

# RECREATION OF THE CMYK PIGMENT PALETTE IN ILLUSTRATED EARTHENWARE FROM L'ALCORA BEFORE SÈVRES CHROMIUM: ASSESSMENT IN PRESENT-DAY FRITS AND NIR REFLECTANCE

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## ABSTRACT

Up until the chromatic revolution following the introduction of chromium in Sèvres in 1802, ceramic pigments in Europe adhered to chemical recipes developed by “trial and error” by “colourist technicians” such as Joseph Olèrys, Joseph Ochando, Julián López or the Causada family in the early period of the l'Alcora Royal Factory of earthenware and porcelain. The European CMYK palette of pigments was based on cobalt blue, haematite-silica incarnate, Naples yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$  and its variations with silica or cassiterite), and cobalt ferrite spinel black ( $\text{CoFe}_2\text{O}_4$  and its compositional variations), together with copper-based greens (Cu(II) verdigris in an acid medium) or ochres obtained by adding iron or cobalt to Sb-Pb yellows.

This paper recreates the l'Alcora technicians' recipes from the 18th century and analyses their performance and NIR reflectance in present-day frits. The results are also compared with remains of enamelled pieces uncovered at l'Alcora (c.f. 1920-1970) that use some of the recreated pigments.

## 1. INTRODUCTION

On 4 September 1725, Pedro Buenaventura Abarca de Bolea succeeded in a lengthy lawsuit initiated in 1706 to be proclaimed IX Count of Aranda and Lord of the Tenancy of l'Alcalatén. That was the start of frenetic activity to set up a factory in the style of France's Louis XIV's minister Colbert (1619-1683) of private manufactures with a strictly regulated production system to guarantee high quality and to achieve over time the necessary experience or know-how and size or scale to compete with sufficient capacity against foreign competitors, granting them exemptions and franchises as royal commissioned manufacturers (1,2). The factory officially started business on 1st May 1727, amid severe disagreements with the town council of l'Alcora regarding the extraction of clays for ceramics. The colours, and the colour master that prepared them, were a key part of the factory, where there are no individual artists but rather the results of a careful manufacturing process that included everybody from the doorman to the senior director of the factory (3). In fact, as Gual (4) points out, the signed works are not a credential of each author (in this case the final painter), but rather a means of controlling each artist's production, so that the chief masters (Olérys, Ochando, López, Causada, Ferrer, Knipffer, Cloostermans) rarely signed pieces and many are in fact unsigned, especially after 1784, when they were compulsorily signed with an A as the factory's trademark. The following recipe books for glazes and pigments have survived till today:

a) *"Recetas de los colores que se usan en mi fábrica de Loza de Alcora (Recipes for colours used at my Alcora Earthenware factory)"* (1749), signed by Olérys, Jacinto Causada, Julián López and José Ochando (2, p. 181-196): It contains 64 colours: Sapphire blue (3), Sapphire black (1), Manises gilts (4), Enamels (2), Naples yellow (7), Orange (4), gilts (3), green (12), purple (7), violet (1), grey (5), black (3), olive (4), pearl (3), Haematite-based red (6), a type of purple (1), gold (1), and "marzacota" ("barrilla" and fritted sand:  $\text{Na}_2\text{SiO}_3$ ) (1)

b) *"Rezetas para Bernizes (Recipes for Glazes)"* (2, p. 197-203): Four glazes ("bernizes") of "rachola, olanda, Talavera and cubierta" (tile, Dutch, Talavera and top coat), are presented, which are frits composed of a lead:tin calcine (1 "arroba" (regionally variable measure of weight): 2 to 8 pounds) that is ground, mixed with sand (1 "arroba"), salt (12 pounds) and "barrilla" (mineral powder) (0-3 pounds) and fritted in a bottom kiln. It then describes 21 colours: yellow (5), orange (3), blue (1), olive (2), green (5), black (1), purple (2), violet (2).

(c) *"Secretos de Christian Kniffer sobre la loza y porcelana (Christian Kniffer's secrets of earthenware and porcelain)"* (2, p. 204-236) (1764), which presents 6 formulations of Pb-Si frits (solvents) and colours: haematite incarnate in a Pb-Si frit (4), Cu green (or zaffer) with Naples yellow (16),  $\text{Co}_2\text{SiO}_4$  glaze blue (1), Holland ochre brown (or  $\text{FeSO}_4$  "caparrosa" (sulphate)) with a Pb-Si frit (3), "musco" (dark brown Fe in a Pb-Si frit) (7), black (3). It then describes the preparation of Au, Ag and Sn dissolved with etching acid and powders for painting noble metals (black precipitates from the Au solution with  $\text{FeSO}_4$ , and from the Ag solution with Fe nails which are removed). It talks of green (Cu green numbered N4) and yellow (Naples) glazes ("bernizes") and describes frits. Finally Knipffer describes the bodies and glazes as well as the firing of porcelain and semiporcelain.

d) "*Quaderno de recetas de vernizes y colores para cuarenta y ocho oras de fuego o cinquenta (Recipe booklet of glazes and colours for forty-eight or fifty hours' firing)*", (2, p. 237-249), compiled by Jacinto Causada for potters or crockery makers in 1765. These are formulations similar to (b), describing 4 glazes ("vernizes") as in (b) then colours with similar formulations: yellow (3), orange (2), olive (Naples with Mn) (2), blue (1), gold (1), pearl (1), grey (2), green (Naples with zaffer) (4), black (Co with Naples and Mn and secondly with Sn), red (haematite road clay) (3), purple (zaffer with Sn-Mn). It then describes 8 mixtures of the above to achieve special colours and 12 coloured glazes using those colours as well as two top coats, two Ag gilts for Manises gold and 4 formulations on Ag and Au for painting, including one for writing ink.

