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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

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Abstract

Cobalt-blue-decorated ceramics with tin glazes have been produced in the Iberian Peninsula since the 14th century AD and in Aragon region since the 15th century until the present time. An important ceramic trade was developed and relations with potters of other important production centres were established. Representative objects from archaeological findings could help in drawing conclusions on the technology used in the manufacture of blue-decoration ceramics. In this work, the composition of bodies and glazes of more than fifty samples of blue-decorated ceramics from Aragon was determined by ICPAES and EDX–Scanning Electron Microscopy (SEM). Based on this information, different ceramic groups could be appreciated and reference values valuable for the subsequent study of the blue decorations by means of other techniques, such as laser ablation (LA)–ICPMS, were also obtained. In particular, the data obtained permitted to unequivocally establish the use of three different types of cobalt pigments, with clear changes between areas and periods. Moreover, it is demonstrated that this evolution in the nature of the blue pigments was related to a different procedure when decorating the object, namely the application of the pigments and the drawing the designs before (under glaze) or after (on glaze) covering the ceramic with the tin glaze.

Keywords: Electron microscopy; Microstructure-final; Spectroscopy; Colour; Traditional ceramics

1. Introduction

A detailed knowledge of the characteristics and production methods of ancient ceramics is crucial not only for solving problems of conservation or authentication, but also for establishing the art and ceramic technological development typical of a population, in a geographical region and in a particular historical period. Since the Middle Age, through the influence of the Islamic culture that introduced the manufacture of tin-glazed ceramics, cobalt-blue-decorated ceramics have been produced in several places in Europe and their beautiful colour has always attracted people's attention.[1–11] In the Iberian Peninsula, blue-decorated tin-glazed ceramics have been produced, at least, since the 14th century AD.[5] Some workshops in Aragon (Fig. 1) have produced this type of decoration since the 15th century until the present time. These products show good quality and, consequently, an important ceramic trade was developed with other areas and relations with potters of other important production centres (e.g. Valencia and Italy) were established.[10,11]

The ceramic workshops of Teruel had begun to be important at the end of the 13th century AD, when the town enjoyed a flourishing economy, and all the Aragon Kingdom was in the culmination of a long period of demographic and fruitful development. At that moment, a tin-glazed ceramic decorated with green and brown designs (Cu and Mn pigments) had started to be produced and continued until the 20th century. In Teruel lustre pottery production is not documented, but in the 15th century potters introduced the fabrication of blue-decorated objects, initially copying the decoration of Valencia lustre ceramics but with their own variety of designs and compositions since the half 15th century. In the beginning, they were only blue decorations on white glazes, but since the 17th century the blue was also combined with green or brown.[10]

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Fig. 1. Map of the Iberian Peninsula showing cities with ceramic workshops (cities in lower case are only indicated to provide a geographical reference). Blue-decorated ceramic from Teruel, 15th century AD.

In the area of Zaragoza, ceramic production attained one of the most splendorous periods about 1500 AD, together with a great economical development of the region. Muel workshops seem to have been the most important site producing tin-glazed pottery in the area, but other places like the town of Zaragoza or other small villages also produced the same type of ceramics. The strong relations among all these places lead to very homogeneous typologies and decorations, this is why ceramic production is said from Muel or called "Muel type".[11] During the 15th and 16th centuries Muel workshops produced tin-glazed ceramics decorated with brown and green designs and with blue drawings from the 16th century, or with combinations of these colours until nowadays. Lustre pottery was also produced in Muel for a long period, but especially in the 16th century, before the expulsion of the Moriscos ("Muslims convert to Christianity") ordered by Philip III in 1610. After this date, ceramic production continued in Muel probably influenced by potters coming from Catalonia (Reus) or Valencia. Afterwards, ceramic manufacture in the area of Zaragoza was also influenced by the arrival of potters and merchants from Liguria (Italy).

Many studies have been carried out on glaze compositions of this type of pottery and on the characterisation of the blue pigments, also currently, in order to know the nature of the glazes and even the possibility of identify the cobalt sources used for the pigments. In this case, the study of a representative group of objects from archaeological findings could help in drawing relevant conclusions on the technology used in their manufacture in the Iberian Peninsula, with questions on materials using, technological changes and pigments. Therefore, the aim of this research was focused on characterise the materials and the technology patterns used for the production of blue-decorated ceramics in a particular area and period, taking into account their special features, and since these workshops collected previous Islamic and Hispano-Moresque ceramic influences in the region and the contacts with other Iberian and European areas at that moment.

2. Methods and techniques

Thirty-two ceramic fragments from the Museum of Teruel (labelled with T) and twenty-two ceramic fragments from the Museum of Zaragoza (labelled as Z and M) were subjected to the study. They belong to objects decorated in blue with white glazes (see Fig. 1). They were dated from the beginning of the 15th century AD to the end of the 18th century AD, found in different archaeological sites in Zaragoza and Teruel, and selected in order to cover a wide chronological period and to study samples produced in the area of Aragon (Spain), in Teruel or in ceramic workshops near Zaragoza, probably in Muel.

A Thermo Elemental Iris Intrepid Radial spectrometer was used for ICPAES analysis of ceramic body, from acid solutions of the powdered samples extracted by drilling in freshly fractured surfaces of the shards. The following elements, present as major or minor elements, were determined: Na, Mg, Al, K, Ca, Ti, Mn, Fe, Sr and Ba.

A JEOL JSM 6400 was used for the Scanning Electron Microscopy (SEM) observations of the ceramics. The SEM was equipped with a system for Energy Dispersive X-ray Analysis, EDXA (Oxford Instruments, INCAx-sight). Cross-section preparations were obtained by cutting with a diamond saw the samples embedded in an epoxi resin. Also small ceramic fragments were cut for direct observation of the glaze surface. For SEM study of the glazes, the acceleration voltage applied was 20 kV, with a 0.6 nA current probe. Bulk glaze analyses were done by scanning a relatively large area (×2000 magnification) of the glaze matrix and by acquiring data from 10 different areas. Samples were prepared as polished ceramic cross-sections and were carbon-coated afterwards for quantitative analysis, or just directly monitored for the observation of the surface characteristics.

