USE OF DIGITAL JET PRINTING IN THE REPRODUCTION AND RECOVERY OF ARCHITECTURAL CERAMIC HERITAGE

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ABSTRACT

In this study a method has been developed for the reproduction of antique ceramics of great historical and architectural value, using characterisation techniques to study the pieces, digitised image processing, and digital jet printers. The method has been applied to the reproduction of earthenware tiles from the Baron de Vallvert palace kitchen (Valencia), dating from the 18th century, which had been stolen and of which only photographic records remained.

In order to reproduce with the greatest possible accuracy the probable appearance of these historical tiles, the glazes of tiles made in the Valencia Region in the 15th, 18th, and early 20th century, loaned from the Manolo Safont Tile Museum in Onda, were characterised. A technique was then developed to separate the digitised photograph into six colour components, since the usual four-colour printing techniques were unable to encompass the entire chromatic spectrum. Inks were formulated with pigments that contributed optical characteristics similar to those of the historical tiles, and applied by digital jet printing, reproducing the original designs. Finally, the appearance of the reproduced tiles was compared with that of the historical tiles used in the reproduction.

1. INTRODUCTION

Historical heritage conservation in general, and ceramic heritage conservation in particular, require a multidisciplinary approach to establish the best conditions for conservation and, where appropriate, the most suitable restoration techniques. Further to be considered is the reproduction of pieces that are extracted from their original locations in order to ensure their conservation, and are replaced by a copy that, logically, needs to be as faithful as possible to the original.

The restoration and/or reproduction of ceramic floor and wall tiles poses a series of specific problems within the framework of architectural heritage conservation. Ceramic materials have evolved notably throughout the centuries and, in regard to their decoration, glazes have been improved and the available colour palette has been extended. This historical variability notably complicates the reproduction of such tiles, since the glazes and colours used in fabricating the piece it is desired to reproduce are often not exactly known, while this information would clearly make the process much easier.

The present study sought to reproduce earthenware tiles from the Baron of Vallvert palace kitchen (Valencia, 18th century). The palace housed the last kitchen with *in situ* Valencian ceramic wall tiling to ceiling height until the theft of these tiles was discovered in August of 2005; some graphic records remained in books on Valencian tiles [1] and in the photographic archives of the Instituto de Promoción Cerámica in Castellón.

Since no originals were available, it was decided to characterise earthenware tile fragments from the same geographic and historical environment (Valencia, from the 15th to the 19th century) and to correlate the results obtained with information provided by bibliographic sources. The evolution of Valencian ceramics was to be studied and it was to be verified whether there were sufficient common features in the appearance, materials, and decorating techniques of the earthenware tiles of that period to allow faithful reproduction of the missing pieces, using other contemporary pieces as references.

The moulding process of ceramics hardly changed after the 15th century. Forming was done with a so-called *graella*, a wooden mould, using clay in a plastic state, after which the body was dried and fired. A white glaze layer was applied by hand and this raw glaze layer was then manually decorated. In order to finish the piece, the tile was then subjected to a second firing, the earthenware tiles being arranged on their edges. Earthenware tile sizes initially varied considerably (though they were generally small), until in the period from about 1735 to 1765 the so-called Valencian 'handspan' (21.5x21.5 cm) was implemented.

The colour palette had already been notably extended in the 18th century since, in addition to copper, manganese, and cobalt, iron (oranges) and antimony (yellows) were also used [1]. However, in regard to that period, it is no longer so simple to determine whether the coloration was due to the direct incorporation of chromophore oxides or to their precursors into the raw glaze, or whether previously prepared pigments were incorporated. A typical example is the yellow pigment $Pb_2Sb_2O_5$, known as Naples yellow, records of whose fabrication in Italy date back to the 16th century, and whose presence in ceramics since the Renaissance has been widely discussed [2]. Geographically much closer, in the manuals of the Alcora ceramics factory (18th century), recipes are already to be found of colorants that ranged from coloured glasses to ceramic pigments, as they are known today [3]. However, the 18th century palette contained no real red, or chrome greens (which did not appear until the 19th century) [4].

Kitchens tiled with earthenware tiles appeared in Valencia about 1770, in a time of full-blown Rococo [5]; the Vallvert palace kitchen dates from 1780. The decorative motifs of the kitchens of that period included handrail borders, garlands of flowers and fruits, food and culinary objects, as well as servants, ladies and gentlemen in everyday scenes. The Vallvert palace kitchen includes a court scene, in which guests are entertained with a service of *turrones* (typical Spanish sweets containing ground almonds) and chocolate.