e) "*Prescripciones de como pintar en diferentes colores sobre porcelana (Specifications on how to paint in different colours on porcelain)*" (2, p. 249-254): Although it is undated, Casal groups this work with (b) and (d), given the similarity of its formulations. Although it uses Cassius' purple formulations, its author may possibly also be Mariano Jacinto Causada. He describes what he calls "*derritientes*" (solvents) (3 Pb-Si frits, although the third one uses Cassius purple in a confusing way) and different pigments which, according to the title, would be applied to porcelain: reds or incarnates (6, based on haematite obtained in different ways, the first one by burning steel and reacting it with sulphur to produce a sulphide which is then attacked with etching acid and the resulting chloride, yellow, is calcined to produce the haematite; the second one uses  $\text{CuSO}_4$  (vitriol from Hungary), which is calcined with a tin sheet. In the last ones, he uses red vitriol  $\text{CoSO}_4$ ), brown and black (8, also based on iron oxide), yellow (1, from Naples), blue (2, from glazes purified with vinegar), green (from copper verdigris, copper acetate, or Co from glazes; the third one uses Cassius purple mixed with Cu green and blue), Cassius purple (he formulates a gold paint dissolved in aqua regia and tin dissolved in etching acid to formulate a Cassius purple and which eventually produces a very clear and perfect formulation of Cassius purple, see p.254). However, the recipes for Cassius purple do not seem to have been applied before 1790, as it is not seen in elaborations prior to that date nor is it reflected in Fig. 1 of the palette of the master colourist Vicente Prats, but it does appear in Cloostermans' porcelain elaborations from 1790 onwards.

f) "*Preparación de colores metálicos y barnices (Preparation of metallic colours and glazes)*" (2, p. 255): this recipe book is a delightful description of the different tasks involved in purifying precursors, as well as describing the characteristics and properties of the various materials (lead, tin, antimony - ....). The writing is very didactic and it is the first recipe book to make an allusion to chemistry ("*Chimica*") and also to dependence on England and Holland as suppliers of some of these raw materials. However, it does not formulate pigments or glazes.

g) "*Compendio Químico*" (A Chemical Compendium). Theoretical and practical theory of the art of manufacturing earthenware, pipes and porcelains, which explains Pedro de Cloostermans' new discoveries and advances at the Alcora factory, when he was the Director and a member of Louis XVI's academy in Paris and Flanders; Austrian. Brought to light by his son, Pedro, painting teacher. Valencia 1st March 1800 (5).

All except the last one were published in the Count of Casal's work (2). In the first recipe book *"it is stated that the "arrobas" and pounds that are named are Valencian, each "arroba" being made up of thirty-six pounds and each pound of twelve ounces.*

*At the foot of each recipe the name of those that composed it is placed, and the one where it says 'usual' in the margin should be used for ordinary and regular consumption by the factory, as from experience it is the best, although the others shall also be good, but not so perfect. Where it is said that the composition of the colour shall enter the kiln at the top, it shall be understood to be above the bottom of the kiln hearth, and where it is said at the bottom, it shall be understood to be next to the pillar that supports the spindle or coil that the flame strikes; and as a general rule, the composition shall be in the kiln until the earthenware is discharged: It is also to be noted that all pots and pans in which compositions are placed in the kiln can be only scalded and not varnished, as the varnish would run and stick with heat, thus damaging the other ingredients" (1,2).*

The "colourists" in the early period of the Royal Factory at l'Alcora developed their ceramic pigments by systematic "trial and error" (1). Up until the colour revolution that followed the introduction of chromium by Brongniart at Sèvres in 1802 (6), the CMYK palette of European pigments was based on cobalt blue, iron-silica magenta (incarnate) or ochre (by mixing haematite or calcined iron with Naples yellow), Naples yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$  and its variations with silica or cassiterite), and cobalt ferrite spinel black ( $\text{CoFe}_2\text{O}_4$  and its compositional variations), together with copper-based greens (Cu(II) verdigris in an acid medium).

With Pierre Cloostermans in charge of technical production at the factory in 1787, the general manager Domingo Abadia requested Vicente Prats, master colourist, to make a compilation of the colouring agents used, which led to a work of great historical and technical value entitled on the cover *"Primeras pruebas de pintura sobre la cubierta sin estar cocida en 23 de Enero de 1790 Por Vicente Prats Mro. De Pintura. de orn. de D.D<sup>o</sup>.A<sup>a</sup>. (First painting trials on an unfired top coat on 23 January 1790 by Vicente Prats, Master Painter, by order of Domingo Abadía)"* which is presented in Figure 1, with 32 colours that Prats divides into 4 spectral families (A, B, C & D in Fig.1.a) emanating from the figure of a Sun (with 6, 6, 8 and 9 colours respectively), and a group of blues between families A and D. In each family, the colour is implemented with different brushes from thin to thick, in steady brushstrokes (sun rays) and applied continuously (rectangles painted with blurring at the edge of the plate). Some show horizontal lines or simple painted motifs that use colour as a test to outline contours within the coloured area. Family A together with I seem to describe the complete basic palette (Fig.1.c): (I) blue (probably common zaffer), (2) deep brown (from haematite occluded in silica), (3) ochre (haematite mixed with Naples yellow), (4) green (from copper verdigris), (5) yellow (Naples), (6) grey (cobalt iron spinel with manganese or zinc), (7) black (cobalt iron spinel). The date reference on the back appears to use these colours, probably in the sequence indicated in Fig.1.b. Families B, C, D seem to be trials with mixtures of the above colours.

This paper recreates recipes from 18th century l'Alcora technicians and analyses their performance and NIR reflectance in present-day frits. It also compares the results with enamelled pieces from l'Alcora collected from the remains of waterwheel-raft implements belonging to Cristóbal Tomás Ferrer (c.f. 1920-1970), which use some of the pigments recreated.





**Figure 1.** First painting trials on unfired top coat made on 23 January 1790 by Vicente Prats (Cabrera Ahís collection, l'Alcora Ceramics Museum).

