

The blue in Portuguese historical azulejos

Index

1	INTRODUCTION	3
1.1	On Portuguese azulejos	3
1.2	On cobalt blue	8
1.3	Purpose of the dissertation and work plan	15
2	PREVIOUS STUDIES	Error! Bookmark not defined.
3	SAMPLES	Error! Bookmark not defined.
3.2-	Macroscopic observations.....	Error! Bookmark not defined.
4	INSTRUMENTAL AND METHODS	Error! Bookmark not defined.
4.1	-EDXRF	Error! Bookmark not defined.
4.1.1	Equipment used.....	Error! Bookmark not defined.
4.1.2	Methods for the characterization of the blue pigments by μ EDXRF.....	Error! Bookmark not defined.
4.2	WDXRF	Error! Bookmark not defined.
4.2.1	Equipment used.....	Error! Bookmark not defined.
4.2.2	Preparation of the samples	Error! Bookmark not defined.
5	RESULTS	Error! Bookmark not defined.
5.1	Analysis by μ -EDXRF	Error! Bookmark not defined.
5.1.1	Tabular presentation	Error! Bookmark not defined.
5.2	Analysis by WDXRF	Error! Bookmark not defined.
5.3	Discussion	Error! Bookmark not defined.
5.3.1	Hispano-Moresque tiles	Error! Bookmark not defined.
5.3.2	Early majolica production and contemporary enxaquetados	Error! Bookmark not defined.
5.3.3	The 17 th Century	Error! Bookmark not defined.
5.3.4	The 18 th century.....	Error! Bookmark not defined.
5.3.5	The 19th century	Error! Bookmark not defined.
5.3.6	The Dutch samples	Error! Bookmark not defined.
6	CONCLUSIONS	Error! Bookmark not defined.
6.1	Composition and possible origin of the pigments.....	Error! Bookmark not defined.

6.2	Shades of blue	Error! Bookmark not defined.
6.3	Geographical provenance of the tiles	Error! Bookmark not defined.
6.4	Chronologic evolution of the composition	Error! Bookmark not defined.
7	THEMES FOR FUTURE RESEARCH	Error! Bookmark not defined.
8	Bibliographic references.....	23
	Annex I Glass standard used for the EDXRF at Universidade Nova de Lisboa.....	102
	Annex II Composition and ratios of all samples.....	103
	Annex III The blue colours in Portuguese Azulejos.....	108
	Annex IV A chronology of events.....	109

1 INTRODUCTION

1.1 On Portuguese azulejos

Glazed architectural ceramics were used in Portugal before 1500 but their history may, according to Reynaldo dos Santos [1], be conveniently made to start with King Manuel I who was impressed by the decorative potential of Hispano-Moresque tiles and during the first decade of the 16th century put a number of orders with workshops of Andalucía for his Paço Real de Sintra (Royal Palace in Sintra). These early *azulejos* still subsist and make up a unique group of great historical importance [1].

Subsequently glazed tiles started being used to decorate walls and vaults in churches and monasteries but also on the palaces of nobility who followed the trend set by their king. These early pre-majolica *azulejos* were probably imported from Spain, although it cannot be excluded that some might also have been manufactured within the Portuguese territory, as defends e.g. Trindade [2]. They follow Moorish, Gothic and Renaissance patterns and the colours were applied as pigmented glaze in cloisonné style (figure 1).



Figure 1- Azulejos “de aresta”



Figure 2- Chequered composition (azulejos “enxaquetados”)

Figures 1 and 2- Convento da Conceição, Beja (S.Portugal).

By 1560 majolica *azulejos* were being imported from Italy and from Flanders [4] and around the same time production started in Portugal – some of the majolica *azulejos* of Quinta da

Bacalhoa on the southern bank of the Tagus river are thought to have been manufactured in Lisbon in 1565 and one of the panels at Church Saint Roch in Lisbon is signed with a Portuguese name and dated 1584 [3]. All those panels bear similitude, either with Italian, or with Flemish productions of the time, although in Portugal they were integrated within architecture in specific places achieving a metamorphosis of the architectural spaces [4] which marks a difference towards some other European productions of the time. Before the end of the 16th century, church walls were starting to be covered with patterned azulejos – either chesstable-like patterns called “*enxaquetados*” in Portuguese - figure 2, or simple *punta de clavo* repetitions made from three different individual tiles. This pattern, called *ponta de diamante* in Portuguese (see sample PT01x in Section 3) probably originated in Talavera [4] but is thought to have also been manufactured in Portugal.

From these early applications resulted a recognizably Portuguese production of patterned azulejo wall coverings [4] manufactured throughout much of the 17th century, using predominantly cobalt blue, Naples yellow and an orange obtained from the mixing of yellow with iron oxide. More rarely, manganese purple and copper green were also used [5]. The patterns themselves and the colours used by the Lisbon workshops allow an approximate dating of the samples [4]. At the same time small figurative compositions were being produced, usually with pious motifs depicted in a rather naïve manner - figure 3.



Figure 3- Early figurative panel (baptism of Jesus),
Convento da Conceição, Beja (Portugal)

In 1640 Portugal revolted against the Spanish rule starting a war that lasted until 1668 during which a new style was introduced, characterized by figures contoured with a very dark manganese-based colour, in cartoon-like manner. This style only lasted for about 25 years, during the third quarter of the 17th century, and is a useful chronological marker [3, 4]. Actually some of these panels lack entirely the blue colour [3, 4] and this seems to be the only period when cobalt blue was absent from a considerable number of panels.