In order to reproduce these types of decorations involving numerous earthenware tiles, each of which was different and for which a small number of units were to be made, the most appropriate technique appeared to be digital jet printing. Applied to ceramics, this decorating system provides a series of advantages over others: since the head does not touch the piece, it is possible to decorate reliefs and, as the system is computer controlled, it allows the pieces to be decorated with an almost unlimited number of designs, and short production runs to be made without prohibitive costs. In comparison, traditional techniques such as screen printing or hand painting are much more expensive.

Inkjet printing is based on the discharge of ink droplets from the nozzles in the printing heads on to the surface to be decorated. There are two main types of heads: thermal and piezoelectric heads. In the former, tiny heating elements are used to drive the droplets of ink from the nozzles; in the latter the ink is driven through the printer head jets by making a cone-shaped piezoelectric crystallite vibrate using electric currents, thus propelling the drops of ink on to the surface to be printed. The most widespread ink proportioning system is drop on demand (DOD), in which the drops of ink are proportioned on demand [6].

Ink exit through the head is the critical point of the system, since it is essential that pigment particle size (which influences the drop formation process) and head outlet size should match for appropriate printer operation [7]. This type of device controls colour by the four-colour printing method, so that four basic colours are required for appropriate operation.

This new ceramic decorating technique seeks to approach four-colour printing, which is fully established in the graphic arts sector. However, the ceramic pigments that are currently available do not exactly match the basic four-colour printing colours (cyan, magenta, yellow, and black). The existing palette of ceramic inks that work with the new printing systems consists of blue, brown, yellow, and black. These four colours allow a broad chromatic range to be obtained, but research is still ongoing into the obtainment of new pigments for jet inks.

2. OBJECTIVE

The purpose of this study was to use digital jet printing as a decorating technique for the reproduction of historical heritage earthenware tiles, and to prepare a set of inks that would allow faithful colour reproduction.

In order to carry out the reproduction, a fragment of the court scene was selected, illustrated in Figure 1, which contained eight different colours: yellow, orange, brown, green, turquoise blue, cobalt blue, purple, and black.

Figure 1. Court scene from the Baron of Vallvert palace kitchen, from the photographic archives of the Instituto de Promoción Cerámica in Castellón (courtesy of J.L. Porcar), and tiles from the 15th, 18th, and 19th century, characterised in this study.

3. MATERIALS AND PROCEDURE

In order to reproduce the pieces, the photographic archives of the Instituto de Promoción Cerámica in Castellón were consulted, and a fragment of the court scene was selected. To determine the nature of the glazes and decorations used at that time and to determine their evolution, fragments of earthenware tiles made in the city of Valencia in the 15th, 18th, and 19th century, loaned from the Manolo Safont Tile Museum in Onda, were characterised. These earthenware tiles, referenced 1 to 5, are shown in Figure 1 together with the fragment of the court scene to be reproduced. Test pieces were cut from the pieces, and observed from the surface and in cross-section with an optical microscope, and an FEG environmental scanning electron microscope (ESEM) with an energy-dispersive X-ray microanalysis (EDX) unit, which provided a semi-quantitative analysis of the glazes.

To decorate the ceramic pieces by digital jet printing, inks based on organometallic complexes that were soluble in an organic medium were discarded, because they offered a very limited chromatic range. For this reason, six inks with a greater saturation were developed, using current ceramic pigments of nanometre particle size. The inks were prepared from solids in suspension and an organic base that provided the inks with the required physical and rheological properties for use in the printing system heads. Of the six prepared inks, four are customarily used in ceramic four-colour printing (blue, brown, yellow, and black), while the other two (pink and green) were specifically developed for this study.

For this purpose, the colorimetric curve of the different colours from the historical tile selected as a reference (piece 3) were measured with a COLOREYE XTH (GretagMacbeth) spectrophotometer, in order to compare this with the one obtained from the developed inks. These inks were applied pure on to previously fired bodies coated with a base glaze; these pieces were then fired in a roller kiln using a 45 min. cycle and peak temperature of 1050 °C. Their colorimetric curve was determined under the same conditions.