Direct analysis of the blue decoration was accomplished by using laser ablation (LA) for sample introduction in the ICPMS. A GeoLas ArF excimer-based LA system (MicroLas) was used, with the 193 nm UV laser beam coming from the Compex102 laser unit (LambdaPhysik). The ablation cell was coupled to the ICP torch via a 3 mm internal diameter Tygon tubing. Ar was used as the carrier gas. All measurements were carried out using a PerkinElmer Sciex DRCplus quadrupole-based ICP-mass spectrometer. More than 30 nuclides were monitored in each sample, although some elements were under detection in several samples or not associated to cobalt pigments and finally they were not used for the characterisation, with a method of 300 laser-pulses/spot (1 μg of sample ablated) and 5 spots/sample. More detailed LA–ICPMS procedure has been explained in precedent papers.[12,13]

Reflectance UV–vis spectra have been recorded on the blue ceramic surfaces, using a Minolta CM-2600d model portable spectrophotometer, equipped with a 52-mm barium sulphate integrating sphere, dual-beam geometry, a 360–740 nm wavelength range with 10 nm measurement intervals of 3 s and irradiating a 3-mm diameter area. From the dispersion of reflectance measurements, colour coordinates (L^*, a^*, b^*) were calculated according to the International Commission on Illumination (usually known as the CIE, Commission Internationale de l'Eclairage), after calibration against a white standard plate. In this method, L^* is the lightness axis [black (0) to white (100)], b^* is the blue (−) to yellow (+) axis, a^* is the green (−) to red (+) axis, and ΔE is the hue variation ($\Delta E^2 = (L^*)^2 + (a^*)^2 + (b^*)^2$).

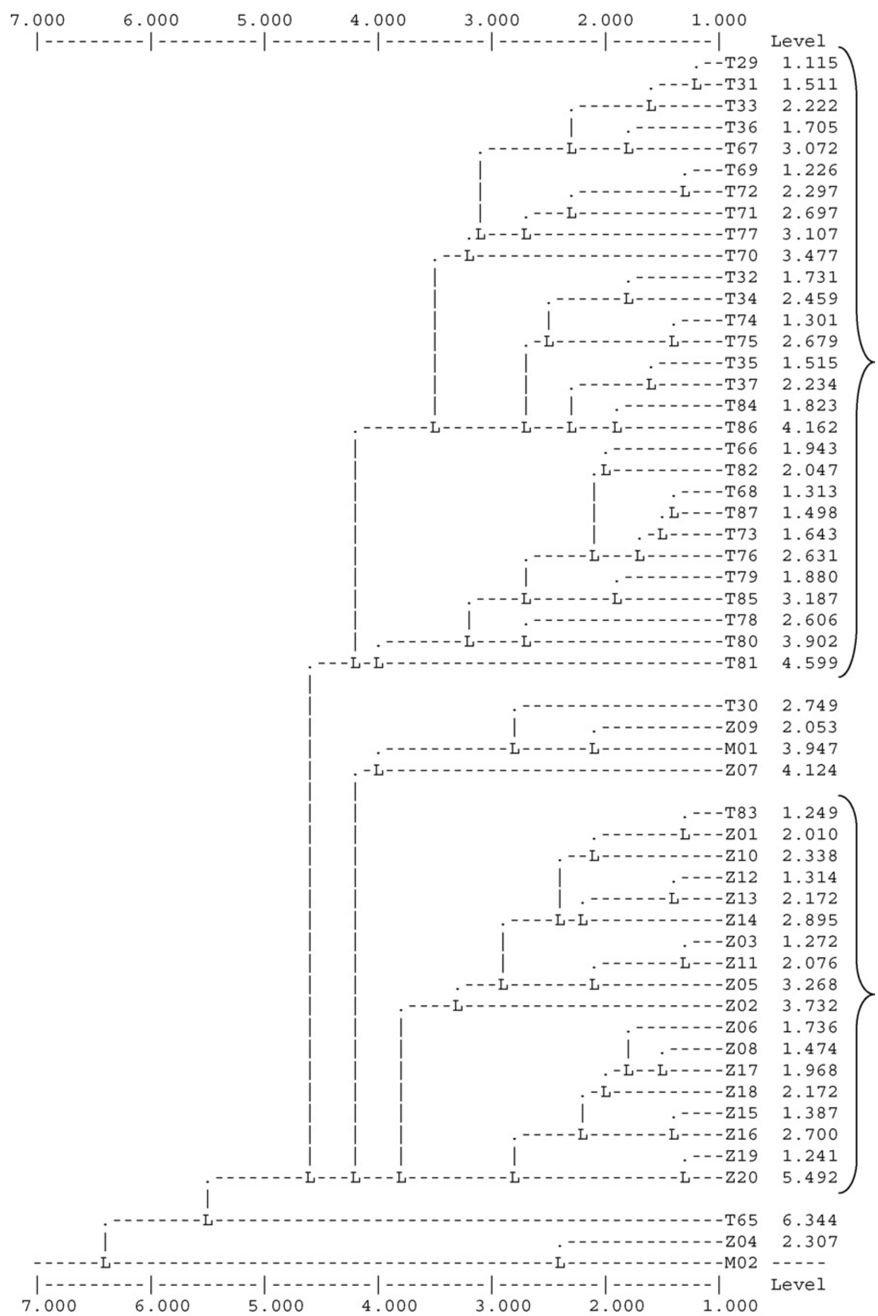

Fig. 2. Dendrogram from the statistical treatment of the ceramic body composition analyses.

Table 1
Chemical composition of the ceramic bodies (wt%, except Ba and Sr in $\mu g\,g^{-1}$). Average composition and standard deviation (SD) of both groups.

	Na_2O	MgO	Al_2O_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Ba	Sr
Teruel	0.431	1.64	16.3	2.72	16.1	0.640	0.0370	5.37	404	371
SD	0.137	0.34	2.2	0.49	3.4	0.080	0.0124	0.90	57	138
Muel	0.628	2.65	13.8	2.64	14.1	0.658	0.0677	5.23	594	352
SD	0.275	0.37	1.6	0.46	2.0	0.100	0.0085	0.55	97	89

3. Results and discussion

3.1. The objects: bodies and glazes

Analytical results of the body chemical composition allowed a good differentiation between the blue-decorated ceramic produced in Teruel and Muel to be established. After a statistical treatment for classifying them (see Fig. 2), excluding some outliers that also showed differences in other aspects (T30, T65, Z04, Z07, Z09, M01, M02), the average composition of both groups is given in Table 1. Only a type of ceramic body was used in each site for blue-decorated tin-glazed pottery. In both cases, objects are made with very fine calcareous clays, with similar proportions of calcium, but other elements like magnesium, manganese or barium, for instance, permit to distinguish both productions very well. This clear differentiation between samples from Teruel and from Muel allows guaranteeing that the studied samples belong to one of both historical sites, and both groups to be defined. The use of this type of calcareous clays is a continuous characteristic in most of the tin-glazed ceramics produced in the Iberian Peninsula[14–18] due to the dissolution of the iron oxides in the clay induced by the presence of calcium and the consequent white-buff colour.[19]