After the end of the war, wealthy customers decided that the local production lacked sophistication and started ordering more professionally painted panels from Holland [4]. These came in the blue and white style inspired by Ming porcelain which was trendy at the time. To be able to compete, Portuguese azulejo-makers resorted to known painters to decorate their local produced panels also in blue over a white majolica ground (figure 4). This step marked the beginning of the so-called Age of Masters which left us magnificent panels of local production, some of which signed. The period lasted until about 1725 [4].

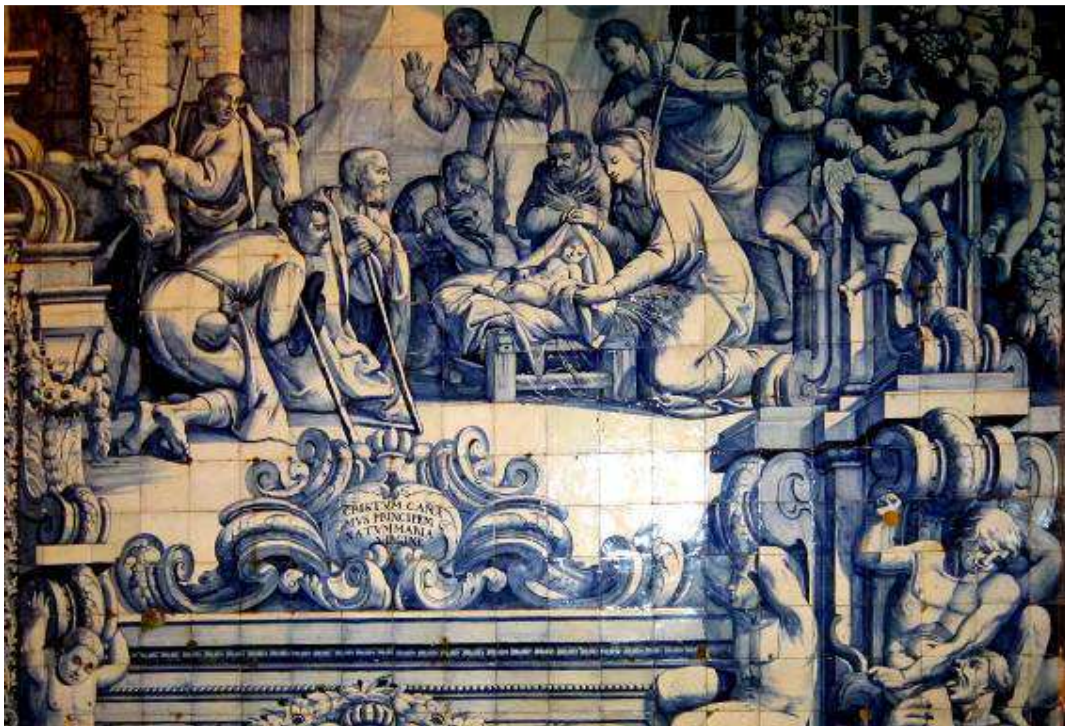


Figure 4- Blue and white interior decoration by António de Oliveira Bernardes, Santuário de Nossa Senhora dos Remédios, Peniche (Portugal)

At the beginning of the 18th century gold was discovered in Brazil and demand increased to the point when established painters could no longer cope with requests. The number of azulejo painters increased but the average quality of their work, often copied from engravings, de-

clined somewhat. As the Baroque taste spread in the country, the azulejo frames that limited the panels became like intricately shaped and decorated windows, from which the scene was observed by the viewers – a period called “Grande Produção” - large production [4] (figure 5).



Figure 5- “Grande Produção” panel with Baroque balaustrade-like frame
Sé de Beja (Beja Cathedral), Portugal.

From ca. 1690 until ca. 1740 both panels and panel frames were exclusively painted in cobalt-blue over white faience but by then the French Rocaille trend was influencing Portuguese decorators and the characteristic shell-like shapes were introduced to the panel frames. Simultaneously other colours than blue returned to the azulejo palette [4]. After that time panel frames could integrate also decorations in green, purple and yellow (figure 6).

In 1755 a strong earthquake destroyed a sizeable part of Lisbon claiming many victims. The date of this event is often considered a turning point, mostly because it brought to power an enterprising minister, the Marquis de Pombal, who presided over the reconstruction. The whole city centre was designed on modern urban conceptions and the stair walls and kitchens of the new multi-storey buildings were often finished with simple patterned azulejos, limited by a linear frame, the so-called *pombalino style* [4]- figure 7. Their production was eventually

set in semi-industrial technology that lowered prices and made azulejos affordable to more people. New patterned designs evolved during the late 18th century (called *Dona Maria style*, from the name of Queen Mary I of Portugal).



Figure 6- Colours return to the frames (ca 1750),
Igreja São Julião, Setúbal (Portugal)



Figure 7- Pombalino Style,
Façade in Lisbon (Portugal)

Portugal went through a troubled period from 1807, when the country was invaded by French and Spanish troops. After the invaders were expelled a period of turmoil ensued until peace was finally restored in 1835 and development could again proceed. The population of the major towns increased and rental housing widespread. After the 1840s azulejos had a revival as a convenient and almost maintenance-free façade covering [4] first in the pombalino style-figure 7, and then with new and colourful designs which continued well into the 20th century, after the setting of modern industrial production.

1.2 On cobalt blue

Cobalt blue is a pigment, including as the active part of its composition a cobalt oxide, that when applied to a raw glaze in the proper proportion and then fired, imparts to it a deep blue colour, commonly known as “cobalt blue”. The cobalt oxide is dark grey but the pigment used by painters (often called “smalt”) is blue (see figure 8) as a result of cobalt-oxygen groups formed through a previous firing with alkali glass. The alkali oxides supply the oxygen ions necessary for the formation of the blue cobalt-oxygen units which then link with silica [6].