For the panel, white-body wall tiles were pressed, measuring 47×47 cm, with a slightly projecting relief and irregular edges, which allowed four pieces of 212×21.2 cm (Valencian handspan) to be obtained from each piece. This body was fired in a roller kiln using a 50 min. cycle and peak temperature of 1140 ºC. It was cut to size and glazed with a bell using an opacified semi-gloss base glaze, with visual characteristics similar to those of the base glaze of piece 3.

The tiles were decorated with an ink-on-demand digital jet system, with piezoelectric technology. The printing system was a laboratory plotter with four printing heads, 512 injectors, and a printing resolution of 180 dpi (dots per inch). The printing conditions were as follows: drop volume: 80 pL, discharge frequency: 4 kHz, printing speed: 0.565m/s, and printing width: 71.8 mm. After they were decorated, the earthenware tiles were fired in a roller kiln using a 45 min. cycle and peak temperature of 1050 ºC.

4. RESULTS AND DISCUSSION

4.1. MICROSCOPIC CHARACTERISATION OF THE GLAZES

In the 15th century piece, the blue decoration had been applied on to a white base glaze, consisting of a silica glass with a high lead and potassium content (66% SiO_2, 17% PbO, 7% K_2O by weight), opacified with SnO_2 (2.5%). Inside the glaze, there was a larger quantity of SnO_2 particles than at the surface, which may be due to partial sedimentation of the opacifier. The blue coloration was due to dissolved Co(II) in the glass, which was associated with Fe and As. The elements associated with Co sometimes allow the origin of the raw materials used in the blue glaze to be determined. In this sense, recent studies [8,9,10] have associated Co in antique ceramic glazes with Ni and Fe or with As. Padeletti [9] proposes a change in the composition of the glazes with Co, since he observed that this element was associated with As in pieces made about 1520, whereas according to Moioli [11] all the Co ores used since the 14th century contained As.

Two pieces from the 18th century were studied: one of these (piece 2), size 11.5×11.5 cm, had a very glossy glaze, with pure pigments of intense hues; the other (piece 3), size 21.5×21.5 cm (handspan), had a semi-gloss texture and less contrasting colour palette, which was broadened by the superimposition of pigments. Table 1 gives the composition of the different colours of the two pieces.

Oxide	Piece 2					Piece 3							
	White	Yellow	Orange	Green	Blue	White	Yellow	Orange	Green	Lilac	Turquoise	Blue
Na_2O	1.1	0.7	0.4	1.1	1.1	0.8	1.0	0.9	1.1	0.7	0.9	1.0
MgO	0.6	0.9	0.8	1.1	1.0	0.6	0.5	0.4	0.5	0.5	0.7	0.5
As_2O_3	--	--	0.7	--	0.2	--	--	0.1	--	--	--	--
Al_2O_3	1.7	2.0	2.5	2.4	1.9	2.2	2.1	2.3	2.3	1.8	2.3	2.0
SiO_2	59.0	51.2	46.9	51.9	59.4	59.4	57.2	50.5	51.1	59.9	59.2	58.8
PbO	24.6	26.2	24.1	24.4	24.6	25.0	24.8	29.6	30.4	22.8	21.9	23.2
K_2O	6.7	5.8	7.1	6.1	6.1	6.6	5.3	5.3	4.9	6.8	6.17	6.4
SnO_2	2.8	--	--	4.9	2.2	2.5	2.5	1.3	1.5	2.9	2.2	2.1
Sb_2O_3	--	5.1	4.5	0.7	--	--	3.1	4.2	1.3	3.1	3.0	2.7
CaO	3.1	3.4	1.6	4.2	2.3	2.4	3.1	2.1	2.6	--	--	--
MnO	--					--	--	--	--	1.0	--	0.3
Fe_2O_3	0.4	0.7	6.1	0.7	0.6	0.5	0.5	3.3	0.7	0.5	0.7	0.7
CoO	--	--	--	--	0.5	--	--	--	--	--	--	0.3
NiO	--	--	--	--	--	--	--	--	--	--	--	0.3
CuO	--	0.6	0.8	2.5	--	--	--	--	3.7	--	2.9	1.7
ZnO	--	3.5	5.3	--	--	--	--	--	--	--	--	--

Table 1. Semi-quantitative analysis of the glazed surface of 18th century earthenware tiles (piece 2 and piece 3), in areas with a different colour.