Also at present, the higher number of ceramic bodies analysed from Teruel, moreover produced in a wide period, leads to conclude that in this pottery site only two types of clay pastes were used in tin-glazed ceramics for centuries: a less-calcareous red clay (around 7.5% CaO) for those decorated with green-and-brown designs (since the 13th century AD to nowadays)[17] and another calcareous cream paste for those decorated in blue. Therefore, the only important technological change for such long period, regarding the ceramic body, was the introduction of this calcareous clay with the first blue-decorated glazes at the beginning of the 15th century AD. However, among the ceramic objects produced in Muel, in spite of the different decorations applied (blue, green or lustre) no change or difference in body composition has been observed.[18]

Chemical composition of tin glazes shows also some slight differences between the two groups, but very similar glazes were used in all the Iberian Peninsula since Islamic and medieval times and later, always with high content of lead.[15,17,18,20–23] Both chemical compositions of tin-glazes are shown in Table 2, obtained analysing only the white areas. These tin-glazes were the result of using a mixture of lead and alkali with sand or quartz and some clay (see aluminium content), but very pure sand and white clay were used, because the iron content is nearly below the detection limits (<0.5% FeO) in all the glaze samples. The tin oxide content ranges from 3 to 12% in samples from Teruel and from 3 to 5.5% in Muel fragments, which is enough to produce opacity, although little quantity is present in some cases. In spite of the similarity between Iberian lead glazes, the composition of the studied glazes shows higher percentages of potassium, a feature presented also in tin glazes with lustre decoration,[18,24] and it could be used to characterise them. This fact could be also linked to a connection between potters making lustre and blue-decorated pottery.

Table 2
Average chemical composition of tin-glazes (wt%) obtained by SEM–EDS analysis (SD: standard deviation).

	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	SnO_2	PbO
Teruel	<0.50	3.31	44.9	4.78	1.83	6.29	36.8
SD		1.09	2.7	0.91	0.60	2.20	3.4
Muel	0.77	3.97	52.7	5.12	2.06	4.52	30.1
SD	0.31	0.44	1.8	0.98	0.55	0.86	2.5

Regarding the microstructure of the tin-glazes, SEM observations indicate that all the glazes have a similar thickness (between 125 and 150 μm). All of them were put on pre-fired (biscuit) bodies and then fired again, as indicated by the very thin interaction layer (<10 μm) observed between glaze and body (Fig. 3).[25] Few non-plastic inclusions, especially quartz, seem to be included in the glazes from Teruel and Muel. The presence of quartz inclusions has been demonstrated to be characteristic of some Islamic tin-glazes (from Zaragoza, Granada or Pechina) or be absent in others (from Murcia and Denia),[15] or be useful to differentiate

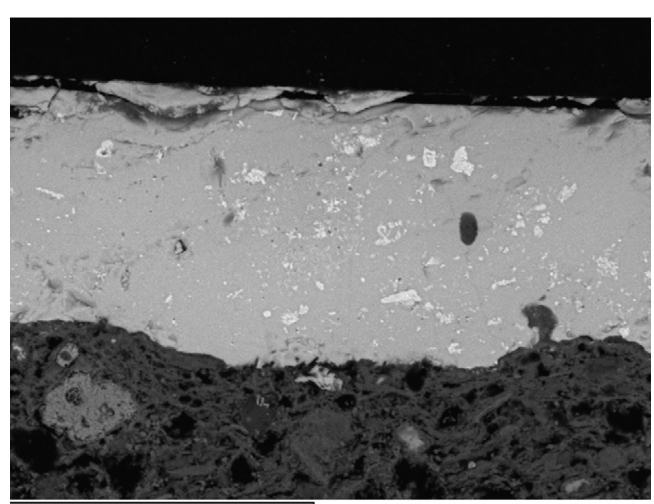

Fig. 3. SEM image (BSE) of a tin-glazed ceramic from Teruel, 15th century AD (image length 200 μm).

groups inside a ceramic production.[17] Tin is present in the glaze as tin-oxide (SnO_2) crystals (cassiterite) that produce the glaze opacification. These crystals appear randomly scattered, causing a high heterogeneity, but, at the same time, grouped in clusters, in such way that there are areas where many crystals are included and other areas where there are no crystals (Fig. 3). In general, the dimensions of tin-oxide crystals are between 1 and 2 μm, so they can be compared with glazes from other periods or places and, for instance, they are bigger than the cassiterite crystals in Islamic tin-glazes,[15] and these dimensions can be related to the fritting and firing processes.[26] In some samples, big fragments of tin oxide with angular forms were even found in the glaze, which could have been originated during the grinding process of the fritted raw materials obtained by heating lead and tin metals and used to produce the opaque glaze.[10]

3.2. *Tin-glazes decorated in blue*

3.2.1. *Blue pigment characteristics*

If we focus the attention on the characterisation of the blue decoration, the chemical composition was identified by LA–ICPMS. Although more than thirty nuclides were monitored by LA–ICPMS, only some of them were finally useful for the pigment characterisation. Cobalt is the element responsible of the blue colour in all glazes. In order to avoid the variability of the pigment amount in each decoration, since deeper blue means more quantity of cobalt and subsequently more quantity of trace elements, all the intensity values were normalized to cobalt signal. In this way, variability of the ratio values would mean variability in the composition of the pigments. Apart from the cobalt, the presence of some elements attributed to the blue glaze could be related to the cobalt source (the mineral ore) or the way to prepare the blue pigment from the mineral ore, and they could be used as markers or "fingerprint" of a ceramic group.

The presence of Fe and Ni (at the $mg\,g^{-1}$ level) in all blue decorations was confirmed and linked to the cobalt pigment, as it is shown by the high correlation between these elements and the Co content (r value between 0.8 and 0.9) and SEM observations would also demonstrate later on. This high correlation observed in all blue samples analysed is important for the investigation on cobalt sources, but unfortunately it makes Fe and Ni not significant for establishing differences into or between the ceramic groups investigated.

