Colour analysis of some cobalt-based blue pigments

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Abstract

The coloring efficiency in different ceramic glazes of the classical Co olivine blue pigment (Co_2SiO_4) was compared with those obtained with a Co-doped willemite ($Co_{0.05}Zn_{1.95}SiO_4$), and with a magnesium-doped Co-Al spinel ($Mg_{0.2}Co_{0.8}Al_2O_4$). The fired pigments and enameled samples were characterized by XRD, UV-VIS-NIR spectroscopy, CIE-$L*a*b*$ color-measurements, and by SEM/EDX. The Co-olivine and Co-willemite pigments dissolved to a higher extent in the molten glazes than the Co–Al spinel. The darker blue color of the Co-olivine probed to be mostly due to Co^{2+} ions incorporated in the glassy matrix. The Co-willemite composition (which only contained a 1.3 Co wt.%) developed the bluest color hue of all pigments in both double and single firing glazes, while the magnesium-doped Co–Al spinel was found the most appropriate blue pigment in the bulk coloration of fast-fired porcelainized stoneware. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Natural and synthetic blue pigments are widely used in the ceramic industry as coloring agents in glazes for floor or wall whitewares, and also in the bulk coloration of polished, unglazed, porcelainized stoneware (commonly known as *gres porcellanato*).[1,2] The traditional and unavoidable source of blue in a ceramic pigment is the cobalt ion.[3] All the blue ceramic pigments known currently (except the vanadium-zircon blue, classified with the DCMA number[4] 14-42-2) contain Co to some extent: for instance, the Co_2SiO_4 olivine (DCMA 5-08-2), the $(Co,Zn)_2SiO_4$ willemite (DCMA 7-10-2), and the cobalt spinels $CoAl_2O_4$ (DCMA 13-26-2), Co_2SnO_4 (DCMA 13-27-2), $(Co,Zn)Al_2O_4$ (DCMA 13-28-2) and $Co(Al,Cr)_2O_4$ (DCMA 13-28-2).

However, the synthesis of cobalt-based blue ceramic pigments must be optimized or rationalized in order to minimize production costs (Co is both scarce and expensive) and also the environmental impact of the manufacturing process (Co is widely considered as toxic or hazardous), while also maintaining an optimal coloring performance in the desired glaze.[5] Thus, a selection of the most adequate pigment type (host lattice) proves to be

essential both to minimize the Co content of the pigment and to enhance its coloring performance and stability in a wide spectrum of ceramic glazes. On the one hand, to minimize production costs and toxicity, the *gahnite* ($ZnAl_2O_4$) and *willemite* (Zn_2SiO_4) structures have been pointed out as interesting host lattices, since nice and intense blue colors can be produced with very low Co doping.[6] On the other hand, the coloring performance of cobalt pigments depends very much on their thermal stability, on their chemical reactivity toward the glaze components, and also on the coordination of Co^{2+} ions (tetrahedral coordination is preferred to octahedral). In this respect, in work of G. Monari, and T. Manfredini,[2] $CoAl_2O_4$ spinel was found to produce a more intense and brighter blue color than Co_2SiO_4 olivine or Co_3O_4 mixed oxide, in the bulk coloration of porcelainized tiles, and the blue color of enameled samples was always attributed to tetrahedrally coordinated Co^{2+} ions. Therefore, it was implicit that olivine did not remain stable in the porcelainized glaze during firing, since a change in the Co^{2+} coordination took place. In this respect, although ceramic pigments are made from oxide crystals which are thermally stable to glaze firing temperatures and which exhibit a substantially low reactivity with molten glazes, reaction with and/or dissolution of the pigment in the glaze cannot be completely prevented. As a result, the same pigment

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can produce different colors in different glazes.[7] For cobalt based pigments, Co^{2+} ions can be incorporated in all kind of glasses as coloring agents, where commonly they adopt a tetrahedral coordination, though octahedral coordination is also possible. In this respect, an evolution from octahedral $[Co^{II}O_6]$ to the most stable tetrahedral $[Co^{II}O_4]$ coordination has been observed with an increase in the alkalinity and also with an increase in the firing temperature of the glass.[8] Therefore, one must expect that the blue color of a ceramic glaze containing a cobalt based ceramic pigment arises not only from the pigment crystals dispersed in the glaze, but also from cobalt ions dissolved in the glaze.