## 2. RECREATION OF PIGMENTS

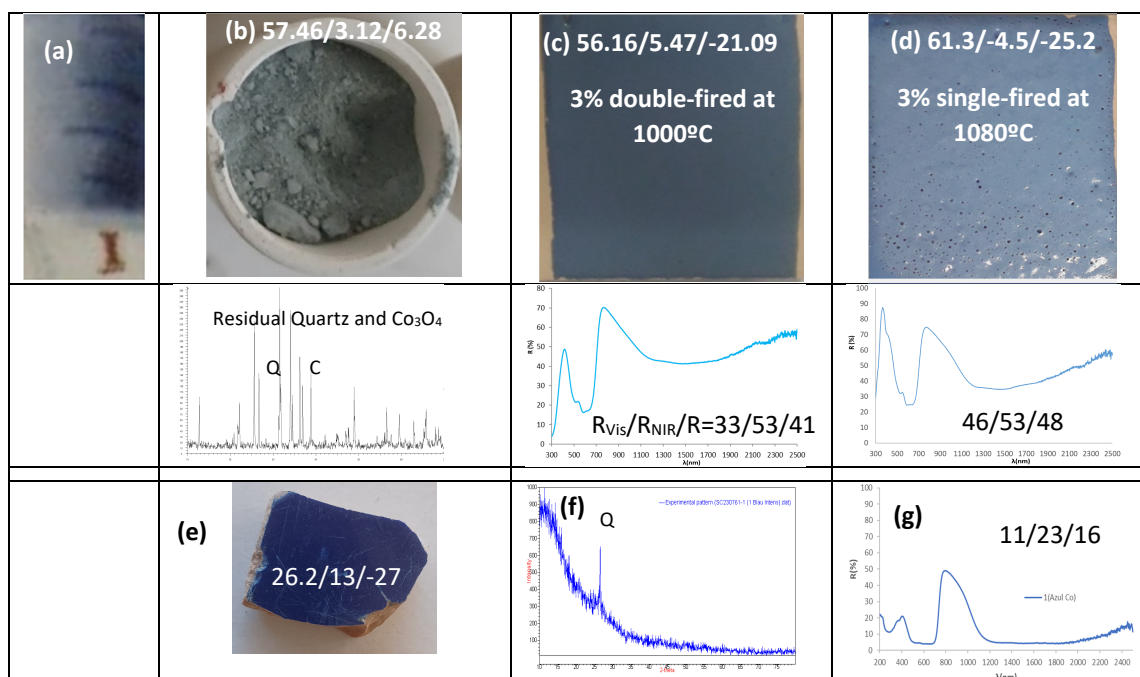
### 2.1. COBALT BLUE

Cobalt blue was produced at the Royal Factory from zaffer (a mixture of Co(II)-Co(III)  $\text{Co}_3\text{O}_4$  spinel and quartz); the quality of the zaffer varied, depending on the concentration of oxide in the mixture and fineness. Recipe book (a) by Olérys-Ochando-López-Causada, possibly the most direct, simple and least verbose of them all, provides 4 recipes for blue with zaffer in the recipe for "Good Holland Zaffer", where it states that zaffer from Delft does not need "any composition" and can be used directly. To guarantee the colour, the other three call for a composition to be made by adding modifiers of approximately 10% glaze (cobalt oxide and lead bisilicate frit), 5% minium (calcined lead or azzarcon), 1.5% sodium carbonate ("barrilla"), and 1.5% manganese oxy-hydroxide ("manganeta"), as the case may be (1,2). 20g of the above composition were prepared using pure  $\text{Co}_3\text{O}_4$  mixed with 25% quartz (recreating common zaffer) and other industrial quality products specified above, mixing them in an electric grinder (@ 20,000 r.p.m.) for 5 min. without calcining (as the recipe says: "grind in the colour mill and use"). The results obtained are presented in Figure 2.

The recreated common zaffer displays better performance in the double-fire frit, as in the single-fire frit, given that calcining of the colour mixture was omitted as the recipe states, pinholing appears, associated with retention of the gases emitted when the  $\text{Co}_3\text{O}_4$  is reduced ( $\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + 1/2\text{O}_2$ ) before dissolving in the molten glaze. The  $\text{Co}^{2+}$  displays a tetrahedral co-ordination in the final glaze, matching its diffuse reflectance spectrum, with absorption bands in the visible at 470, 580 and 670 nm (reflectance minimums are shown in Figure 2)(7).

In the enamelled pieces from l'Alcora (c.f. 1920-1950) (Fig.2.e), the blue colouring is more intense ( $L^*=26.2$   $a^*=-27$ ), which could indicate that a higher concentration than the usual 3% of modern standard applications was used.

X-ray diffraction at grazing angle shows quartz crystallisation in the glaze and the diffuse reflectance spectrum presents the same bands in the visible range, but the strong reflection in the ultraviolet region observed at 350 nm in the recreated pigment disappears (see highlighted area in Fig.2.g) - this absorption is associated with the presence of lead in the historical glaze formulation.