One of the elements monitored by LA–ICPMS that is characteristic of one of the groups was Cu. Samples from Teruel dated in the 15th century and the beginning of the 16th century AD showed a high Cu/Co ratio (see Fig. 4 and Table 3). These 15 samples were included in a group, with also lower content of As (≈50 times compared with other glazes), and labelled Teruel1. This second element, As, is another significant element in the blue-decorated glazes. Fragments dated in the 16th century AD or later have always a higher As/Co ratio (see Fig. 4 and Table 3). This difference in ceramics from the Iberian Peninsula was already noted in previous papers,[12,13,27] and also in other European blue-decorated ceramic materials.[8,9,28] Among samples with higher As/Co level, fragments from Teruel and Muel are both included but, if we also consider the Mn/Co ratio, two new different groups can be separated: one with high Mn/Co proportions including samples from Teruel, dated in the middle-16th and 17th centuries AD (labelled Teruel2), and the second one with very low content of Mn generated for the 17th and 18th centuries ceramics from Muel, including 15 samples, labelled Muel1 (see Fig. 4 and Table 3). These three elements help objects to be differentiated and grouped by provenance and chronology.

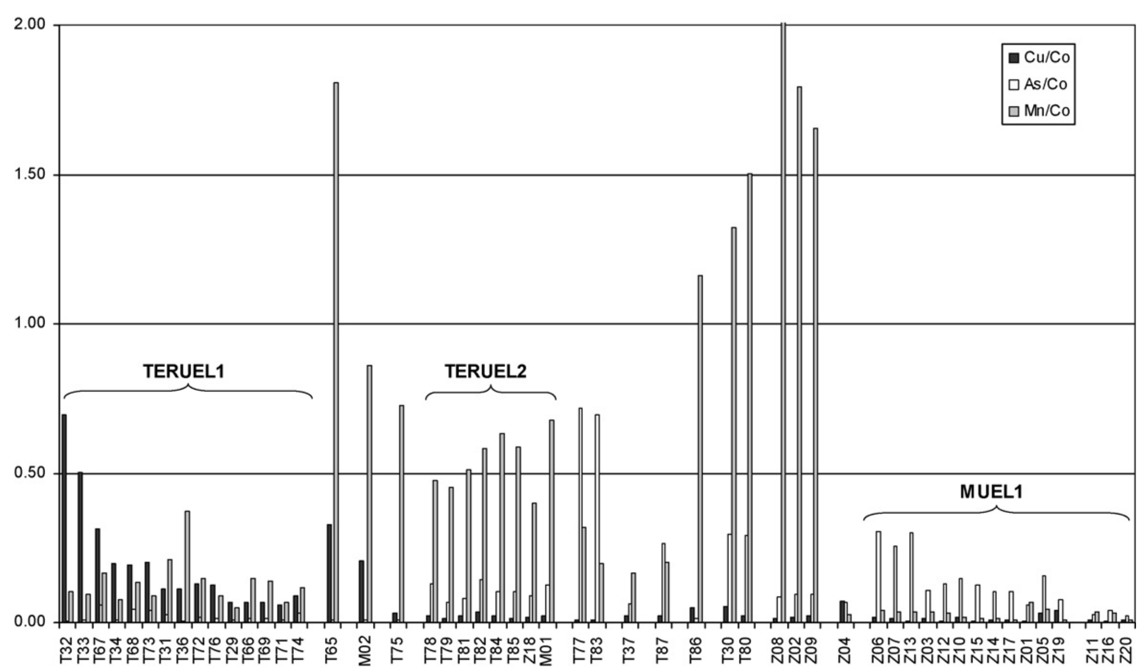

Fig. 4. Normalized signal intensity values for the elements of interest (Cu/Co, As/Co, Mn/Co) in blue decoration of the ceramics using LA–ICPMS.

Table 3
Summary of the main characteristics of blue decorations (Cu/Co, As/Co, Mn/Co are normalized signal intensity values).

	Cu/Co	As/Co	Mn/Co	Co source	Chronology	Decoration
Teruel1 ($n=15$)	0.06–0.70	0.005–0.03	0.05–0.20	Co–Cu–Fe–Ni (Mn, As)	15th–beginning 16th century	Under
Teruel2 ($n=8$)	0.01–0.03	0.07–0.14	0.40–0.65	Co–Mn–As–Ni–Fe (Cu)	Middle 16th–17th century	On
Muel1 ($n=15$)	0.002–0.03	0.04–0.30	0.01–0.06	Co–As–Ni–Fe (Mn–Zn)	17th–18th century	On
Muel2 ($n=3$)	0.01–0.02	0.08–0.10	1.6–3.5	Co–Mn–As–Ni–Fe	16th century	On

There are also other samples that could be clearly distinguished by the highest Mn/Co ratio. Some fragments from Muel (Z02, Z08, Z09) have this high Mn/Co ratio, with similar As proportions to Muel1 (labelled Muel2), in this group are included ceramics dated in the end-16th and 17th centuries AD (see Table 3). Also sample T30 (outlier in body analysis) and T80 have these features and they are dated in the second-half 16th century. Other samples from Teruel, like T65 (outlier), T75 and T86, have a very high proportion of Mn and, however, low contents of As (like Teruel1), but they additionally have different chronologies (dated in the 15th century (T65, T75) and the 18th to 19th century (T86)). It is more difficult to establish a provenance for this fourth group with the highest quantity of manganese, due to the small number of samples and their diversity; it could belong to workshops in Teruel or in the area of Muel, or even have more than one origin.

Other samples could not be grouped, including some of them with highest As/Co ratios (T77 and T83). Among exceptions, fragments T37 and T77 (dated of the 16th century) show also higher Zn content, although other samples (T78 and T80, both 16th-century dated, see above) showed also high Zn/Co ratios. High Zn proportion seems to be characteristic of blue-decorated ceramic of more ancient chronology in the Iberian Peninsula,[13,27] but very few Iberian samples have been still studied from this early period to establish a relation between chronology and Zn content.

Therefore, using the ratios of these three elements (Cu, As and Mn), a good differentiation according provenance and chronology could be established for blue-decorated ceramics from the area of Aragon, and these elements can serve as "markers" of the main pigments used in this ceramic production (see Table 3).