In the present study, the coloring efficiency in different glazes of the classical Co-olivine blue pigment (Co_2SiO_4) has been compared with those obtained with a Co-doped willemite ($Co_{0.05}Zn_{1.95}SiO_4$), and with a magnesium-doped Co–Al spinel ($Mg_{0.2}Co_{0.8}Al_2O_4$), in which the Co content has been reduced to minimize both costs and environmental impact. The Co_2SiO_4 olivine contains approximately hexagonal close packed oxide layers, with SiO_4 tetrahedra and with Co^{2+} ions in octahedral coordination. In Co-doped willemite (an orthosilicate of the phenacite group), Co^{2+} ions are to be found in tetrahedral coordination substituting for Zn^{2+} ions that occupy 3/8 of the tetrahedral sites. In the Co–Mg aluminate normal spinel, Co^{2+} (and Mg^{2+}) ions also occupy the tetrahedral sites of the cubic lattice.

The glazes selected in this work are representative of the main wall- and floor-tile production sectors (or firing schedules): double firing (DF), single firing (SF), and porcelainized stoneware (PO). Single firing formulations contain a higher proportion of alkaline-earth oxides to increase the melting temperature of the glaze and to let body-decomposition reactions complete before this melting temperature is achieved. Accordingly, single firing glazes are fired at higher temperatures (around 1100°C) than double firing glazes (around 1000°C). Firing schedules of porcelainized stoneware are even more severe, and temperatures as high as 1200°C are employed.

2. Experimental procedure

A Co-olivine (O), a Co–Al spinel with a 20 mol% Mg doping (S), and a willemite sample with only a 2.5 mol% Co doping (W) were prepared by the traditional ceramic procedure (mechanical mixture of the oxide precursors). The nominal compositions and nomenclature of the samples is shown in Table 1. As may be seen, the cobalt content of spinel and willemite samples was much lower than that of olivine sample. Quartz, MgO, AlO(OH), all of industrial quality, chemically pure commercial ZnO, and commercial cobalt oxide (Co_3O_4) were employed as precursors.

Table 1
Samples prepared, nominal composition and Co wt.%, and firing treatment (maximum temperature/soaking time)

Samples	Nominal composition	Nominal Co wt.%	Firing treatment
O	Co_2SiO_4	56.1%	1300°C/1 h
W	$Co_{0.05}Zn_{1.95}SiO_4$	1.3%	1300°C/1 h
S	$Co_{0.8}Mg_{0.2}Al_2O_4$	27.7%	1400°C/3 h

The corresponding precursor powders were suspended and homogenized in acetone in an agate ball mill (25 min at 800 rpm). Residual acetone was removed by evaporation and the dried powders were finally homogenized in an agate mortar and fired in a muffled electrical furnace. Firing treatment consisted in heating the powders to the appropriate temperature to obtain the pigment structures as major phases (1300°C for the olivine and willemite samples, and 1400°C for the spinel), with a heating rate of 10°C/min and with a soaking time of 1 h (O, and W) or 3 h (S).

In order to test their efficiency as blue ceramic pigments, the fired compositions were enameled with two different transparent (vitreous) glazes (formulations representative of single-firing and double-firing glazes) onto commercial ceramic biscuits. With this aim, the calcined pigments were first milled in water (agate milling medium) during 30 min (these milling conditions were estimated sufficient to bring all the fired pigments to a similar particle size distribution), and the powders were then sieved at 45 μm to guarantee an adequate dispersion in the glazes. A mixture (12 g) of each glaze with the sieved pigments (weight ratio pigment:glaze equal to 1:5) was homogenized in a ball mill during 10 min after adding an appropriate (and constant) amount of water (8 ml). The obtained slip was dip-coated onto ceramic biscuits obtaining a uniform glaze layer (around 1 mm thick), which was then fired following a fast firing scheme (60-min with a maximum temperature of 1000°C for the double-firing glaze, and 52-min and a maximum temperature of 1085°C for the single-firing glaze). The approximate oxide composition of both glazes expressed as Seger formula (molar) can be seen in Scheme 1. As may be seen, the single-firing glaze has a higher basicity [a lower ratio $(MO_2 + M_2O_3):(MO + M_2O)$] than the double-firing glaze.