In both pieces, the decoration had been applied on to a white base glaze that had the same composition, and was similar to that of the 15th century piece. It is a glaze that consists of SiO_2, PbO, and K_2O, in which the low Na_2O, Al_2O_3, and CaO content stands out. A heterogeneous glaze is involved, with large quartz and potassium feldspar particles (up to 150 μm), spherical bubbles, and groups of small SnO_2 crystals, measuring 2 μm (Figure 2a and b). The surface of the piece contains groups of acicular cristobalite crystals, indicating that the firing cycle has been sufficiently prolonged to allow the partly dissolved quartz to recrystallise [8]. The cristobalite crystals are also observed on the edges of quartz particles in the glaze, but they are more concentrated at the surface, probably, because higher temperatures were reached during firing in that area. The white base has a pink hue, which might be related to the low quantity of SnO_2 and, perhaps, to the presence of Fe_2O_3.

In the case of the yellow and orange glazes (Figure 2c and 2d), the pigment particles were in the upper part of the glaze. In the blue and green glazes, the top layer had a more concentrated and uniform colour, the colours also being observed, albeit somewhat more tenuously, in the bottom cross-section of the glaze, near the body surface.

A lead-antimony pigment (Naples yellow) with a variable composition was used for the yellow glaze [12,13,14]. In piece 2, with an intense hue, the pigment concentration was so high that the quartz and feldspar particles in the base glaze are not observed. In contrast, in the light yellow of piece 3 (Figure 2g), the pigment crystals are observed to be very isolated, with numerous quartz particles between them, which means that the pigment is diluted in the base glaze. A variant of the Naples yellow that contained iron was also used for the orange glaze [15] (Figure 2c and 2d).

Zinc was detected in both the yellow and the orange glaze of piece 2, which was not observed in piece 3. Since the main lead mineral was galena (PbS) and this ore could be accompanied by blende (ZnS), the presence of zinc could be related to the origin of the lead used in each case. However, in *Li Tre Libri dell arte del vasaio*, Piccolpasso (16th century) describes a Naples yellow recipe that contains zinc. Dik [13] reproduced that pigment and concluded that structures of the type $Pb_2Sb_{2-x}Zn_xO_{6.5}$ could form.

The green glaze (Figure 2h) contains copper dissolved in the glass and the hue is clarified with a yellow pigment addition. In the cross-section, this element is detected throughout the thickness, which suggests that the decoration might have been applied on to a base glaze, since copper is able to diffuse extensively in the melt. In addition, the glaze composition that gave rise to this glaze could have contained Cu dissolved in water.

In piece 2, the coloration is due to cobalt dissolved in the glass, associated with iron and arsenic, elements that came from the cobalt ore used as raw material. The top part of the glaze is a quite homogeneous glass, with some partly dissolved quartz inclusions, the absence of SnO_2 crystals standing out. The lower part of the glaze is very heterogeneous: small particles of SnO_2 are close to the surface of the body and some large light-coloured crystals are observed, located approximately in the middle of the glaze layer, consisting of Pb-As-Ca (Figure 2e and 2f). The use of this phase as an opacifier in the Pb-As glazes occurs much later, which is why it may be inferred that the crystals have formed by reaction of the arsenic present in the cobalt ore with lead and calcium in the melt [8].

In contrast, in the dark blue glaze of piece 3, the cobalt is associated with Fe, Ni, and Mn. Some As/Pb/Ca crystals are observed in the cross-section, but they are very few in number, indicating that the pigment probably comes from an arseniate mixed with a different cobalt, which has been processed in a different way, since practically all the arsenic has been eliminated. The shade of blue is less intense than in piece 2 and it is clarified with brushstrokes of manganese black, which could explain the presence of this element in the glassy phase. The light-blue glaze is obtained by the application of a much more diluted pigment, since needles of cristobalite, and quartz and SnO_2 particles of the base glaze are observed from the surface (Figure 2j).

Only in piece 3 do the colours present an outline, whose hue varies from brown to black depending on the colour with which they are mixed. In every case, the analysis on these lines exhibits a high concentration of manganese and calcium, which is consistent with the literature, indicating that the black lines were obtained by outlining with manganese [16]. This element is usually accompanied by the chromophores on which it is applied. For example, when the outlining is located in the blue area, the analysis presents relatively high quantities of Fe, Co, and Ni in addition to Mn, forming diopside-type crystals.