Figure 8- Cobalt pigment as smalt

In pottery, cobalt blue was used singly over a white glaze to decorate the magnificent blue Ming porcelain that was made accessible in Europe through the Portuguese Far East trade routes and greatly impressed the local markets. Consequently the blue-on-white decoration became very stylish in European produced faience and, particularly, in Dutch and Portuguese glazed tiles [3]. Cobalt compounds have been used to colour both glass and glazed pottery with an intense blue for 4000 years [6]. There are many fragments that prove the use of cobalt compounds to obtain this deep blue since Antiquity, but only in 1735 AD did G. Brandt isolate a new element - cobalt - and demonstrated that it was the source of the blue colouration [6]. There are many studies on the use of cobalt pigments through time, but there are not yet definitive results as to the geographic location of most of their early sources and commercial routes [7].

Cobalt is a metal that can be found in limited quantities in the Earth crust. It is never found in pure elemental form. Its mineral ores (see Table 1) can be associated with other minerals of Fe, Ni, Mn, Cu, Bi and other metals [6].

Table 1 – Some of the most common cobalt minerals

<i>Cobalt mineral</i>	<i>Chemical formula</i>	<i>Origin</i>
Cobaltite	CoAsS	Sweden
Safflorite	(Co,Fe)As ₂	Saxony, Germany
Erythrite	Co ₃ (AsO ₄) ₂ ·8H ₂ O	Morocco, Schneeberg (Germany)
Skutterudite (includes Smaltite)	CoAs ₃	Schneeberg, Saxony (Germany)
Chloanthite	(Ni,Co)As ₃	Schneeberg, Saxony (Germany)
Linnaeite	Co ₃ S ₄	Iran (Qamsar)

Some elements associated with cobalt in the blue pigmented glazes can be related to the source of its mineral ore but their presence and relative content may also depend on the way in which the blue pigment was obtained from the ore. The presence or the absence of some elements could thus be used as markers or “fingerprints” of a possible cobalt source. Only a chemical characterization can help to pinpoint the origin of each different type of cobalt-bearing pigment. But it must also be borne in mind that the presence of an unexpected element may be alien to the cobalt source- it may be there because another compound was added to alter its original proprieties (including the shade of the resulting colour) or to reduce the cost. In such cases the full composition may, then, be useful to characterize the provenance of a ceramics production, but not necessarily the source of the ore from which the pigment was obtained.

The principal sources of cobalt known in the past were [7; 8; 9; 36]:

- Qamsar (present-day Iran) known since ancient times;
- Europe: *Saxony* and *Bohemia* (in present-day Germany and Czech Republic) known from at least 1500;

- China and present-day Sumatra, also known since before 1500;
- Spain (known from around 1720);
- several other locations in Germany (known from around 1700) and, later, Norway;
- Morocco, known for certain since the 19th century.

To introduce the question of the sources of the cobalt ore and its processing to obtain the pigment, we could hardly find better words than Josef Horschik's in his 1979 review published in Keramos [7]:

When we survey the European ceramics of the 16th to the 19th centuries, we perceive the prevalence of blue colours. Faience and porcelain decorations are dominated by blue colours (...) Blue decorations required the discovery of suitable pigments and their local availability or procurement through trade routes. (...) As we consider the broad use of blue ceramic colours spreading in ancient and medieval times, the question arises of what minerals were used at that time to prepare the blue pigments. This problem has been incompletely addressed so far. Many publications lack specific information about the pigments used. A differentiated description of the very different shades of blue is not often found. It is, for example, customary to refer to any deeper blue as "cobalt blue", without thinking whether at the country of origin of the ceramic piece existed, at the time of its manufacture, conditions to produce or import the necessary pigments for this colour. Historically, the mining of cobalt ore began in Europe in 1500, in close connection with the silver and bismuth mining in the High Saxon-Bohemian Erzgebirge. At this point begins the proliferation of ever-increasing use of cobalt in the central and northern European pottery and glassworks. In Spain, Portugal, and Italy, the appearance of the colour occurred about a century earlier, when it was imported by sea from far away countries through the Western Mediterranean. Since the formulae for the paint mixtures and the suppliers of the raw materials to produce blue colours were a closely guarded secret among producers and merchants well into the 18th century, our knowledge of the origins of those cobalt deposits is scant. Probably the Venetians and Genoese imported firstly the colour from Persia, as did the Portuguese. Spain likely obtained the colour through the Moors of Morocco, where cobalt ores exist in surface deposits.

Dutch researchers found just how hard it is to enlighten the cobalt history several years ago, when trying to determine details of the blue colour production in their own country during the 16th century.

From the 16th until the late 18th century the main source of the cobalt pigment used in Europe was the Erzgebirge - literally “ore-mountains” - [7] and we shall examine the local production and refining technique first. The Erzgebirge is a mountain range about 150km long by 40km wide (see figure 9) whose crest closely marks the border between Saxony and Bohemia (now respectively part of Germany and the Czech Republic). The fact that the mines were distributed on both sides of the border is important because often in History turmoil only affected one of the regions and thus supply as a whole to foreign markets could be maintained by the region that was unaffected. Examples of potential threats to a steady supply that involved only one of the regions were the 1618-1621 Bohemian rebellion and the 1630-1645 Saxon involvement in the Thirty Years War.