On the other hand, related to the possible cobalt sources of the three pigment groups, although it was out of the aim of this study to find the cobalt origin, it must be taken into account that not only these three elements but also others are associated to cobalt, like Ni and Fe, even with high correlation in objects from both production areas. For instance, Cu is characteristic of 15th century samples from Teruel for its highest proportion (Teruel1), but Cu and Co seem to be also slightly correlated (*r* value is circa 0.7) in fragments from Teruel2 and Muel1 in spite of their low content. Something similar happens for As, it becomes distinctive in blue samples since the 16th century (Teruel2 and Muel1), but As and Co are also linked (*r* value is circa 0.8) in early glazes (Teruel1). This element shows also a certain association with Bi (*r* value is 0.6 between As and Bi, in samples from Muel1). Manganese is an element with very high correlation with Co in the three groups (*r* values are 0.92 in Teruel1, 0.99 in Teruel2 and 0.75 in Muel1). Finally, Zn and Co have a correlation coefficient (*r* value) higher than 0.9 for Muel1 samples. Then, cobalt pigments must be linked to cobalt ores with minerals where the quantity of Co is related to compounds with Fe, Ni, Cu, As, Mn, Bi or Zn. Cobalt pigments of every ceramic group could be summarised as: Co–Cu–Fe–Ni (Mn, As) for Teruel1, Co–Mn–As–Ni–Fe (Cu) for Teruel2 and Co–As–Ni–Fe (Mn–Zn) for Muel1 (in parentheses appear elements correlated to Co but included in low proportions in the pigment).

For a chemical association of Co–As–Ni–Bi–Fe in ceramic samples produced between the 16th and 18th centuries AD, several authors[9,28] proposed Schneeberg mines (Erzgebirge mountain range, Germany) as the cobalt ore source, which could correspond to pigment used in Muel1 group. Pigments must have been prepared from a cobalt–arsenic mineral, like the German ores, but these minerals are also present in the Pyrenees (Gistain Valley, Huesca) and were commercially extracted (San Carlos mine) since 1730 until 1945, therefore, could have been also the source of cobalt during the last period of ceramic production in the area of Zaragoza.

The fact that As content in blue pigments increases from the 16th century AD (like Teruel2, Muel1 and Muel2) in other European areas has been explained for some authors because of a different way of preparing the pigment from the mineral ores since the introduction of the zaffre manufacture by Peter Weidenhammer in 1520,[9,29] and the commercial production of "smalt" in Saxony in the 16th century,[2] assuming that the source of materials was the same across a long historical period. Some fragments from Teruel dated of the 18th to 19th century showed again low As/Co proportions, probably already suggesting the more recent use of very pure cobalt pigments.

For cobalt pigments used in glass and ceramic where Co is associated to Cu or Mn, more ancient chronologies (from the protohistory to the 13th century AD) and a cobalt source of unknown origin have been proposed.[28] This is not the case of the samples analysed, because Teruel1 and Teruel2 groups have chronologies from the 15th to the 17th centuries AD but their cobalt pigment is highly related with Mn and Cu. For Teruel1 group, cobalt source should be related to a cobalt-associated copper mineral and this could have been a probable source, since cobalt production is usually linked to copper mining and there are important copper ores (chalcopyrite, $CuFeS_2$) in Teruel area that could have been exploited in that period and used as local small sources of the mineral.[1] The more important presence of Mn in Teruel2 group could be linked to the use of a cobalt-associated manganese mineral for preparing the pigment.

Due to the fact that Co in both Teruel groups is highly correlated to Mn, if the same or a very near source of cobalt was used in both cases, a different way of extracting the cobalt from the mineral since the 16th century or a diverse manipulation of the pigments could also explain the differences for Cu and Mn between Teruel1 and Teruel2. During the previous preparation of pigment used in Teruel1, Cu could remain in the same phase than Co, whereas As and Mn went to another phase; however, with a different preparation As and Mn could keep with Co and then Cu could be separated. A correlation between Mn and Cu, that would reinforce the hypothesis of a common source, has been also observed in manganese pigments used to decorate tin-glazes with black lines on ceramics produced in Teruel in the 13th century until the 16th century AD where Mn appears as responsible of the colour but always with small quantity of Cu.[17]

3.2.2. *Blue pigment application for decorating glazes*

Before discussing other possible reasons for chemical differences between the studied groups, another technological feature in the pattern of application of these blue pigments on the ceramic must be considered. Cross-sections of all the samples were studied by Light Microscopy and SEM and an interesting difference was observed between samples: all fragments from Teruel dated in the 15th century or the beginning of the 16th century showed a dark blue layer between clay and glaze (Fig. 5a). By SEM–EDS it was confirmed that these layers corresponded to remains of cobalt pigment (probably as Co oxide), always with high quantities of Fe and Ni (also probably as oxides) (Fig. 5b). Both elements appear together with Co, but usually in opposite correlation even in the same sample: high Fe proportion with low Ni content or high Ni percentage with low Fe quantity. Because these oxides are the result of some pigments unsolved or partly solved into the glaze, the quantitative results showed high variety (high standard deviation) and no numerical correlation between these two elements could be extracted. This group of samples from Teruel corresponds to Teruel1 group, classified by the trace-element study, and in this case also Cu was detected in the pigment remains in small quantities (up to 2–3.5% CuO). The elements identified by EDS confirm that the cobalt-based pigment was applied as oxides, obtained from the roasted mineral ore.

Although cobalt blue is always a so-called in-glaze decoration (because Co ions responsible of the colour are solved inside the glass phase), samples from Teruel dated of the 15th century or the beginning of the 16th century appear to be decorated applying the pigment directly on the body fabric and then covered with the glaze and fired again, following the tradition of under-glaze decorations. Cobalt was then solved into the glaze and it was possible the decoration to be observed because Co ions diffused to the glaze surface (Fig. 5a). Spanish potters call this way of decorating ceramics as "bajo-cubierta".

However, samples dated of the 16th century AD or later show an opposite pattern of Co and colour diffusion, from the glaze surface to the interior (Fig. 6a), explained because pigments were applied on the surface of the glaze before firing. This decorating method is called "sobre-cubierta" by Spanish potters. This way of decorating the glaze is present in samples from Teruel since the 16th century (Teruel2 group and other samples) and in all samples from Muel (all of them dated of the 16th century