The remaining colours of piece 3 were obtained by combining or diluting the previously described glazes with the base glaze. Thus, the brown glaze consists of an application of black on to orange (or of orange on to black). In the analysis of the lilac colour, manganese and antimony were detected, which is in accordance with the practice of applying a first watered-down yellow base and painting on top with manganese oxide [1]. Finally, the turquoise blue glaze (Figure 2i) is due to the joint presence of copper dissolved in the glass in a smaller concentration than in the green glaze, and crystals of Naples yellow.

The analysis of pieces 4 and 5 shows that, in the 19th century, the composition was practically maintained of the white base glaze ($PbO-SiO_2-K_2O$) with SnO_2 as an opacifier and the addition of quartz and feldspar. The blue glaze continued to have cobalt dissolved in the glass, together with some iron. Naples yellow was still used, without zinc. The green glaze was different: the glass contained a smaller quantity of cobalt and iron than the blue glaze and no copper, and there were some yellow pigment crystals, which is why the green glaze may have been obtained with a diluted mixture of blue and yellow. A coral-coloured pigment appeared in piece 4 (not found in the colour palette of the previous century), which consisted of Pb-Sb crystals with an inverse Pb/Sb ratio with respect to the yellow pigment of the 18th century dispersed in a glass with iron. The black glaze was also different, and was formed by crystals of an iron oxide, possibly magnetite, which suggests that the glazed piece was fired in reducing atmosphere.

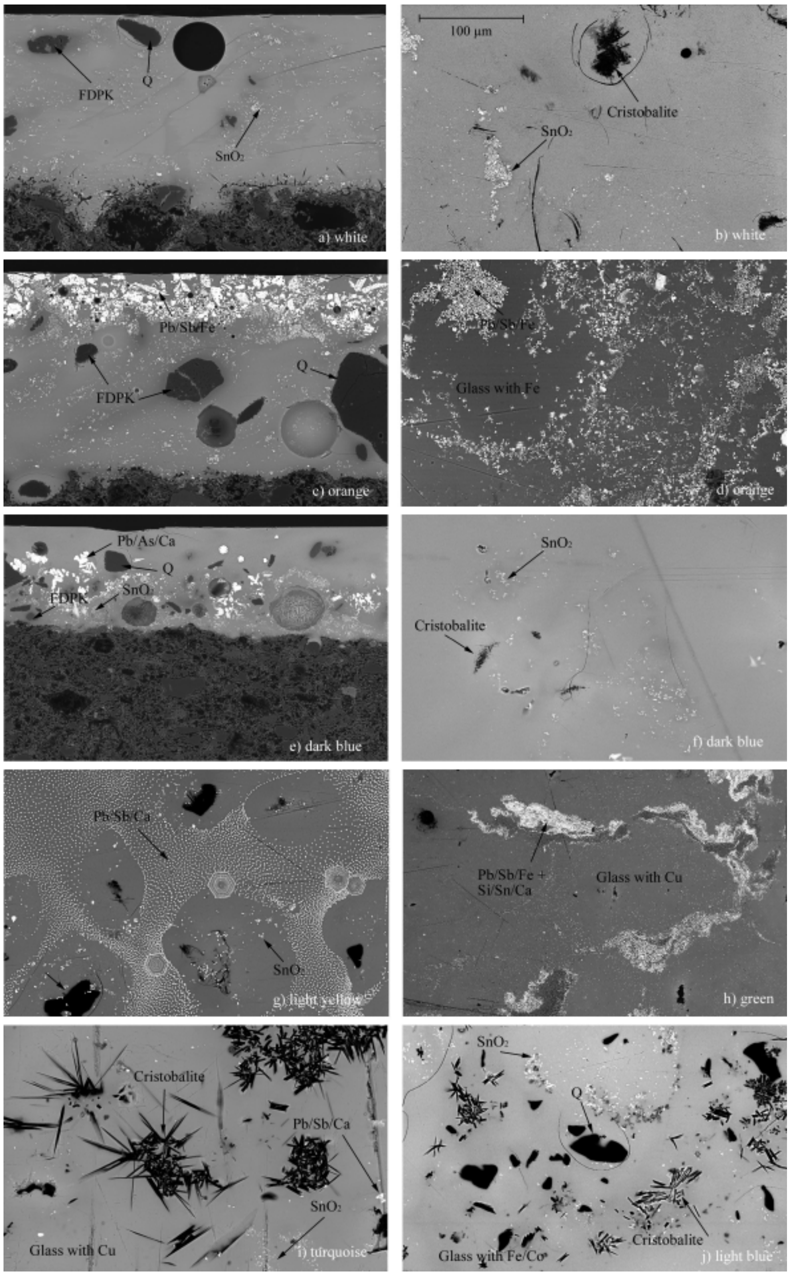

Figure 2. Surface and cross-section of glazes with different colours in the pieces from the 18th century.