Figure 9- The Erzgebirge Mountains

Significant mining activities seemingly began locally in the 12th century in Freiberg and other lower regions of the Range producing silver, tin, copper and lead. During the first half of the 15th century bismuth started being explored as well and found use (e.g. in lead alloys). Bismuth was extracted by roasting the ore over an open fire until it melted out. The resulting fractured slag was called “bismuth barley”, considered worthless and thrown in the dumps. This however contained cobalt, which could only be extracted at a higher temperature. Its utility as a pigment had not yet been locally discovered [7].

According to concurring German sources listed by Horschik [7] around 1500 “colour” (zaffre) started being manufactured in Saxony from bismuth barley by a South German immigrant called Peter Weidenhammer who sold it to Venice. The Italian connection is particularly interesting as the same author mentions local traditions according to which Venetians were active

in the Erzgebirge during the 15th century purchasing ore and metals and sending them to Venice. They may have found about the use of the bismuth barley much earlier than the locals did.

Around 1550 Cristoph Schürer, a glassmaker established locally, found that he could melt cobalt-bearing slag in his glass furnace and when the ashes were mixed with the raw materials necessary to make glass, a beautiful blue glass resulted. By grinding it he produced smalt that could be used as a blue pigment by artists. The colour was taken to Nuremberg and the Dutch got word of it there. Schürer explained his method and that was the source of the Dutch trade in the blue cobalt pigment [7].

In 1679 Johannes Kunkel [10; 25] wrote on how the cobalt ore was processed at the time: *This cobalt is initially thrown in a furnace. When it starts to glow it smokes a white smoke (figure 10) that comes out of it. Such is collected in a wooden construction and this is the arsenic. This fumed and then roasted cobalt is then thrown into a crushing mill. When it goes through it several times the cobalt is the smallest fraction that passes through a narrow sieve and taken into a storage. From this cobalt is taken one portion and mixed well with two or more parts of the finest and smallest crushed gravel pieces which the miners call quartz, mixed and fired together, put in barrels until it is hard and strong like stone.*

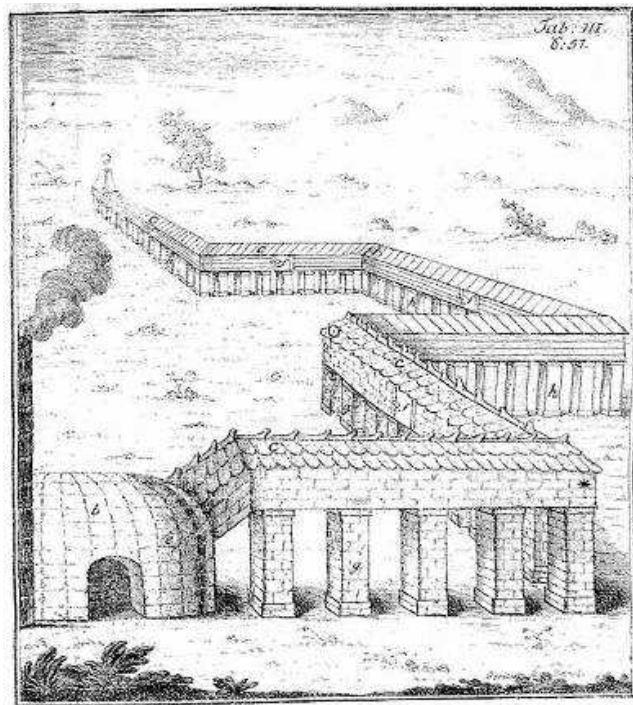


Figure 10- Furnace to roast cobalt [10; 27]

After a long period, finally it is again crushed with iron mallets. Such gravel will be sent away to the Dutch and other nations and used to paint their fine tableware and other things with it. And this is precisely what many mountain people and particularly miners call "zaffre". It is also known that if this fumed cobalt with a certain part of sand and potash is again mixed and molten the glass then carefully crushed and ground in a known mill between two particularly hard stones, a powder is obtained and then separated in different kinds. There is always one more beautiful than the others and sold in portions by an important trader from which a not small revenue is obtained. The sand is from Meissen and no other material is mixed so that the strength of the blue needed in other countries that the (...) painters also call "blue smalt" cannot be imitated or reprocessed at a profit. The same process is schematised by Alfred Lange referring to the late 18th century adding however how nickel and bismuth are separated when smalt is prepared [26].

The important point to retain from these descriptions is that the potters' pigment (zaffre) is not the painters' pigment (smalt). Zaffre for ceramics use was basically calcinated slag in which cobalt was oxidized and arsenic partially expelled. It was ground to powder with little processing. Its content in cobalt was relatively low, said to be around 70% in the 18th century [27] but certainly much less earlier as seen from details of the fine processing needed to refine it. It also included a high content of impurities that were present in the slag and survived the roasting process such as iron and nickel that could not be extracted at the roasting temperature (under 1000°C) and thus remain associated with the cobalt. This is an important point because the pigment carries thus a chemical "fingerprint" from which its geographic origin may eventually be identified. Smalt, the artists' cobalt blue, is obtained through a lengthy refinement process that aims at making it as pure as possible. It was particularly important for the manufacture of artists' smalt that bismuth be separated because it was harmful to the blue colour [7]. Arsenic was tolerated at a low content because it had a favourable effect on the colour [7]. Smalt was sold in several qualities and colour shades [11]. It should still carry a chemical fingerprint but only as relatively low-content impurities.

The Erzgebirge location was the only confirmed source of cobalt in continental Europe until the second half of the 17th century, when new sources were discovered elsewhere in Germany: in Thuringia (1660s), the Black Forest (early 18th century), Hesse, etc. In 1800 there were, besides the Saxon works, fourteen other blue colour mills in Germany alone [7; 9]. Discoveries followed in other countries (figure 11): Austria, Norway, Spain and Hungary. By the mid 19th

century, the colour mills in Saxony no longer used local ore but rather imported, better quality, raw material from abroad [7].