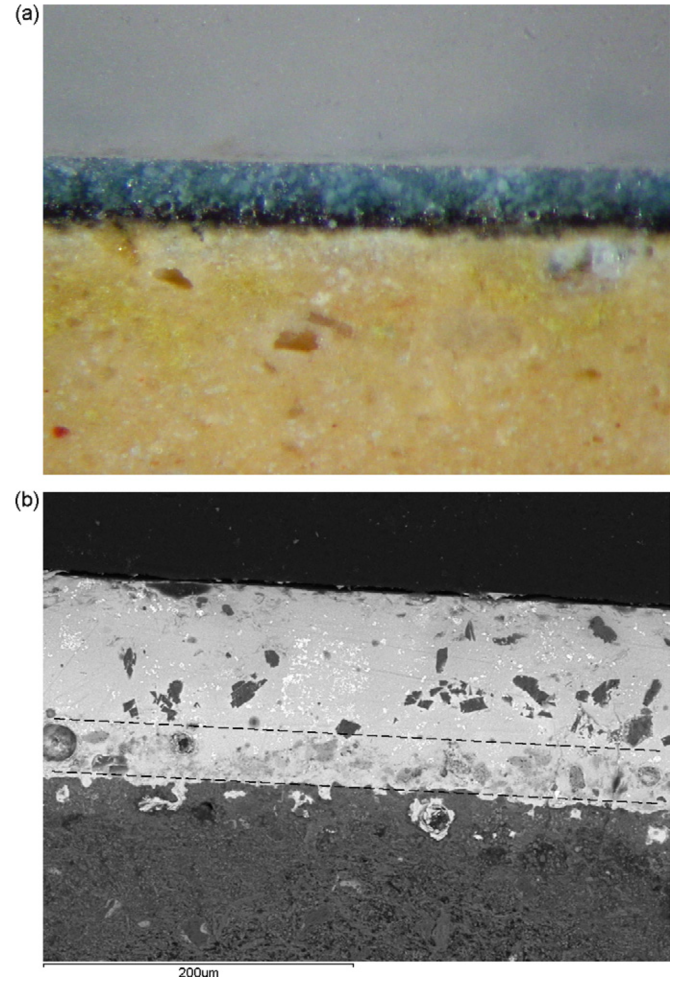

Fig. 5. (a) OM image, and (b) SEM image (BSE) of the cross-section in a glazed ceramic from Teruel, dated of the 15th century (dashed lines enclose blue-pigment area) (a: image length 1 mm and b: image length 400 μm).

or later). In SEM cross-section observations, cobalt pigments always seem well dissolved into the glaze without remains on the surface. Only in few cases where it was possible to be analysed, the composition of small particles corresponded to Co–Ni oxides (Fig. 6b).

This difference in the method of applying cobalt pigments was also verified when glaze surfaces were observed by SEM. Samples with under-glaze decoration always have very homogeneous surfaces, similar in blue and white areas (Fig. 7a, black spots in the BSE image correspond to quartz inclusions). However on-glaze-decorated fragments clearly showed a different treatment of the glaze surface between blue and white areas (Fig. 7b). The fact that cobalt was accumulated in the surface or in the interior of the glaze was also suspected by LA–ICPMS measurements because Co-signal intensity was 3–5 times higher in samples on-glaze decorated than in under-glaze cases (Teruel1).

Therefore, the changes observed in the use of different cobalt pigments for decorating tin-glazes could be related to important modifications in the blue-decoration technology, because the break between the chemical composition of blue pigments approximately in the middle of the 16th century also corresponds

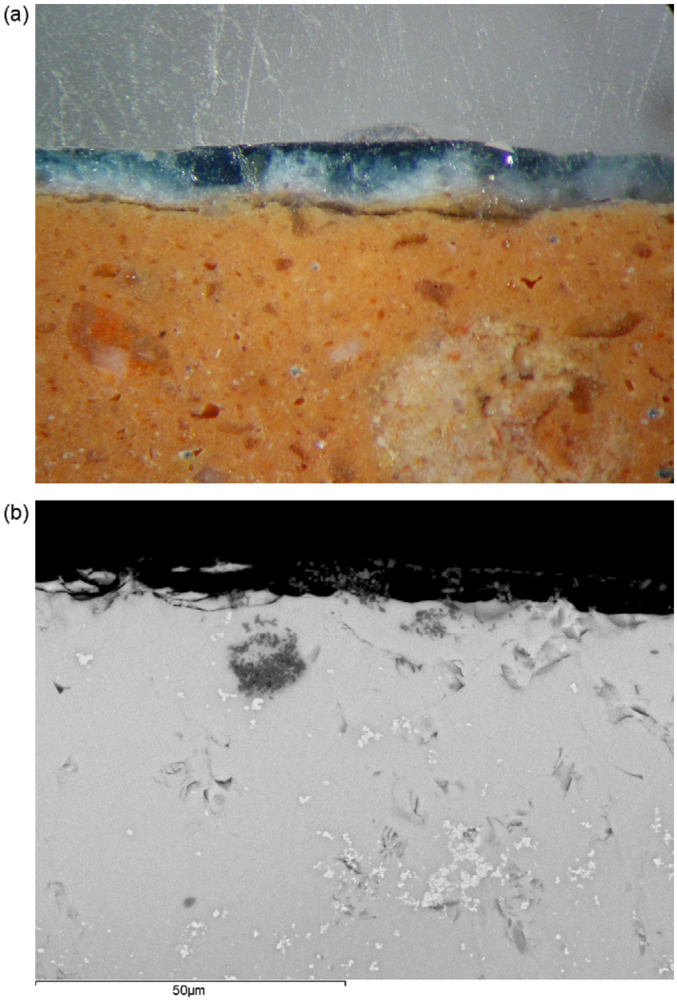

Fig. 6. (a) OM image, and (b) SEM image (BSE) of the cross-section in a glazed ceramic from Teruel, dated of the 18th century (a: image length 1 mm and b: image length 100 μm).

to another important change in the decoration technique: cobalt designs were painted under the glaze in early objects and pigments were applied on the glaze after the middle of the 16th century, with an opposite diffusion way of the cobalt ions.

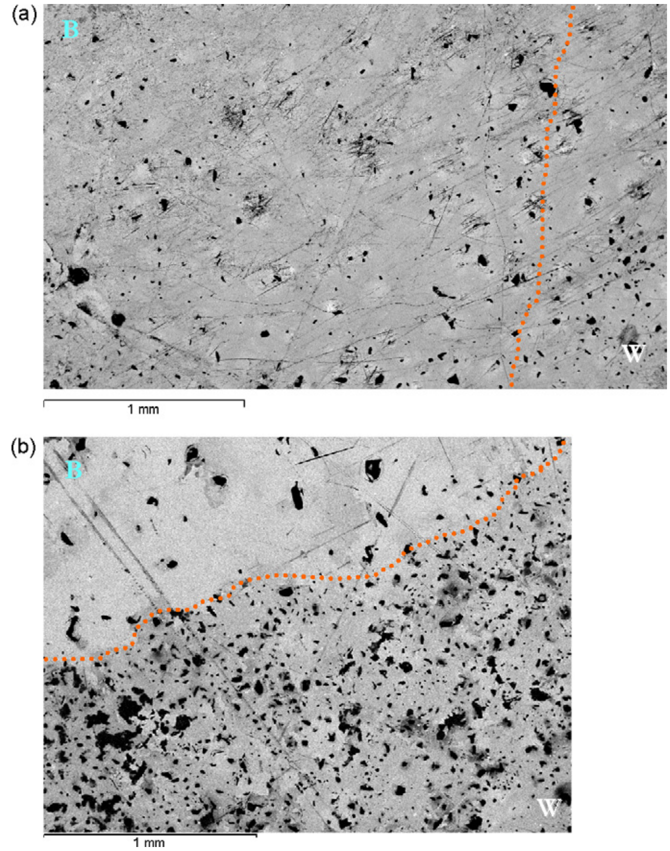

Fig. 7. SEM images (BSE) of the glaze surfaces. (a) Fragment with "under-glaze" decoration; (b) sample with "on-glaze" decoration (points mark the limit between blue (B) and white (W) surfaces) (a: image length 3 mm and b: image length 2.5 mm).