From the characterisation of the pieces and the references [1,17] it may be concluded that the base glaze was, in all cases, a lead glaze, with a high potassium content and a more or less matt appearance, which possibly depended on the quantity of unmelted added materials.

When piece 3 is compared with the court scene of the Vallvert palace kitchen (Figure 1), it may be observed that they have very similar hues; and further, in both cases, the size of the earthenware tiles is the Valencian handspan and the decoration is polychromatic with a manganese outline. In the characterisation it was verified that piece 3 displayed the typical features of tiles fabricated in the city of Valencia in the last quarter of the 18th century. Its decoration matches the basic colour palette of the Rococo period [1] and includes Naples yellow; orange (obtained by adding iron to the yellow pigment); cobalt blue, which allowed different shades of blue as a function of the dilution and addition or non-addition of black glaze; copper green, which could take on shades ranging from turquoise (in more alkaline glazes) to a bottle green (more leaded glazes), via luminous colours if it was combined with Naples yellow; and manganese purple that, with yellow pigment, gave warm colours, and combined with blue pigment, cold violets. In order to delineate or to darken some colours, manganese oxide was used. Its great chromatic variety was obtained by more or less watered-down basic pigments being brushstroked on top.

Piece 3 has been selected, therefore, as a reference for the gloss and the hue of the glaze, and for the chromatic characteristics of the inks to be used in the reproduction.

4.2. SELECTION OF THE BASE GLAZE AND THE SET OF JET INKS

The gloss of the white base glaze was measured. This was found to be 45‰ (measured at 60°), which corresponded to a semi-gloss texture. A glaze was chosen, therefore, that provided this texture and it was judiciously reformulated to obtain the appearance of the white glazes of the 18th century.

The colorimetric curves of the most significant colours of piece 3 are presented in Figure 3. It was not possible to determine the curve of the black, because it only appeared in piece 3 in the outlining and the curve changed depending on the pigments with which it was mixed.

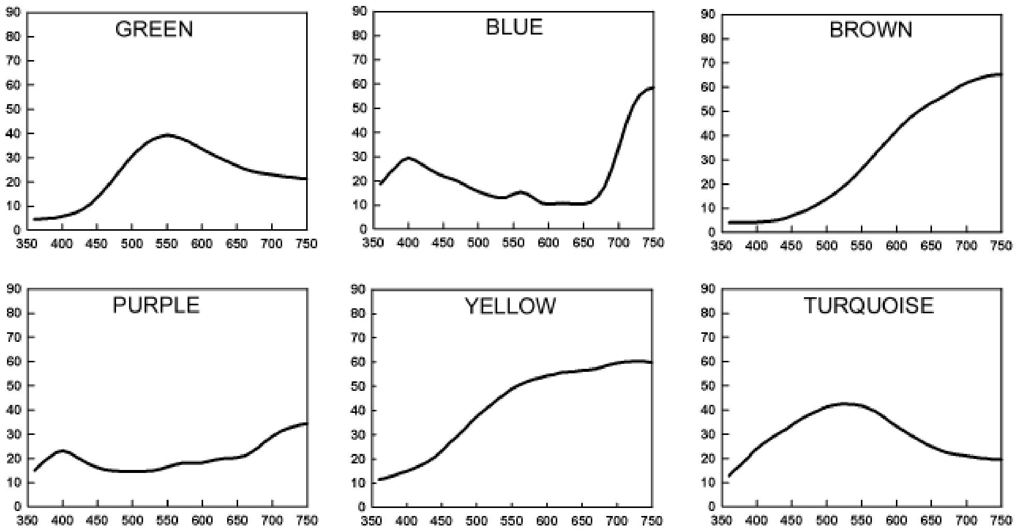

Figure 3, Spectrophotometric curves of the glazes in piece 3 (18th century). Reflectance in % versus wavelength in nm

For the reproduction, a set of six compatible jet inks were selected, prepared from current ceramic pigments, in an attempt to reproduce the chromatic characteristics of the basic colours of piece 3. The four basic pigments that are customarily used in ceramic four-colour printing (blue, brown, yellow, and black) could not reproduce the subtleness of the colours obtained by applying watered down brushstrokes of manganese or copper green on to the other pigments. A pink ink and a green ink were added, therefore, to the basic palette. These two inks, by mixture with the others, allowed the magenta and cyan of classic four-colour printing to be simulated. A cobalt pigment was selected for blue. The colorimetric curves of the glazes obtained by application of the pure inks are presented in Figure 4.