Josef Horschik called to attention the matter of the geographical sources of the blue potter's cobalt pigments and their chronologies. An early source certainly existed in Persia that supplied mid-East potters since before 1300. This pigment probably circulated through the Islamic World, possibly into Spain, and was certainly exported to China according to local contemporary written sources cited by several researchers and compiled by Horschik [7]. In the 15th century, during its age of sea exploration, China is also reported to have obtained cobalt pigment from Sumatra [14;16].

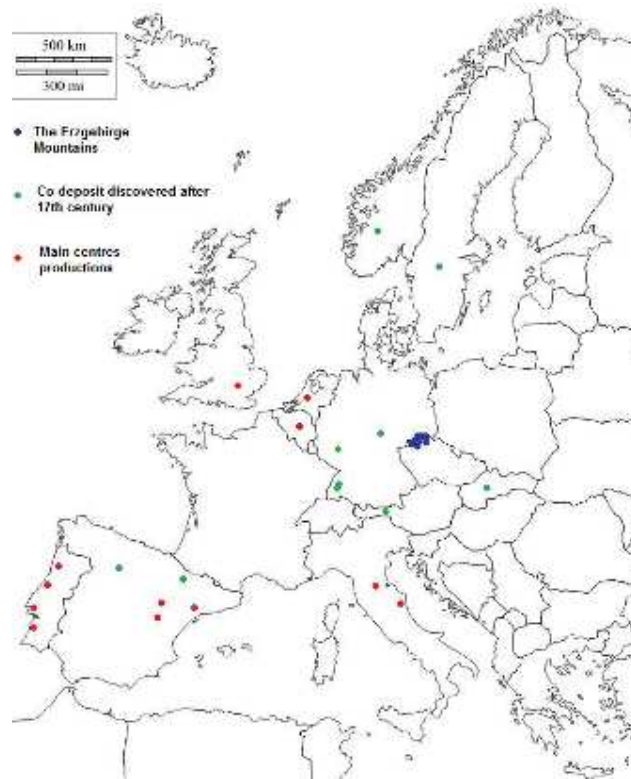


Figure 11- Cobalt deposits and main production centers

The potential sources available to the Iberian Peninsula before the German cobalt became prevalent are of interest to this work. Some authors mention the possibility of exploration of local Spanish cobalt even before 1500 [21]. However they do not offer any undisputable proof. Cobalt occurs in Spain under several mineralogical forms, in association with Fe, Ni and As, but also in cupriferous pyrite [36] from which results an association with copper but the ear-

liest written source mentions in 1846 that cobalt was first found in Spain in the early 18th century [36]. Another possibility is present-day Morocco, where sizeable deposits of cobalt are mined to this day. Besides the obvious connections between Morocco and the Al-Andalus, the Portuguese took Ceuta in 1415 and during the next decades expanded south creating a number of commercial outposts in the coast of Morocco, one of them near Agadir from where cobalt mined 250 km to the interior is exported today [6]. However, no contemporary source has yet been found mentioning clearly any imports of ore or zaffre, nor is there any reference we are aware of ascertaining that the Moroccan cobalt was recognized as a source of blue before the 19th century.

1.3 Purpose of the dissertation and work plan

Although Portuguese azulejos are such an important heritage asset, having been extensively studied from the Art Historian viewpoint, the knowledge concerning the raw materials used and the details of the technological manufacturing process is very limited. The research project behind this dissertation was aimed at improving the present knowledge as concerns the composition of the blue pigment used in the 17th and 18th centuries. A representative set of azulejos spanning at least 200 years from ca. 1600 to 1800 was selected and the composition of the blue colour in their glazes analysed. The results were assessed aiming to answer the following main questions:

- i- What are the characteristic compositions of the colour (pigment and impurities) and how do they relate with the chronology of the azulejos?
- ii- What are the compositional traits that bear on the shades of the blue colour?
- iii- Can Portuguese azulejos be separated from Dutch and Spanish productions, at times when they co-existed in Portugal, solely by the composition of the blue colour?
- iv- Is the composition of the blue colour related with provenance of azulejos within Portugal?
- v- Are there grounds to suspect that at some time the Portuguese used, besides the well-known German zaffre, alternative sources of blue colour imported through their wide sea trade routes?










The workplan included the following main steps:







- i- Study of Portuguese azulejos and their history (visits and bibliography review);
- ii- Bibliographic study of the cobalt blue problem and of previous research results on the matter;
- iii- Selection of ca. 50 samples on the basis of chronology and perceived colour shades;
- iv- Analytic campaign based on non-destructive μ -EDXRF and interpretation of results;
- v- Selection based on previous results of ca. 10 samples for quantification with WDXRF;
- vi- Discussion of results and writing of the dissertation.










It is understood, from the analytic means available, that no fine fingerprinting based in trace elements present in the pigments is possible and so the conclusions have to be based on major elemental associations representing relatively high contents of impurities. A finer research would, however, collide with the present absence of reference data of given ore provenances with which new results might be compared.