All the fired pigments were also enameled on typical porcelainized whiteware or *porcelanatto* (PO) body (fabricated by spray-drying a mixture mainly consisting of kaolinitic white clays, feldspars, and quartz). This time, to imitate the most usual industrial practice, the dried (and 45 μm-sieved) pigments were mixed in bulk with the same PO body (spray-dried powder), also having a pigment:porcelanatto weight ratio of 1:5, and then homogenized in a ball mill during 10 min after adding water (as before, 8 ml for 12 g of pigment/porcelanatto

(a) transparent double-firing glaze (DF):

K$_2$O	0.094				
Na$_2$O	0.576				
MgO	-	Al$_2$O$_3$	0.633	SiO$_2$	6.916
CaO	0.193				
PbO	0.137				

(b) transparent single-firing glaze (SF):

K$_2$O	0.106				
Na$_2$O	-				
MgO	-	Al$_2$O$_3$	0.323	SiO$_2$	1.972
CaO	0.565				
ZnO	0.329				

Scheme 1. Seger formulae of the glazes.

mixture). The obtained slip was dip-coated onto the same green-pressed, porcelainized whiteware, and the whole set (green-pressed porcelainized body + bulk-colored porcelainized coating) was fired following a fast firing scheme (60-min with a maximum temperature of 1185°C).

To determine the crystalline phases formed in the fired powders and also in the enameled samples, X-ray diffraction (XRD) patterns were obtained in a Siemens D-500 Diffractometer with Ni filtered CuK$_\alpha$ radiation.

UV-vis-NIR spectroscopy (diffuse reflectance) of fired pigments and enameled samples also was performed with a Perkin-Elmer (lambda 2000) spectro-photometer at a range between 300 and 1600 nm. In addition, $L^*a^*b^*$ color parameters of both fired powders and enameled samples were measured with the same Perkin-Elmer spectrophotometer using a standard lighting C, following the CIE-$L^*a^*b^*$ colorimetric method recommended by the CIE (Commission Internationale de l'Eclairage).[9] On this method, L^* is the lightness axis [black (0)→white (100)], b^* is the blue (−)→yellow (+) axis, and a^* is the green (−)→red (+) axis. From the diffuse reflectance (R) spectra obtained with the spectrophotometer, it was also possible to obtain the Kubelka-Munk absorption function, conventionally referred to as Remission Function, $[F(R) = (1-R)^2/(2R)]$. The employment of $F(R)$ spectra is strongly advantageous to better compare the color intensity of ceramic pigments and also to relate color intensity to pigment concentration, as suggested by Eppler and Eppler.[10]

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis techniques also were used to characterize the fired pigments and enameled samples, employing a Leo-440i Leyca electron microscope equipped with an EDX attachment.

3. Results and discussion

3.1. XRD and SEM/EDX characterization

Table 2 summarizes the crystalline phases detected both in fired powders and in enameled samples. Focusing first on the fired powders, the cobalt olivine (Co$_2$SiO$_4$) did not form as a single phase during the firing (1300°C/ 1 h) of the O sample, since small amounts of unreacted Co spinel (Co$_3$O$_4$ introduced as Co precursor), and of CoO were observed as residual phases in this fired composition. On the other hand, the structure of zinc silicate (Zn$_2$SiO$_4$ or willemite) formed as the major crystalline phase in W sample (a small amount of unreacted ZnO also was detected). In this sample, the characterization performed by XRD did not show the presence of any purely cobalt-containing oxide phase; accordingly, a solid solution of Co^{2+} in the willemite lattice was accomplished in these samples (more information about the ranges of solid solution between Co$_2$SiO$_4$ and Zn$_2$SiO$_4$ can be found in a previous work).[6] EDX mapping analysis performed on this powder (not shown) confirmed the formation of the solid solution. With regard to the spinel sample (S), XRD characterization indicated the formation of the normal CoAl$_2$O$_4$ spinel as the major crystalline phase; in addition, XRD peaks of extremely weak intensity associated to the inverse Co$_2$AlO$_4$ spinel also were detected, indicating that some Co^{2+} ions could have entered octahedral sites in the spinel lattice. Moreover, the XRD pattern of S fired pigment showed almost indiscernible MgO (periclase)

Table 2
Crystalline phases[a] detected by XRD in the fired powders and in enameled samples