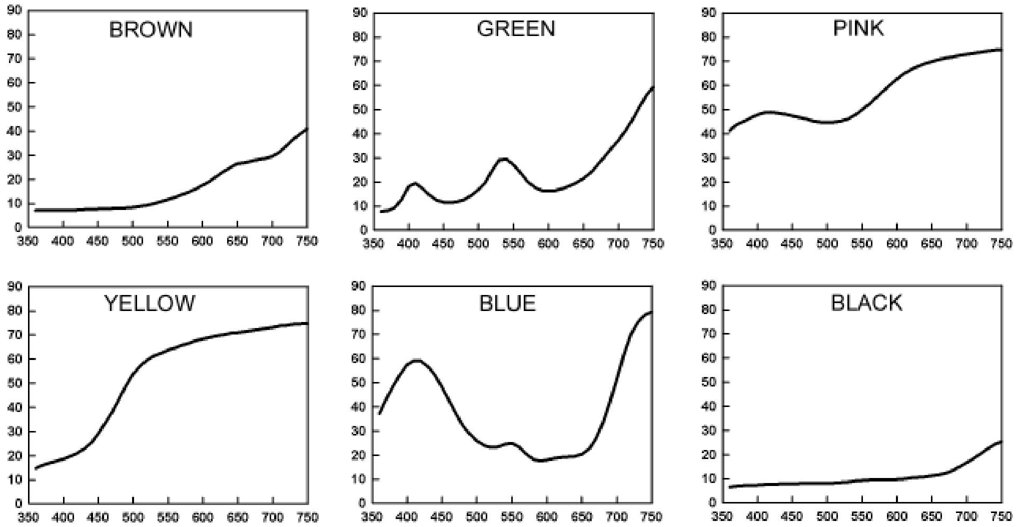

Figure 4. Spectrophotometric curves of the glazes obtained by applying the pure inks. Reflectance in % versus wavelength in nm

The most important physical characteristics of the prepared inks were as follows: viscosity (10-15 cP), electric conductivity (100 µS), surface tension 28-30 mN/m, and particle sizes between 200 and 400 nm.

4.3. IMAGE PROCESSING

A 5x7 cm slide was available of the entire ceramic ensemble, which was scanned in order to be able digitise the image; this meant a limitation of the final resolution of the reproduced pieced, because in order to be able to print at real size, it was necessary to magnify the digital image 400 times. This image was processed by Photoshop CS2 editing software in order to eliminate image background noise. The intensity of the colours in the entire image was compensated in order to correct the reflections that existed due to deficient lighting when the photograph was taken of the ceramic ensemble.

The tile-to-tile joints of the earthenware tiles were also eliminated in order to obtain a continuous image, without these joints appearing in the print. The size of the image was processed in order to make the position of the earthenware tile joints coincide with the ones existing in the original tiling. The result obtained is shown in Figure 5.

Figure 5. Image obtained after eliminating the tile joints.

The image was processed using the CMYK colour model at a resolution of 254 dpi. It was necessary previously to obtain the profile of the system (base glaze plus the four developed inks corresponding to the CMYK colours). This step was needed in order to be able to visualise the chromaticity of the CMYK ceramic inks on the computer screen after firing. Two additional alpha colour channels were then created to complete the design and obtain the eight different colours observed in the original pieces.

The fragment that has been reproduced consists of 8x9 pieces, and measures 170x190 cm.

4.4. DECORATION BY DIGITAL JET PRINTING

The pieces were printed in two steps, since the plotter only had four heads and it was necessary to apply six inks. In the first step the four-colour printing model was used with four inks: blue, brown, yellow, and black; in the second, the two inks (pink and green) developed specifically for this study were applied, thus completing the areas of the design where the chromatic range obtained with four-colour printing was insufficient.