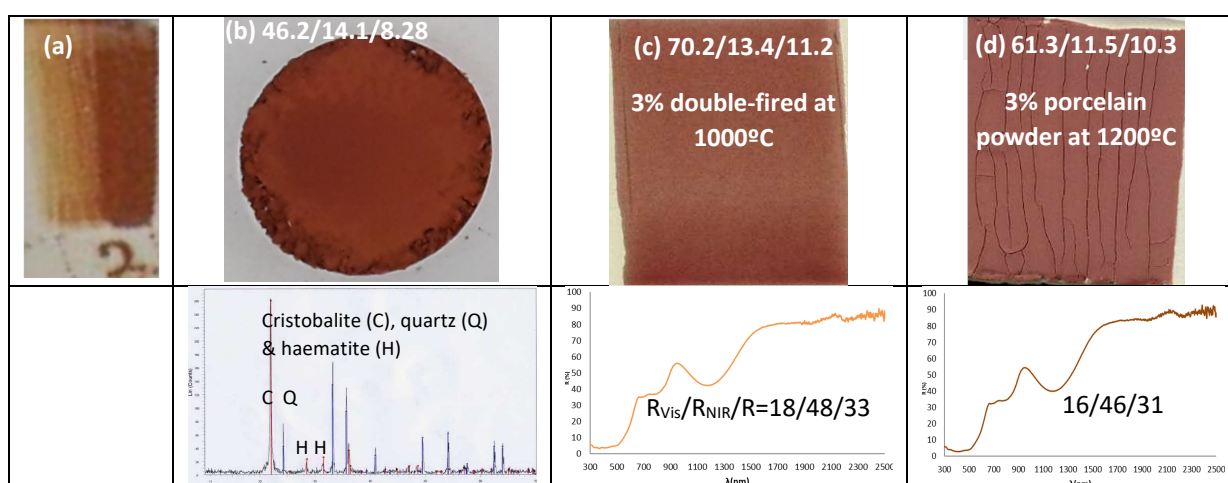
**Figure 2.** Cobalt blue with indication of CIEL\*a\*b\* values: (a) view Fig. 1, (b) initial composition with X-ray diffractogram (XRD) below, (c) glazing at 3% in double-fire frit with diffuse reflectance spectrum below indicating the visible ( $R_{\text{Vis}}$ ), near infrared ( $R_{\text{NIR}}$ ) and total ( $R$ ) reflectances, (d) glazing at 3% in a single-fire frit with diffuse reflectance spectrum below, (e) rest of glazed pieces from l'Alcora (c.f. 1920-1950) with their XRD incidence at grazing angle (f) and its diffuse reflectance spectrum.

## 2.2. MAGENTA

### 2.2.1. "ROXO", RED OR INCARNATE

All the recipe books contain formulations for reddish hues and all of them are based one way or another on fritted haematite, either on its own, with sand, or with a Pb-Si frit (this is the case of Knipffer's so-called "derritientes" or solvents). For example, Julián López's description of "colorado" (red) on p. 192 (2): "Red clay from the road is dissolved in water, passed through a sieve, left to dissolve, and the water runs clear; when the body is ready, it is put in a well-covered pot in the kiln bottom, taken out of there, it is made into powder, and it is composed as follows = Red clay powder, nine ounces-: "Marzacota", an ounce and a half-: ground glass, one ounce-: molten lead, one ounce-: the dry, remixed composition is put inside a well-covered pot and fired again in the same place in the kiln, taken out, ground with water and used".

The formulation describes the use of a highly ferruginous clay (this recipe uses "red clay from the road", others call for clay from Franchellas in Onda or from near the marsh, all of which are red). The clay is washed thoroughly and calcined in a *sagell* or *rastell* kiln, eliminating solubles and carbonates and enriching it with iron. It is ground to a fine powder and the approximate mass ratio of Fe/Si/Pb/K oxides=3/7/1/0.5 (red clay, "marzacota" and glass/minium/"marzacota" and glass) is formulated. In our recreation, red iron oxide (haematite, Quimialmel) 10%, quartz (Sibelco) 85%, minium (1%), and potassium carbonate (4%) were used. The mixture in an electric mill was calcined at 1100°C/2h and glazed at 3% in a double-fired frit and porcelain stoneware powder (like the pigment used in the factory for porcelain and today to colour porcelain stoneware). No colouring occurs in the single-fired frit at 1080°C (8). The results in Fig. 3 indicate brown colourings with  $a^*$  values of between 11.5 (porcelain body), 13 (double-fire frit with 6% PbO) and 14 (micronised powder), while glazing in single-fire alkaline frits produces no colour. The XRD of the powder shows crystallisation of cristobalite with the presence of quartz and weak peaks of haematite. Reflectance spectra, with octahedral Fe<sup>3+</sup> absorption bands, indicate significant NIR reflectance of around 46%.



**Figure 3.** Haematite-silica incarnate showing CIEL\*a\*b\* values: (a) view Fig. 1, (b) initial composition with X-ray diffractogram (XRD) below, (c) glazing at 3% in double-fire frit and diffuse reflectance spectrum below showing visible ( $R_{Vis}$ ), near infrared ( $R_{NIR}$ ) and total reflectance ( $R$ ), and (d), glazing at 3% in porcelain powder with diffuse reflectance spectrum below.

### 2.2.2 OCHRE

The 1749 recipe book uses two strategies to prepare orange (ochre) hues:

a) Naples yellow modified with Dutch ochre ( $\text{Fe}_2\text{O}_3$ ). A basic yellow is prepared (*"Preparation of yellow for orange. B. Lead six pounds -: Antimony six pounds; calcined once or twice in the kiln top spread with the finger so that it fires well"*) to which they add *"Ochre, an ounce and a half, two ounces or two and a half"* according to three formulations in succession: *"it is coarsely ground in the grinder, it is taken out in a basin, it is left to stand or to brown, the water is removed, and it is left to be rinsed until it is ready, it is cut - in small thick sticks measuring "dos cantos de real de a ocho" (expressed in terms of old Spanish coin ("real") thickness), and put on scalded plates it shall be fired uncovered in a pot kiln, and if it remains the same colour as the sticks on the bottom side, it shall be returned to the kiln, and if it is dark on the top side and a little less so on the bottom, it is well prepared and shall be ground and used"*.

b) Naples yellow modified with burnt iron ( $\text{Fe}_2\text{O}_3$ ). *"Antimony, a pound and a half -: Litharge, nine ounces :- "Azarcon" (bright orange), nine ounces :- Burnt anchor iron, eight ounces :- to be chopped fine and mixed, putting it three times in scalded dishes to be calcined in the top of the kiln; and again at the bottom; it may be ground; and used"*.