At the moment of the research, it is not possible to give the reason of this technological change. It could be the result of historical changing in the ceramic influencing groups or arrival of new potters, for instance, but it could also be produced for new characteristics of the pigments regarding their behaviour in the glaze. Under-glaze cobalt application has been also observed in the tin-glazed ceramic production from the Valencia area dated to the 14th and 15th centuries AD.[30] Cross-sections showed in

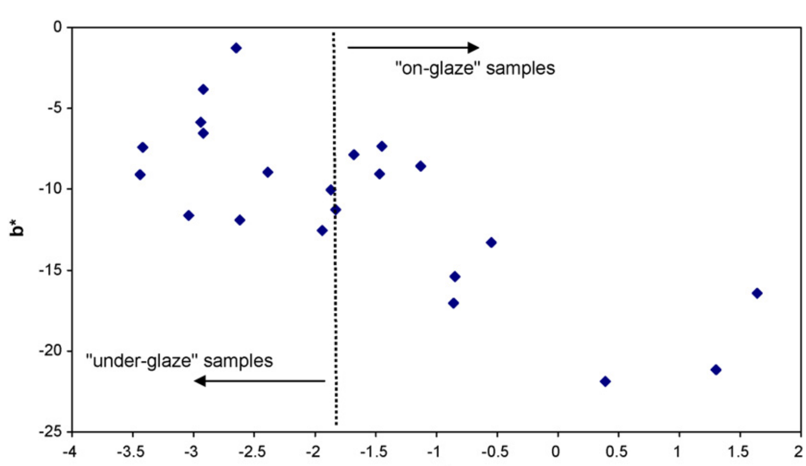

Fig. 8. Differences in colour coordinates (a^*b^* plane of the CIELab colour space) among blue ceramic samples decorated following the two methods.

studies by SEM and OM followed in blue-decorated ceramics found in Liguria (Italy) seem to have the cobalt not accumulated in the surface but concentrated in the glaze interior, in objects dated of the 12th century imported from northern Africa[4] and in some productions of the 16th century from Savona (Italy),[31] although no evidence for an under-glaze application is given in these studies. Studies of blue decorations of earlier Islamic eastern tradition seem to utilise only the on-glaze application of the cobalt pigments in tin-opacified glazes.[2,3,32]

Optical behaviour and colour parameters of the blue objects decorated following the two different methods (Teruel1 and Teruel2) have also some distinctions. Apart of differences in $L^*a^*b^*$ coordinates (Fig. 8), reflectance spectra show a diverse optical behaviour between 360 and 480 nm. Firstly we find a reflectance peak at circa 558 nm in all the samples, but in glazes decorated on the glaze surface is another clear maximum of reflectance at 400–408 nm. These peculiarities do not produce a clear difference in the b^* parameter among samples from both groups (Fig. 8), although on-glaze decorations seem to tend to a more blue hue (more negative b^* value). Nevertheless, under-glaze decorated samples (Teruel1) can be grouped on the left of the graphic (Fig. 8), with more negative a^* values (less than -1.9), and on-glaze decorated surfaces, on the right, have a slightly tendency to the red (higher a^* value), although these values are always low. L^* coordinate values are between 34.5 and 53.5 without any apparent difference between both groups, so with similar intensities of colour in both of them.

Although spectra were recorded in reflectance mode, in Fig. 9 are displayed the spectra of two representative samples (T71—under-glaze and T79—on-glaze) expressed in absorbance for easier comparison with the data reported in literature. Considering the absorbance spectra, all the blue samples showed similar behaviour. Peaks at circa 530, 600 and 650 nm

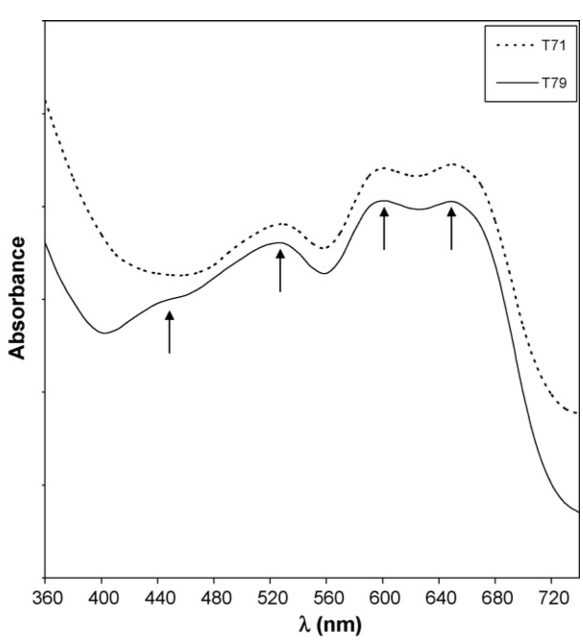

Fig. 9. Absorbance spectra of two representative blue-decorated glazes (T71—under-glaze decorated and T79—on-glaze decorated) (arrows mark the different maxima or shoulders).

are due to the presence of Co(II) in the glaze, but they do not provide any information about its coordination number because this particularity appears in the near-IR region (800–1800 nm).[33] However, several studies on cobalt in similar amorphous glass phases have demonstrated that this element is in the form of high-spin Co(II) ion in a tetrahedral (or pseudo-tetrahedral) coordination in the glassy matrix.[6,33–36] The three signals have to be attributed to the Jahn–Teller splitting of the $A_2 \rightarrow T_1(P)$ bands because of the distortion of the tetrahedral structure[37] or to an interaction between L and S quantic numbers.[38] The peaks appear slightly red-shifted compared to those expected, like other potash glasses and smalt pigments, thus indicating a smaller ligand field strength in the presence of potassium.[33,34]

Moreover of these characteristic bands, common to all samples, only absorbance spectra of on-glaze decorations showed a slight shoulder at 450 nm (Fig. 9) that distinguishes this group from under-glaze decorations. A peak at 480 nm and shoulders at 443 and 457 nm have also been observed in pure deep cobalt blue (or Thénard's blue from Zecchi) and blue glasses, respectively,[33] a shoulder at 440 nm in blue windows panes[34] and at circa 430 nm in blue-decorated majolica.[6] This shoulder could be compatible with the presence of Fe(III), as reported by some authors,[34] because the quantity of this element solved from the pigment can be higher when the decoration is applied on the glaze surface (1–2 wt% Fe_2O_3).