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Table 2- The samples analyzed with origin, chronology, description








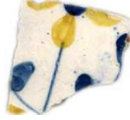
Sample	Origin Chronology	Description	1  10cm
MM01	Spain Early 16 th century	Early Hispano-Moresque production, <i>Azulejo de aresta</i> (manufacturing technique similar to <i>cloisonné</i>). Not majolica.	
MM02	Spain Early 16 th century	Early Hispano-Moresque production, <i>Azulejo de aresta</i> , geometric motifs.	
MM03	Spain Late 15 th , early 16 th centuries	Hispano-Moresque production, <i>Azulejo de corda seca</i> (dry string technique). Not majolica.	
PT01x	Portugal or Spain (?) 1590/1615	<i>Ponta de diamante (punta de clavo)</i> , blue and yellow on white majolica. Early example of Portuguese azulejos production in faience, but maybe this tile came from Spain where the <i>punta de clavo</i> motif was diffused	
PT02x	Spain or Flanders or Portugal (?) 1590/1615	Flemish influence(?), abundant use of orange, yellow. Flemish potters known to have worked in Lisbon around this time Dull glaze, very different from Portuguese	
PT03Sx	Spain or Flanders or Portugal (?) 1590/1610	Flemish influence (?), abundant use of orange, yellow. Dull glaze but different from PT02x. Very thick ceramic body, same creamy colour as typical Portuguese tiles.	
PTE04	Portugal 1600/1615	<i>Azulejos enxaquetados</i> (chess-table pattern): monochrome tiles in two alternating colours (white-blue or white-green), which shows a diagonal grid of great power and visual dynamism. One such azulejo. Coloured glaze- not majolica.	
PTE05	Portugal 1600/1615	Single piece from a panel of <i>enxaquetados</i> as above. Coloured glaze, not in the majolica technique.	



FD01	Flemish/ Dutch 1600/1625	Detailed use of many colours (deep blue, green, yellow and orange) and high decorative style (vegetable and floral pattern). Dull glaze, as in PT03Sx, but ceramic body red-orange.	
PT06S	Portugal 1600/1620	Sample with rare use of red, recovered in Lisbon from strata of rubble corresponding to the 1755 earthquake.	
PT07x	Spain or Portugal (?) 1610/1630	Early Portuguese(?) majolica production, detailed drawing with inaccurate contours. Colours: greenish blue, yellow, maybe also orange.	
PT08	Portugal (not Lisbon) 1615/1650	Very odd specimen manufactured in a workshop from some unidentified town (not Lisbon). The glaze appears cracked and is very dull. The yellow is very brilliant and deep; the blue very dark, almost black.	
PT09	Portugal (not Lisbon) 17 th century	Very different blue. The majolica background is creamish-white. Colours and production technique are not typical of Lisbon's workshops	
PT10	Portugal 1620/1660	Deep blue, usually called "cobalt blue" and yellow. Pure white majolica and very shiny glaze.	
PT11	Portugal (Lisboa) 1620/1640	Early <i>azulejo de padrão</i> , this is half the centre piece of an <i>enxaquetados</i> pattern. Presence of light blue in association with deep blue (often found in Persian kashi-kari tilework and other Islamic productions). Pure white majolica and very shiny glaze.	
FD02	Dutch 1620/1640	Early Dutch blue on white production, using two shades of blue. Glaze off white, maybe decayed. Central scene (plants and animal pattern).	
PT12S	Portugal 1620/1660	The Portuguese production went on using the two colours (blue and yellow) eventually with orange on a white majolica. Sometimes presence of a little frame.	
PT13S	Portugal 1620/1660	Same style as PT12S	

PT14S	Portugal 1620/1660	Again, same style.	
PT15	Portugal 1630/1680	Deeper, rather dark blue used for areas and the contours too in association with deep yellow, floral motifs.	
PT16S	Portugal 1630/1640	Same as above but also with brownish orange.	
PT17S	Portugal 1630/1670	Main colours (white, blue, yellow and orange/brown). Presence of linear contour	
PT18S	Portugal 1630/1640	White, blue and yellow/orange	
PT19S	Portugal 1630/1640	Deep and shining blue and yellow	
PT20S	Portugal 1630/1640	Same as above: blue, white and yellow orange	
PT21S	Portugal 1630/1640	White, blue and yellow/orange	
PT22S	Portugal 1650/1670	Early use of the opaque green colour obtained from mixing the yellow and green pigments. Vegetable motifs.	

PT24S	Portugal 1650/1680	Motifs contoured in black, in a cartoon-like manner, very light blue.	
PT25	Portugal 1650/1700	Floral motif in blue, yellow and orange on a white background	
PT26S	Portugal 1650/1670	Very similar to PT22S	
PT27S	Portugal 1657/1660	Intense and brilliant blue in association with yellow and white background. The samples PT27S, and PT28S may be parts of a single tile.	
PT28S	Portugal 1657/1660	As above.	
PT29	Portugal 1657/1660	The samples PT28S and PT29 are the same - we decided to repeat the analysis with the aim to confirm the unusually high As content obtained by S. Coentro.	
PT30	Portugal 1650/1680	Floral motif (camelia?), deep and shining blue and white. Paint applied very thick. Represents early use of single blue (two shades) on white majolica, in Portugal.	
PT31	Portugal 1650/1680	As above but shade of blue is very different, like the so-called "midnight blue" but muted and slightly greenish.	
PT32	Portugal 1650/1680	Camelia motif, as above but painted with very similar blue as PT30 (cobalt blue). Again very thickly applied paint.	