Samples	O	W	S
Fired powders	O (m), C (w), C′ (vw)	W (vs), Z (m)	S (vs), S′ (vw), P (vw)
Enameled sample (double-firing)	Q (m-w), CR (w), O (vw), A (vw), K (vw)	W (m-s), Q (m-s), CR (m-s)	S (s), Q (m), CR (w)
Enameled sample (single-firing)	CR (m), AN (s), K (vw)	CR (m), AN (s), K (vw)	S (s), AN (s), CR (w)
Enameled sample (porcelainized glaze)	Q (m-s), L (s), M (m-s), A (vw), K (vw)	Q (vs), L (m-s), M (m-s), A (vw), K (vw)	S (s), Q (s), L (s), M (s)

[a] Crystalline phases: O (cobalt olivine, Co$_2$SiO$_4$), C (cobalt spinel, Co$_3$O$_4$), C′ (cobalt oxide, CoO), W (willemite, Zn$_2$SiO$_4$), Z (zinc oxide, ZnO), S (normal Co-Al spinel, CoAl$_2$O$_4$), S′ (inverse Co-Al spinel, Co$_2$AlO$_4$), P (periclase, MgO), Q (SiO$_2$, quartz), CR (SiO$_2$, cristobalite), A (albite, NaAlSi$_3$O$_8$), K (orthoclase, KAlSi$_3$O$_8$), AN (anorthite, CaAl$_2$Si$_2$O$_8$), M (mullite, Al$_6$Si$_2$O$_{13}$), and L (sillimanite, Al$_2$SiO$_5$); Intensity of XRD peaks: vs (very strong), s (strong), m (medium), w (weak), and vw (very weak).

peaks, and, therefore, almost all Mg^{2+} doping ions (20 mol%) formed as expected a solid solution in the Co aluminate spinel substituting for cobalt ions.

Considering the enameled samples (see X-ray diffraction patterns of samples enameled with the PO glaze in Fig. 1), the major crystalline phases formed in the cooled molten glazes were different in each case: crystallization of quartz and cristobalite were observed in DF glaze (in agreement with its high SiO_2 content), anorthite crystals were predominant in SF glaze due to its higher CaO content, while mullite and sillimanite crystallization occurred in the PO glaze, in agreement with its composition rich in Si and Al oxides. As a relevant fact, XRD peaks corresponding to Co-olivine and Co-willemite pigment crystals were only detected in DF glaze (very weak peaks for the olivine sample, and medium-strong peaks for the willemite), while the spinel phase of cobalt aluminate was clearly detected (peaks of medium-strong intensity) in all glazes enameled with S sample. Therefore, this result indicates that olivine and willemite pigments dissolved to a higher extent in the molten glazes than the magnesium-doped cobalt aluminate, and reaction of the former was probably triggered by the higher firing temperatures employed in SF and PO glazes.

SEM/EDX analyses on enameled samples were also conducted to confirm the assumptions made from XRD results. Fig. 2 shows representative SEM micrographs obtained with the backscattering detector corresponding to O, and S fired pigments enameled with the porcelainized glaze, and to W fired pigment enameled with the double-firing glaze. In backscattered electron images, darker regions are those rich in lighter elements (in our case Si, Al, Na, etc.), while brighter or whiter regions are those rich in heavier elements (in our case, Co, Zn, and so on). On the other hand, the EDX mappings

corresponding to the same details of Fig. 2 are presented in Figs. 3–5.

The EDX mapping of O-PO sample (Fig. 3a) let us appreciate an even distribution of Si, Al, Na and K elements in the glaze, along with Si rich crystals; however, Co element is not observed to be associated to Si, which

(a)

(b)

(c)