These mixtures were not recreated.

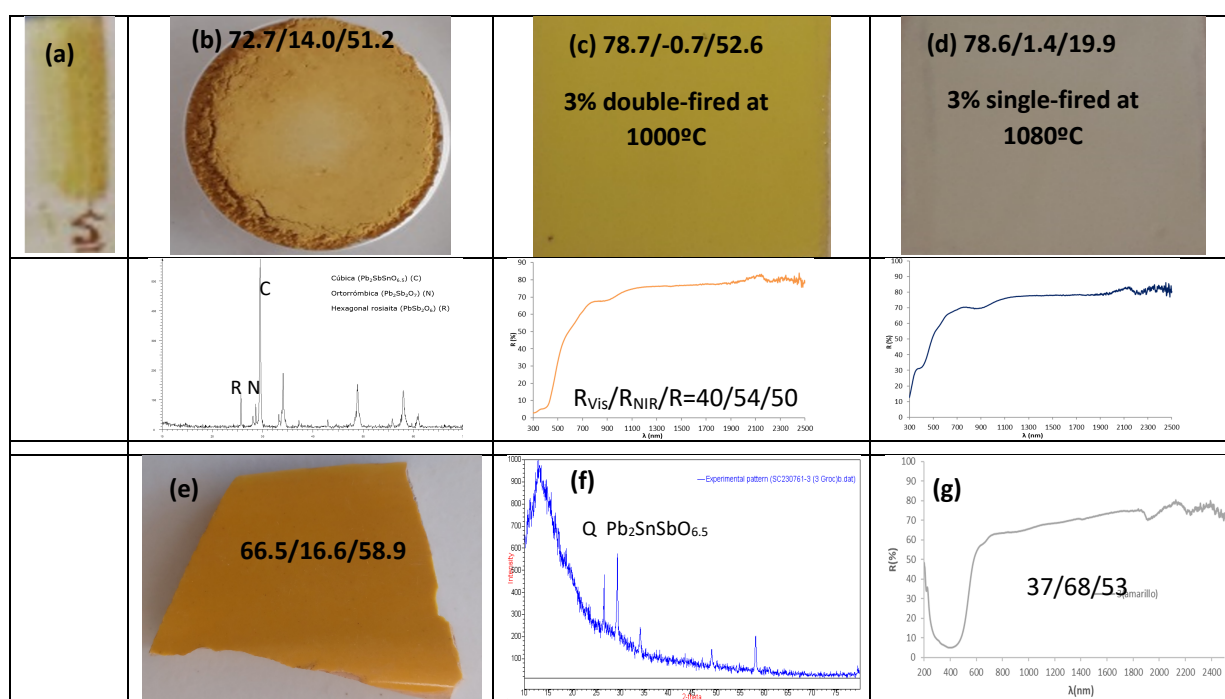
### 2.3. YELLOW

Yellow in those days (15th-18th century) was based on Naples yellow and its related predecessors: Pb-Sn yellow type I (orthorhombic  $\text{Pb}_2\text{SnO}_4$ ) and its Si-doped modification called Pb-Sn yellow type II (cubic pyrochlore  $\text{PbSn}_x\text{Si}_{1-x}\text{O}_3$ ), which were initially used for ceramics and glass and later also in oil painting (e.g., Titian in *Bacchus and Ariadne*, 1520-23), or Velázquez in *Apollo in the Forge of Vulcan*, 1520-23). In the 18th century, lead antimoniate yellow or Naples yellow  $\text{Pb}_2\text{Sb}_2\text{O}_7$  were the most common formulation, an evolution of Pb-Sn yellows, although it had been previously used in Babylon, Mesopotamia and Assyria (9,10).

The 1749 recipe book contains 9 yellow formulas based on Naples yellow formulations: (a) two formulations of Sb-Pb-Zn (antimony, "azarcon"/calcined lead, tutia) with mass ratios 2/3/1 and 3/3/1, (b) three formulations with Sb-Pb-Si-Na (antimony, "azarcon"/calcined lead, sand, "barrilla") with mass ratio 8/10/10/18, 8/12/4/3 and 3/6/3/11, and (c) three more basic Sb-Pb formulations (antimony, "azarcon"/calcined lead) with mass ratio 6/6, 3/6 and 12/24, although the last one is said to be for preparing "olive". In this instance, one or two calcinings are always prescribed: *"it is put to calcine in the kiln, in scalded dishes, taken out, it is remixed and chopped again, and put a second time in the kiln; it is ground and used"*. Recipe book (b) contains a formulation with tin: *"To make yellow, put a pound of good firewood, two pounds of antimony, a pound and a half of litharge and a pound and a half of "Alarca" and you shall have good yellow. To make orange, 18 ounces antimony, 9 ounces litharge, 9 ounces of "Alarca", 8 ounces of "Ladrado" iron and you fire it three times, twice when scalding and once when firing, noting that it must always be chopped when you put it in"* (2, p 197). "Alarca" is *"a mixture of one "arroba" of lead and five pounds of tin"*; however, later it describes six other basic formulations with Pb and Sb, some with "barrilla" and/or sand and others with no antimony (it is probably a misprint and instead of antimony it says "amoniaco" (*ammonia*)).



According to Cerro et al (9), to recreate the pigment that is shown in our tests, we chose the recipe with tin and the formulation of  $2\text{PbO} \cdot 3\text{Sb}_2\text{O}_5 \cdot 0.5\text{SnO}_2$ , which is the solid solution of Sn in Naples yellow pyrochlore ( $\text{Pb}_2\text{Sb}_{1.5}\text{Sn}_{0.5}\text{O}_{6.75}$ ) and an excess of 2.25 moles of  $\text{Sb}_2\text{O}_3$ , an excess that is common in all the above formulas. 20g of the above composition were prepared using industrial quality  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{SnO}_2$ , mixing them in an electric grinder (20,000 r.p.m.) for 5 min and calcining at  $1000^\circ\text{C}$  for 3h before grinding the product by hand in an agate mortar. The results obtained are presented in Figure 5.