3.2.3. Cobalt and blue decoration in Mediterranean ceramics

Blue-decorated ceramics from the area of Aragon produced between the 15th and the 18th centuries show features that could be compared with other productions from the Iberian Peninsula and the Mediterranean area, in order to observe influences or differences. Considering clays used to produce this type of objects, in spite of the use of local sources, the preference of a calcareous type seems to be a shared characteristic with all tin-glazed ceramic productions, since Islamic times in al-Andalus to Renaissance and later periods, in the Iberian Peninsula and also in other places (i.e. Italian majolica).[4–8,14,16,31,39–43] The glaze elemental composition used in every production centre is expected to depend on raw materials and workshop recipes, however, in blue-decorated ceramics from Teruel tin-opacified glazes were produced using high content of lead (25–35% PbO), the type called lead-alkali glaze,[23] like all the Iberian production and Italian majolica.[4–9,15,16,22,24,30,31,39–45]

About the use of the blue pigment, Teruel workshops utilised a cobalt pigment characterised by the association Co–Cu–Fe–Ni in the 15th century until the first half of 16th century. This feature also appears in Valencia ceramics produced during the 14th and 15th centuries.[13,27,30] Cobalt pigments associated to Cu used in this historical period are not very well known, but some in-depth studies of "della Robia" blue ceramics of the Italian Renaissance have demonstrated that cobalt pigments used since the middle 15th century until 1514–1517 had a similar element association.[9,46] The pigments were Co–Ni–Fe oxides with strongly varying ratios of the three elements, probably the called zaffre (documented in Valencia ceramic workshops since 1333).[47] Similar pigments were found in blue tin-opacified glazes of Samarra faiences (9th century) and "underglaze" blue painting of Persian "faiences" (quartz-frit bodies) (12th–14th century), although in both cases glazes were of alkaline type.[2] Until the beginning of the 16th century, potters from Teruel used these pigments painting under tin-opacified glazes to decorate ceramics, as Valencia potters did,[5,30] but this way of decorating pottery is not documented in Italian majolica. In spite of the different type of glaze, this tradition of under-glaze painting with cobalt pigments seems to be very similar to that described in the Abu'l-Qasim's treatise on ceramics (Kashan, Persia, 1301 AD) to paint "on a white ground with blue colour".[48] In his comments to this manuscript translation, the author quotes part of the text by Schindler[49] describing the production and use of cobalt where he told about the preparation of a fine powder with cobalt pigment and quartz to be applied with gum "under the glaze".[48]

In the 16th century Aragonese ceramic workshops modified the way to decorate white opacified glazes with blue designs and the pigments were applied on the glaze. This type of decorating tin-opacified glazes appears as a general feature of Iberian and Italian majolica since the 16th century,[6–9,30,31,39–45] although there are some differences in the blue pigment used. The previously stated fact that As content in blue pigments increases since the 16th century AD in the Aragonese pottery, like in other Iberian centres,[13,27,30,39] is also present in Italian majolica.[6–9,31,39–46] The transition to the use of a cobalt pigment with significant amounts of As is dated between 1517 and 1520 in Robiane ceramics,[9] but also in some lustre ceramics by Mastro Giorgio, where blue was also included, cobalt pigments have higher proportions of As in objects between 1527 and 1540, and it is not detected in those produced in 1510–1528.[44] However, in spite of the common significance of the As, Teruel potters seem to use a different pigment where also Mn is significant, whereas in the area of Muel the blue has a similar association of elements (Co–As–Ni–Fe) to other Renaissance ceramic objects.[6–9,31,39–46] In both centres of production, blue pigments were applied on the glaze as impure cobalt oxides and never as "smalt" (a potassium-silicate glass containing Co),[6,7,41] because no increasing of potassium and silicon contents were detected between the blue areas and the white glaze, and no compositionally distinct glaze layer associated to the blue was observed in glaze cross-sections, nor other inclusions related to pigment (i.e. Pb–Ca arsenates).[9,41,43]

4. Conclusions

In summary, regarding to the evolution until the 18th century, tin-glazed ceramic production from the 13th century shows a first change with the beginning of the blue-decorated manufacture: the selection of more-calcareous clays in Teruel when objects were decorated in blue on white glaze, with a similar composition for the glazes. Coming to the evolution of the blue-decorated ceramics, in Teruel, when the production of blue pottery started in the 15th century, a cobalt pigment linked to copper was used in the decoration that was changed between the beginning and the middle of the next century by other different blue pigment with more quantity of manganese and arsenic. These two groups from Teruel, diverse considering the blue pigment, have the same body composition and no difference was found in glaze compositions, the only distinction is in the nature of the blue pigment.

In Muel the blue decoration started in the 16th century and most of the glazes were painted with a cobalt pigment richer in arsenic, although few objects let us to suspect that a different pigment with also high proportion of manganese could be also used in some cases. Clay composition, even calcareous, and glaze features allow Muel samples to be distinguished from other similar ceramic productions, like Teruel. The chemical and microstructural differentiations allow to group ceramics by provenance and chronology, establishing possible blue pigment origins, in an attempt to better understand contacts and ceramic evolution.

Another important technological feature observed was the fact that blue pigments were applied directly on the body fabric under the glaze until the beginning of the 16th century, in spite of the use of tin-opacified glazes, whereas the blue decoration was painted on the glaze since about the middle 16th century.

All the studied pigments react with the ceramic glazes, diffusing Co(II) ions from their coordination sites in the pigment (either tetrahedral or octahedral) to be preferentially accommodated in tetrahedral sites of the glassy matrix, giving the blue colour. However, both types of decoration patterns (under-glaze and on-glaze) show slightly different optical behaviour, with some variations in colour coordinates and reflectance spectra.

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