Fig. 2. SEM micrographs (backscattering detector) of representative enameled samples: (a) Olivine-PO glaze, ×5000, (b) Willemite-DF glaze, ×595, and (c) Spinel-PO glaze, ×10,000.
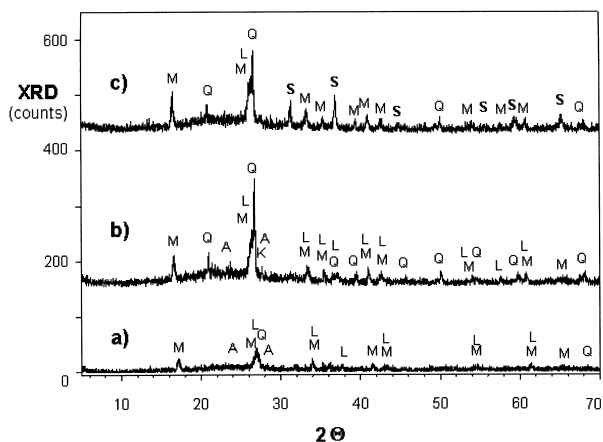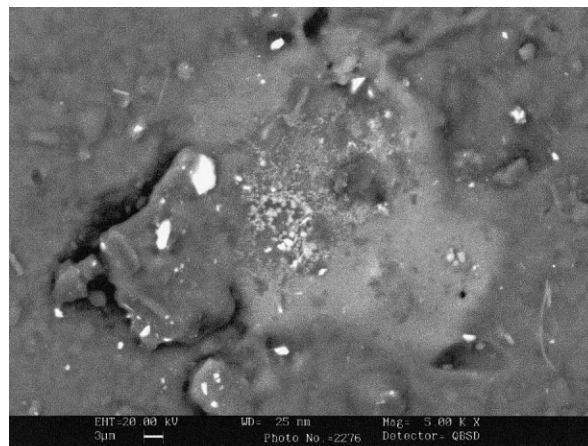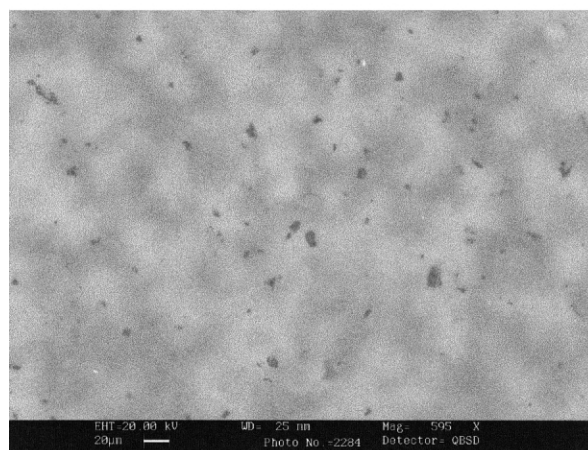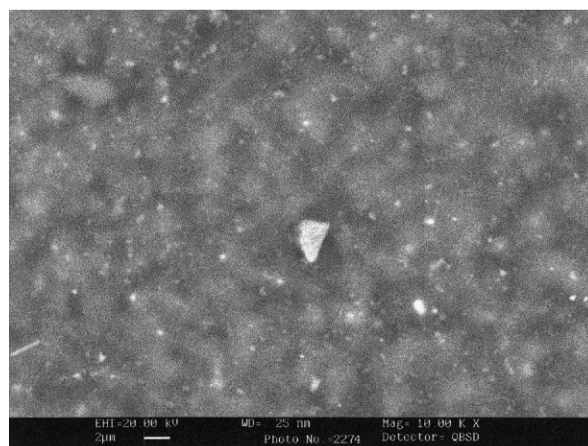

Fig. 1. XRD patterns of representative samples enameled with the porcelainized (PO) glaze: (a) O (Co_2SiO_4), (b) W ($Co_{0.05}Zn_{1.95}SiO_4$), and (c) S ($Co_{0.8}Mg_{0.2}Al_2O_4$). Crystalline phases: S (normal Co–Al spinel, $CoAl_2O_4$), Q (SiO_2, quartz), A (albite, $NaAlSi_3O_8$), K (orthoclase, $KAlSi_3O_8$), M (mullite, $Al_6Si_2O_{13}$), and L (sillimanite, Al_2SiO_5).