**Figure 4.** Naples yellow with indication of CIEL\*a\*b\* values: (a) view Fig. 1, (b) initial composition (top) and X-ray diffractogram (XRD) below, (c) glazing at 3% in double-fire frit and diffuse reflectance spectrum below, indicating visible ( $R_{\text{Vis}}$ ), near infrared ( $R_{\text{NIR}}$ ) and total ( $R$ ) reflectances, (d) glazing at 3% in single-fire frit with diffuse reflectance spectrum below, (e) rest of glazed pieces from l'Alcora (c. f. 1920-1950) with their XRD at grazing angle (f) and their diffuse reflectance spectrum.

The recreated yellow displays a yellow-orange colour and the X-ray diffraction indicates the presence of a mixture of crystalline phases: the most significant one is the cubic phase ( $\text{Pb}_2\text{SbSnO}_{6.5}$ ). It also reveals the pyrochlore lead antimoniate phase in reference to the Naples yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$ ) and the hexagonal rosiite ( $\text{PbSb}_2\text{O}_6$ ), both of which appear with very similar peak intensity to what is stated in the literature (Fig. 4.b shows the most intense peaks for each phase C, N and R respectively). The enamelled powder displays good performance in a double-fire frit but in a single-fire frit, it disappears due to the dissolution of the ions in the glaze, rendering it void of any pigmenting capacity. The diffuse reflectance spectra are similar in both frits (very weak absorption bands at 400 and 790 nm), although obviously reflectance is higher in the practically white piece from the monoporosa frit.

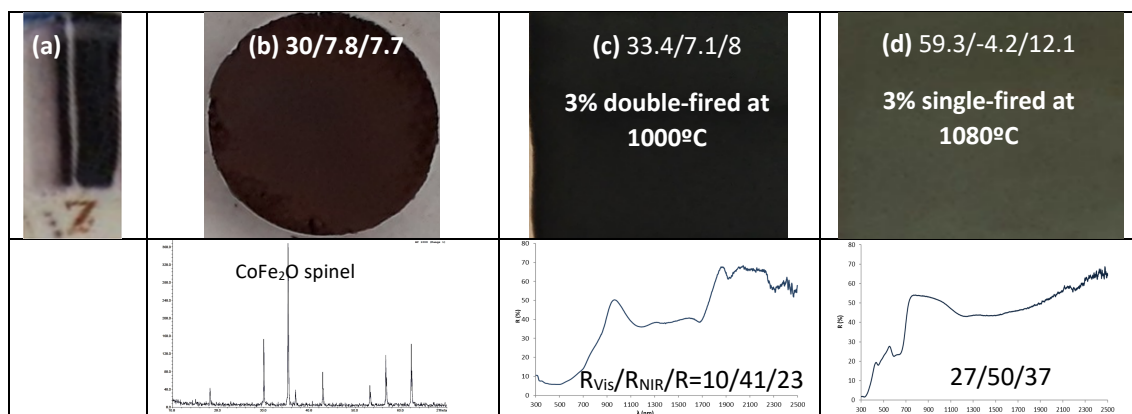


In the remaining enamelled items from l'Alcora (c.f. 1920-1950) (Fig. 4.e), the yellow colouring is more intense ( $L^*=66.5$   $b^*=58.9$ ) indicating a concentration in glaze over the usual 3% used in modern applications. Grazing angle X-ray diffraction indicates the crystallisation of quartz in the glaze and peaks of remarkable intensity associated with the cubic phase ( $\text{Pb}_2\text{SbSnO}_{6.5}$ ). The diffuse reflectance spectrum shows the same bands in the visible although weaker, as well as strong absorption in the ultraviolet region, which is associated with the presence of a high concentration of lead in the historical glaze formula.

## 2.4. BLACK

To obtain black, the colourists at l'Alcora developed cobalt ferrite  $\text{CoFe}_2\text{O}_4$  (spinel) with different variants. For example, the N.A. Black on page 213 (2) is made from rust ( $\text{Fe}_2\text{O}_3$  from oxidised iron or rust), which is sieved and fired (it is made into embers) and the powders obtained are ground with enamels and N.2.P solvent in a proportion of 1/1/2, involving an Fe/Co/Pb/Si mass ratio of 1/0.5/1/1.5 (rust/Co from the enamels/Pb from the frit/Si from the enamels and frit): *"mixing these three materials, passing them across the grinding stone with a little water, the paste shall be dried in the sun, put in a clay crucible, which shall be placed at the bottom of the kiln to melt it; [once] melted, it shall be made into powder and passed through a silk sieve, passing it again across the stone with water, and dried in the sun, it is ready to serve"*. Alternatively, the Black Colour (p. 219), from which they omitted iron: *"We shall take Aragon blue and put it in a crucible, which for three times we shall make an ember come to the bottom of the kiln and use it. By way of explanation, 1 ounce of Aragon blue (calcined), 2 and 1/2 ounces of solvent N.5.B (frit made of 6 ounces of quartz (clear stone) and 6 ounces of white lead). This is then ground with water on the stone and dried in the sun, it is ready"*. That gives a Co/Pb/Si mass ratio of 1/2/1 (Co from Aragon zaffer/Pb from the frit/Si from the Aragon Co and frit), which would produce dark blue as it does not contain iron.