PT33	Portugal (not Lisbon?) 1660 ca.	Main colours: rather greenish blue and pale yellow with brown contours- fired too hot? Early example of manganese-contoured tile.	
PT34	Portugal 1660/1680	Use of mixed colour: opaque green (yellow+blue mix) with a greenish blue. Dark contours. Maybe from Coimbra?	
PT23S	Portugal 1650/1670	Azulejos characterized by black outline (Mn) and use of colours (yellow, blue, green, purple). Short period production (starting around 1650, abandoned before 1680).	
PT35	Portugal 1660/1680	Same as above	
PT36	Portugal 1660/1680	Azulejos characterized by black outline (Mn) and use of colours (yellow, blue, green, purple). Very dark Prussian blue-like shade. Short production period, as above.	
PT37	Portugal 1680/1730	Freeze from <i>Ciclo dos Mestres</i> (Age of Masters) period. Golden Age of the Portuguese blue on white Azulejos. Muted greenish blue.	
PT38	Portugal 1680/1730	Same as above but the shade of the blue changes to a very dark blue, not found in other samples.	
FD03	Dutch 1700 ca.	Dutch production characterized by central motif in blue on a white background, floral decoration on the corners. This is from the period of Portuguese imports from Holland.	
PT39	Portugal 1700/1715	Floral motif, deep blue and white from the late <i>Ciclo dos Mestres</i> period.	
PT40	Portugal 1700/1720	Animal motif in white and blue (use of light blue for the nuance). Late <i>Ciclo dos Mestres</i> frame.	

PT41	Portugal (Coimbra) 1700/1750	Coimbra production, presence of deep and light blue in association with the white. Similar to some earlier Dutch tiles. Size of tiles smaller than in Lisbon. Quite different blue.	
PT42	Portugal 1715/1745	Floral motif in deep and light blue, use of blue contour.	
PT43	Portugal 1730/1757	"Grande Produção" period.	
PT44	Portugal (Coimbra) 1715/1750	Main colours: blue (deep and light), purple on creamish-white. Blue is slightly greenish, associated with Coimbra production. Size of tiles smaller than in Lisbon	
FD04	Dutch 1750 ca.	Dutch production characterized by central motif in blue on a white majolica background, floral decoration on the corners	
FD05	Dutch (Friesland) 1775/1825	Floral decoration with blue (deep and light)	
PT45	Portugal 1780/1800	<i>Pombalino</i> style as used for kitchens, stairs and other interiors. Simple decoration, vegetable and floral patterns. Reintroduction of colours: green, yellow, blue but with predominance of white (still hand painted). This is a late example using a light blue which once had a yellow over-paint (now faded) to return a green colour.	
PT46	Portugal 1790/1810	<i>Dona Maria</i> style. A time of experimenting with geometric and floral motifs in several colours for interiors. Characterized by larger white background areas than usual until then. Dark slightly greenish blue.	

FD06	Dutch (Friesland) 1825/1850	Dutch production characterized by central scene in blue inside a circle. White background and floral decoration on the corners	
PT47	Portugal 19 th century	Imitation of <i>pombalino</i> style but now done with the “estampilha” technique - painted with paper masks. Early industrialization example, still with parts hand-painted.	

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Bibliographic references

- 1- Reynaldo dos Santos, *O azulejo em Portugal*, Editorial Sul, 1957;
- 2- Trindade R.A.A. *Imagens de Azul*. Revista de História da Arte: Imagem, Memória e Poder pp.236-263; Instituto de História da Arte; Lisboa, 2011;
- 3- Meco, J, *O azulejo em Portugal*, Publicações Alfa, Lisboa, 1993;
- 4- Henriques, P; Almeida, A; Pais, A.N; Loureiro, F; Monteiro, J.P. *Roteiro do Museu Nacional do Azulejo- segunda edição*, Instituto Português de Museus, Lisboa, December 2005;
- 5- Coentro, S. X, Mimoso, JM, Lima, A.M, Santos Silva, A, Pais, A.N, Muralha, V.S. *Multi-analytical identification of pigments and pigment mixtures used in 17th century Portuguese azulejos*, Journal of the European Ceramic Society nr. 32, January 2012;
- 6- Young, R. (ed.), *Cobalt – its chemistry, metallurgy and uses*, American Chemical Society and Reinhold Pub.Co, New York, 1960;
- 7- Horschik, J, *Beiträge zur Geschichte der Kobaltfarbe und ihre Verwendung in der Keramik*. Keramos, 1979, 85, pp. 119-142 (translated by J-M. Mimoso, LNEC 2011);
- 8- Gratuze, B., Soulier, I., Blet, M. and Vallauri, L., *De l'origine du cobalte: du verre à la céramique*. Revue d'Archéométrie, 1996, 20, pp. 77-94.
- 9- Taylor, J.R., *The origin and use of cobalt compounds as blue pigments*. Science and Archaeology, 1977, 19, pp. 3-15.
- 10- Harley, R.D, *Artists' Pigments c.1600-1835. A study in English Documentary Sources*, Second Revised Edition, Archetype Publications, 2001, pp. 29-58,