These printing heads printed at a resolution of 180 dpi. In order to be able to increase the printing resolution to 360 dpi, a computer simulation was performed in the plotter of the operation of an industrial digital jet printing system with a double printing head for each ink.

The foregoing allowed reproduction of the selected fragment from the Baron of Vallvert palace kitchen with optimum characteristics in regard to definition, colour, and hue, as illustrated in Figure 6.

Figure 6. Reproduction of the court scene in the Baron of Vallvert palace kitchen.

5. CONCLUSIONS

A methodology has been developed to reproduce the decorative motifs and chromatic range of heritage tiles. The methodology allows damaged or lost pieces to be replaced, and original ones located in exposed places to be replaced with a copy, in order to assure conservation of the originals under appropriate conditions. The methodology is based on three phases: characterisation of the materials to be reproduced using SEM-EDAX; acquisition and digital processing of the decorative designs to separate the different colours; and development of a set of inks for digital jet printing which allow the chromatic range of the tiles to be reproduced. The methodology has been validated by the reproduction of tiles from an 18th century Valencian palace kitchen, characterised by the complexity and chromatic wealth of the decoration.

REFERENCES

[1] VIZCAÍNO, M.A. Azulejos barrocos valencianos. Valencia: Federico Domenech, 1999.

[2] BULTRINI, G. et al. Characterization and reproduction of yellow pigments used in central Italy during Renaissance. Appl. Phys. A. 83, 557-565, 2006.

[3] ESCRIVÁ DE ROMANÍ, M. Historia de la cerámica de Alcora estudio crítico de la fábrica, recetas originales de sus más afamados artífices, antiguos reglamentos de la misma. Madrid: Aldus, 1945.

[4] LUCAS, F. et al. Rediseño industrial de azulejos tradicionales valencianos. Bol. Soc. Esp. Ceram. Vidr. 39 (1), 39-53, 2000.

[5] PÉREZ GUILLÉN, I.V. La azulejería rococó. La cocina valenciana del proveedor de nieve. Narria, 65-66, 13-21, 1994

[6] SONG, J.H., EDIRISINGHE, M.J., EVANS, J.R.G. Formulation and multilayer jet printing of ceramic inks. J. Am. Ceram. Soc., 82 (12), 3374–80, 1999.

[7] TENG, W.D. EDIRISINGHE, M.J., EVANS, J.R.G. Optimization of dispersion and viscosity of a ceramic jet printing ink. J. Am. Ceram. Soc., 80 (2), 486–94, 1997.

[8] ZUCCHIATTI, A. et al. The "Della Robbia Blue": a case study for the use of cobalt pigments in ceramics during the italian Renaissance. Archaeometry, 48, 131-152, 2006.

[9] PADELETTI, G. et al. First-time observation of Mastro Giorgio masterpieces by means of non-destructive techniques. Appl. Phys. A, 83, 475-483, 2006.

[10] ROLDÁN, C.; COLL, J.; FERRERO, J. EDXRF analysis of blue pigments used in Valencian ceramics from the 14th century to modern times. J. Cult. Herit. 7, 134-138, 2006.

[11] MOIOLI, P.; SECCARONI, C. Analysis of art objects using a portable X-ray fluorescence spectrometer. X-Ray Spectrom. 29, 48-52, 2000.

[12] BULTRINI, G. et al. Characterizsation and reproduction of yellow pigments used in central Italy for decorating ceramica during Renaissance. Appl. Phys. A, 83, 557-565, 2006.

[13] DIK, J. et al. Early production recipes for lead antimoniate yellow in italian art. Archaeometry, 47, 593-607, 2005.

[14] SAKELLRIOU, K. et al. Spectroscopic investigation of yellow majolica glazes. J. Raman Spectrosc. 35, 61-67, 2004.

[15] PADILLA, R. et al. Microanalytical characterization of surface decoration in Majolica pottery. Anal. Chim. Acta, 535, 201-211, 2005.

[16] COLL CONESA, J. Historia de la Cerámica Valenciana. [en línea] Valencia: AVEC, [s.a.] http://www.avec.com/historia_de_la_ceramica_valenciana.asp [Consulta: 2007-09-13]

[17] AURA, E. Desarrollo de procedimientos metodológicos para la caracterización, restauración, y conservación de piezas cerámicas medievales (Siglos XIII-XV) de Paterna y Manises. Valencia: Universidad Politécnica de Valencia. 1996. [Tesis doctoral]