To recreate the pigment, the composition of the first two was prepared with an approximate stoichiometry of  $\text{CoFe}_2\text{O}_4 \cdot 0.3\text{Fe}_2\text{O}_3 \cdot 0.7\text{PbO} \cdot 1.2\text{SiO}_2$ , starting in this case from industrial oxides mixed in an electric mill for 5 minutes and calcined at 1100°C for 3h. The results are presented in Figure 5 and the pigment obtained displays an acceptable black hue, albeit with  $a^*/b^*$  values of around 7. The XRD of the powder only shows crystallisation of the  $\text{CoFe}_2\text{O}_4$  spinel, the stoichiometric excesses of iron and unnecessary Pb and Si are not detected, as they probably form an undetected amorphous glassy phase. The double-fire glazing retains the colour tone while the monoporosa fares worse, as it turns to grey. The absorption bands are the result of overlapping d-d transitions of  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  ions in the  $\text{CoFe}_2\text{O}_3$  inverse spinel (80%) (11) and, therefore, with co-ordinated IV and VI environments for both cations, which makes assigning bands very complicated. In all cases, NIR reflectance is excellent for a black pigment, around 40%.



**Figure 5.** Cobalt ferrite spinel black showing CIEL\*a\*b\* values: (a) view Fig. 1, (b) initial composition with X-ray diffractogram (XRD) below, (c) glazing at 3% in double-fire frit with diffuse reflectance spectrum below, showing visible (R<sub>Vis</sub>), near infrared (R<sub>NIR</sub>) and total reflectance (R), and (d) glazing at 3% in single-fire frit with diffuse reflectance spectrum below.

## 2.5. GREEN

Prior to Cloostermans being at l'Alcora, green was created using two strategies:

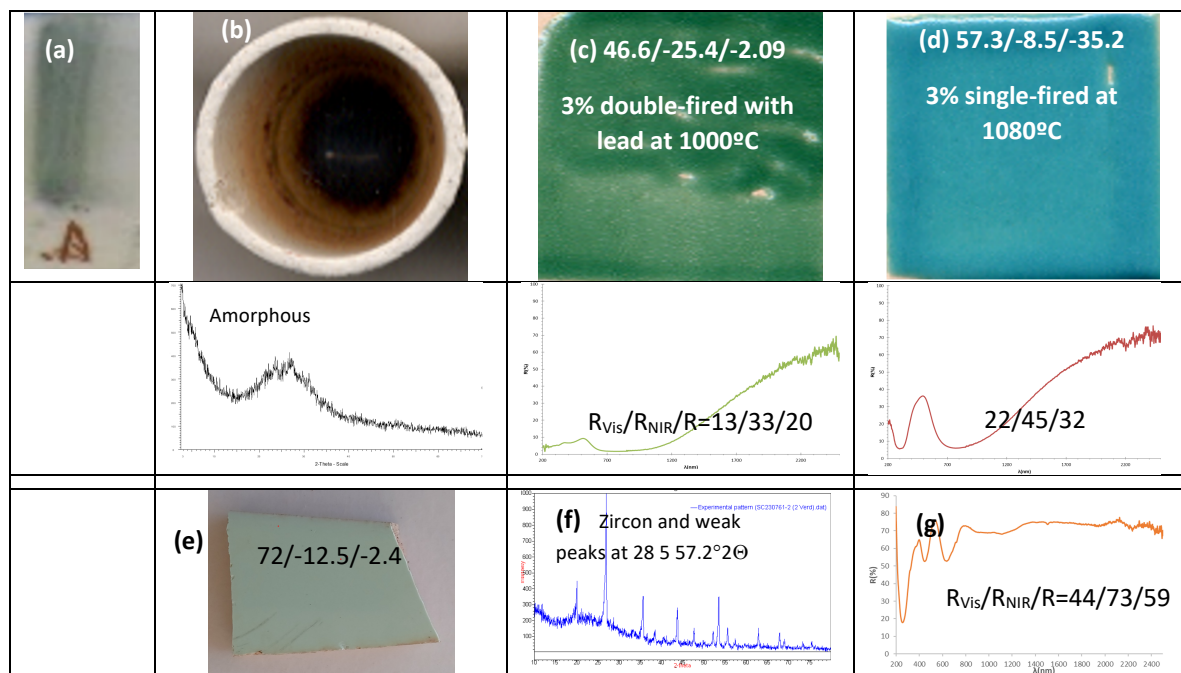
a) Mixing cobalt blue and Naples yellow. The 1749 recipe book contains 12 formulations based on this strategy; for example, the first one on page 186: "Calcined lead, one ounce :- Antimony powder, four ounces :- Glaze sand, six ounces :- "Barrilla", two ounces :- Calcined tin, one ounce :- Enamels, two pounds and four ounces= Mix it into powder and put it in a well-covered pot with clay to calcine in the kiln; grind it, and use it". This formulation implies a Pb/Sb/Sb/Si/Na/Co-Si dosage with an approximate mass ratio of 1/4/6/2/2/1/28 (calcined lead/antimony/sand/"barrilla"/tin/Co-Si from enamels).

b) Knipffer's 1765 recipe book describes copper-based green with solvent N.2.P (frit Si/Pb in mass ratio 1/2/0.5 (calcined flint/minium/white lead), which is melted in a crucible and ground, as stated on p.202). They are formulated for example: (b.1) green for porcelain and semiporcelain by mixing copper with Naples yellow: "Green colour N. 2 K. Take copper powder, purify it well, put it in a glass beaker, pour a portion of etching acid over it, leave it for a month in infusion, then remove the etching acid that it has and pour clean water over it several times until it is completely clean of all that the etching acid causes on the copper, leave it to dry in the sun, the rest that remains on the ground, which is what is necessary for this colour. For the same colour, verdigris is taken and it is also put in a glass vessel, a portion of vinegar or white wine is added, but very strong, and it is left in the sun for a month in infusion, then all the vinegar is removed and clear well water is added several times until it is known that there is no vinegar left, then the mass is put to dry in the sun and served with the other ingredients. By way of explanation...1 pound of copper powder, 1/2 pound of distilled verdigris, 1/2 pound of yellow N.1 (1 pound of Naples yellow and 3.5 of solvent N.5.B (frit of Si/Pb in proportion 1/1 (powder of calcined flint/white lead) and 5 pounds of solvent N.2.P). All that remains is to mix these materials, moisten them with well water and grind them on the stone".