- 11- Hammer, P., *Das Sächsische Blaufarbenwesen und der Handel mit Kobaltfarben – nach Unterlagen der Bücherei der Bergakademie Freiberg*. In VII International Symposium “Cultural Heritage in Geoscience, Mining and Metallurgy: Libraries – Archives – Museum”: “Museum and their collections”, Scripta Geologica Special Issue, 2004, 4, pp. 108-117 (translated by J-M.Mimoso, LNEC 2011).
- 12- Barilaro, D, Crupi, V, Interdonato, S, Majolino, D, Venuti, V, Barone, G, La Russa, M.F, Bardelli, F, *Characterization of blue decorated Renaissance pottery fragments from Caltagirone (Sicily, Italy)*. Applied Physics A, Materials Science & Processing, 2008, 92, pp. 91-96.
- 13- Roldán, C, Coll, J, Ferrero, J, *EDXRF analysis of blue pigments used in Valencian ceramics from 14th century to modern times*. Journal of Cultural Heritage, 2006, 7, pp.134-138.
- 14- Feng, D., BaoRu, S., *Further study of sources of the imported cobalt-blue pigment used on Jingdezhen porcelain from late 13 to early 15 centuries*. Science in China Series E: Technological Sciences, 2008, vol.51, 3, pp. 249-259.
- 15- Pérez-Arantegui, J, Resano, M, Garcíá-Ruiz, E, Vanhaecke, F, Roldán, C, Ferrero, J, Coll J, *Characterization of cobalt pigments found in traditional Valencian ceramics by means of laser ablation-inductively couple plasma mass spectrometry and portable X-ray fluorescence spectrometry*. Science Direct, 2008, 74, pp.1271-1280.
- 16- Wood, N, Tite, M. S, Doherty, C., Gilmore, B, *A technological examination of ninth-tenth century AD Abbasid blue-and-white ware from Iraq, and its comparison with eighth century AD Chinese blue-and-white sancai ware*. Archaeometry, 2007, 49, pp. 665-684.
- 17- Mühlethaler, B., Thissen, J., *Smalt*. Studies in Conservation, 1969, 14, pp. 47-61.
- 18- Wen, R, Wang, C. S, Mao, Z. W, Huang, Y. Y, Pollard, A. M, *The chemical composition of blue pigment on Chinese blue-and-white porcelain of the Yuan and Ming Dynasties (AD 1271-1644)*. Archaeometry, 2007, 49, pp. 101-115.
- 19- Rehren, Th, *Aspects of the production of cobalt-blue glass in Egypt*. Archaeometry, 2001, 43, pp. 483-489.
- 20- Calligaro, T, *PIXE in the study of archaeological and historical glass*. X-Ray Spectrometry, 2008, 37, pp. 169-177.
- 21- Porter, Y., *Origines et diffusion du cobalt utilisé en céramique à l'époque médiévale. Etude préliminaire*. La céramique médiévale en Méditerranée. Actes du 6^{ème} Congrès de l'AIECM2. Éditions Narration, Aix-en-Provence, 1997, pp. 505-512.
- 22- Llusar, M, Forés, J.A, Badenes, J, Calbo, M.A. Tena, Monròs, G. *Colour analysis of some cobalt-based blue pigments*. Journal of the European Ceramic Society, 2001, 21, pp. 1121-1130.

- 23- Velez, Z, *In quest of a useful blue in Early Modern Spain* in "Trade in artist's materials to 1700", Archetype Pubcs, London 2010.
- 24- Zucchiatti, A., Bouquillon, A., Katona, I. and D'Alessandro, A., *The Della Robbia blue: a case of study for the use of cobalt pigments in ceramics during the Italian Renaissance*. *Archaeometry*, 2006, 48, pp. 131-152.
- 25- Kunkel, J, *Ars vitraria experimentalis*, Berlin, 1679.
- 26- Lange, A, *Das sächsische Blaufarbenwessen um 1790*, in *Freiberger Forschungshefte D.25*, Berlin 1959 (translated by J-M Mimoso, LNEC 2011).
- 27- Gruijl, M., *Zaan Blue – from zaffer to smalt to ultramarine*. Amsterdam. (personal communication by Johan Kamermans of the Tegelmuseum, Otterlo, Holland- translated by J-M.Mimoso, LNEC 2011).
- 28- Pérez-Arantegui, J, Montull, B, Resano, M, Ortega, J.M, *Materials and technological evolution of ancient cobalt-blue-decorated ceramics: Pigments and work patterns in tin-glazed objects from Aragon (Spain) from the 15th to the 18th century AD*. *Journal of the European Ceramic Society*, 2009, 29, pp.2499-2509.
- 29- Cipriano Piccolpasso, *The three books of the potter's art (Il tre libri dell'arte del vasaio), a fac-simile of the manuscript at the Victoria and Albert Museum*, translated by Ronald W. Lightbown & Alan Caiger-Smith, Scolar Press, 1980.
- 30- Yunhui Mao, *Lead-Alkaline Glazed Egyptian Faience: Preliminary Technical Investigation of Ptolemaic Period Faience Vessels in the Collection of the Walters Art Gallery*, *Journal of the American Institute for Conservation*, Vol. 39, No. 2. (Summer 2000), pp. 185-204.
- 31- International Atomic Energy Agency, *Intercomparison of PIXE spectrometry software packages*, Report IAEA-TECDOC-1342, (www-pub.iaea.org/MTCD/.../te_1342_web.pdf), February 2003;
- 32- Pereira, S; Mimoso, J.M; Santos Silva, A, *Physical- chemical characterization of historic Portuguese tiles*, Repport 23/2011-NPC/NMM, LNEC 2011 (available on the Internet at: <http://www-ext.lnec.pt/AzTek/publication.html>)
- 33- Serrão, J.V, *História de Portugal, Vol. V (1640-1750)*; Editorial Verbo, Lisboa, 1996.
- 34- Kleinmann, B., *Cobalt-pigments in the early Islamic blue glazes and the reconstruction of the way of their manufacture*. In *Archaeometry '90 International Symposium on Archaeometry*, eds. E. Pernicka and G. A. Wagner, Basel: Birkhauser, 1991, pp. 327-336.
- 35- Berke, H., *The invention of blue and purple pigments in ancient time*. *Chemical Society Reviews*, 2007, 36, pp. 15-30.

36- Monografía sobre recursos minerales de cobalto en España, Instituto de Recursos Geológicos y Mineros, Madrid, 2003.

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