(b.2): a copper-based green mixed with enamels (p. 211): *"Another green colour N.1.º By way of explanation: 1 pound copper, N.O., 1/2 pound enamel that is boiled with vinegar, 2 pounds of solvent N.2.P. And said materials shall be mixed together and put in a crucible to melt them and the same operation shall be done as the last one" ("it shall be taken out, trodden on, passed through a sieve and ground with water on the stone and it is a perfect colour")*.

In the first case (b.1), from the chemical point of view, it uses a Cu/PbSb<sub>2</sub>O<sub>7</sub>/Pb/Si composition with a precursor mass ratio of 1+0.5/0.1/1.7/3.4 (Cu Nitrate+Cu Acetate/Naples Yellow/Pb<sub>3</sub>O<sub>4</sub> in frits/SiO<sub>2</sub> in frits). The introduction of yellow is not very significant in the mixture, accounting for little more than 6% of the chromophores, and even less so when applied on porcelain or semiporcelain with more intense firing. In the second case (b.2), it uses a Cu/Co+Si/Pb/Si ratio of 1/0.2+0.3/1.5/0.5 (Cu Nitrate/Enamels/Pb<sub>3</sub>O<sub>4</sub> in frits/SiO<sub>2</sub> in frits). Including Co with the enamels is, as in the previous case, also circumstantial; the colourists of the time seem to have thought that the zaffer and Naples yellow gave the colour more intensity and so at least they prevented any absolute failure in their colouring efforts. To recreate this type of colour, a composition with copper (II) nitrate, quartz and a lead bisilicate frit (45% SiO<sub>2</sub> and 48.5% PbO) in a mass ratio of 1.5/1/1.5 similar to b.1 and calcined at 1100°C for 1h was used. The results are shown in Figure 7.

The recreated verdigris melted in the calcine to produce a dark blue-green glass (amorphous to X-ray diffraction). In the glaze, it displays green colouring in the double-fire frit with lead (6% in PbO) and in the alkaline one (Na<sub>2</sub>O, K<sub>2</sub>O, ZnO, MgO and CaO make up 26% of the mass) for porous single-firing, it produces an elegant turquoise blue, with moderate reflectance, especially in the case of green. Diffuse reflectance spectra indicate in the green an absorption band with a minimum reflectance at 420 nm and a relative maximum reflectance at 530 nm, so that it absorbs the blue and also the orange-red range, with a broad band between 600 and 1200 nm. Turquoise, on the other hand, has an absorption band at 300 nm (associated with the charge transfer of the glass which does not occur in the lead frit), with a maximum at 500 nm and reflected with certain intensity in the blue range at around 400 nm; it also has a broad, intense absorption band between 600 and 1200 nm. The green colour occurs in low crystal field intensity environments, such as the reticulum of the lead frit, where the co-ordination is octahedral (O<sub>h</sub> group), whereas in alkaline environments, field distortion is high and the Jahn Teller effect of tetragonal distortion occurs, with square planar co-ordination (D<sub>4h</sub> group) and the colour is blue (the spectrum shifts to shorter wavelengths). The observed broad bands could be the overlap of the three forbidden d-d absorption bands of Cu<sup>2+</sup> in the visible region around 800 nm (<sup>2</sup>B<sub>1g</sub>→<sup>2</sup>B<sub>2g</sub>), 630 nm (<sup>2</sup>B<sub>1g</sub>→<sup>2</sup>E<sub>g</sub>) y 570 nm (<sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>1g</sub>) (12).



**Figure 6.** Green with indication of CIEL\*a\*b\* values: (a) view Fig. 1, (b) initial composition with X-ray diffractogram (XRD) below, (c) glazing at 3% in double-fire frit with lead and diffuse reflectance spectrum below indicating visible ( $R_{Vis}$ ), near infrared ( $R_{NIR}$ ) and total ( $R$ ) reflectances, (d) glazing at 3% in single-fire frit with diffuse reflectance spectrum below, (e) rest of glazed pieces from l'Alcora (c.f. 1920-1960) with their grazing angle XRD, (f) and their diffuse reflectance spectrum.

The pieces of the light green transparent glaze collected at l'Alcora in Fig. 6.e. show an intense X-ray diffraction peak associated with zircon  $ZrSiO_4$ , which began to be used as an opacifier in l'Alcora in the mid-1960s, and the diffuse reflectance spectrum indicates reflectance minimums associated with  $Cr^{3+}$  in octahedral co-ordination (10). Chromium was not used in l'Alcora until long after Cloostermans' arrival in 1787, chromium coming from Sèvres to l'Alcora.

### 3. CONCLUSIONS

CMYK and green pigments were prepared recreating the basic palette used at the Royal Earthenware and Porcelain Factory of l'Alcora (cobalt blue, haematite-silica, Naples yellow, cobalt-iron black, and copper green), adhering to the recipe book legacy of its "technical colourists". The behaviour of these colours was studied using modern-day double-fire frits (with 6% PbO in their formulation) and an alkaline monoporous frit, as well as with porcelain stoneware powder for  $\text{Fe}_2\text{O}_3\text{-SiO}_2$  red. A decrease in colour performance was seen with respect to the performance observed from the remains of some of the pigments glazed in lead bisilicate frits uncovered at l'Alcora (1920-1970), especially in the single-fire frit, which matures at relatively higher temperatures. The pigments show fairly high reflectance in the infrared region, the blues based on  $\text{Co}_3\text{O}_4$  and the blacks based on cobalt ferrite being of special interest, although they include lead-based modifiers that were widely used in those days, but which could invalidate them for modern applications.

### 4. ACKNOWLEDGEMENTS:

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