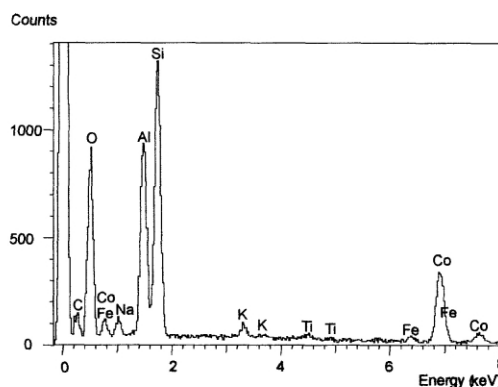indicates that the white region does not correspond to olivine crystals. Cobalt appears in this mapping to have diffused to the glaze, and this cobalt rich region could have arisen from olivine crystals decomposed or dissolved in the glaze, or from CoO or Co_3O_4 residual phases which also were detected in the fired powder by
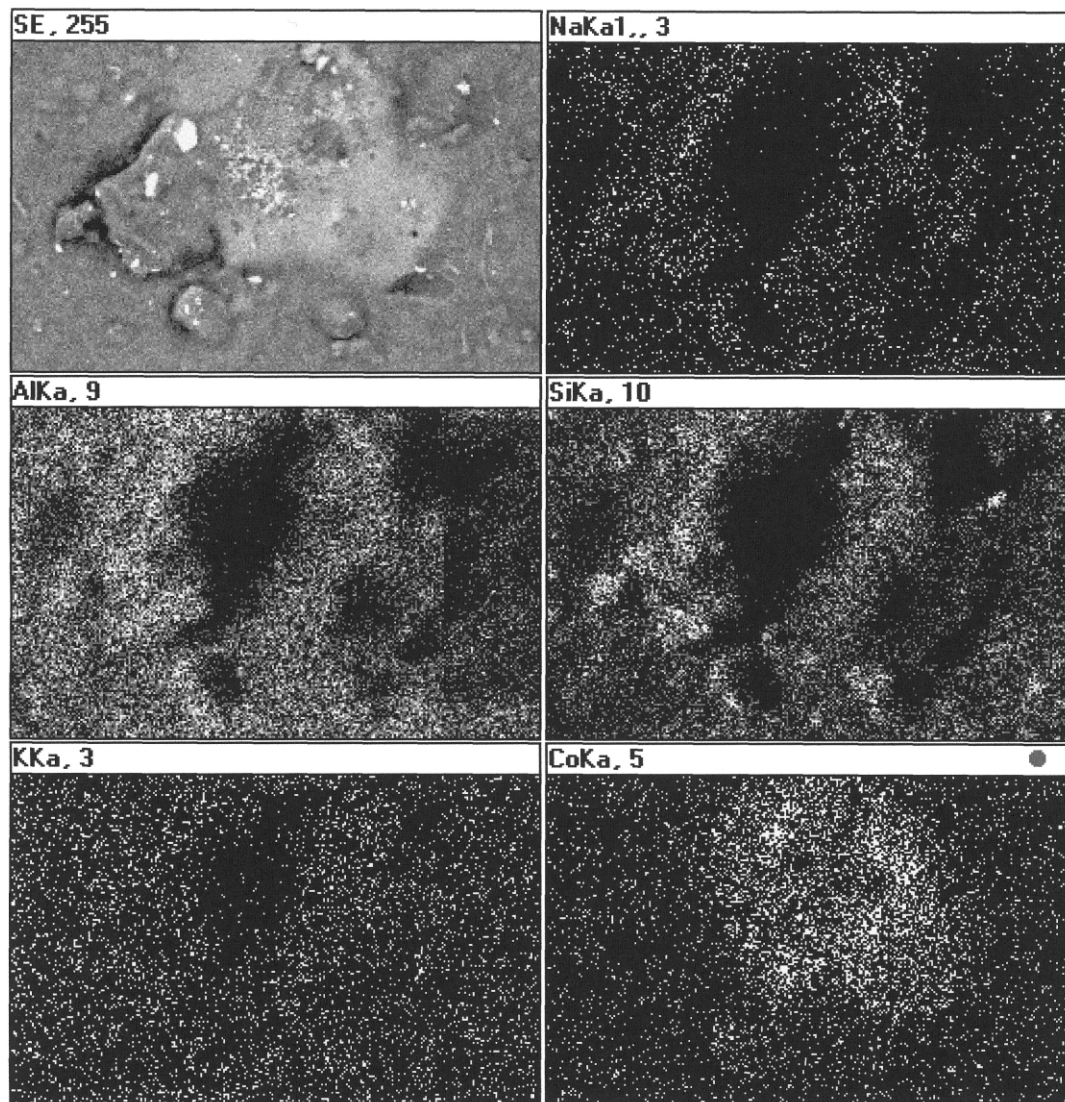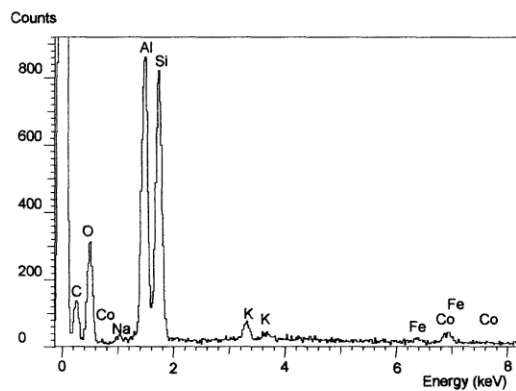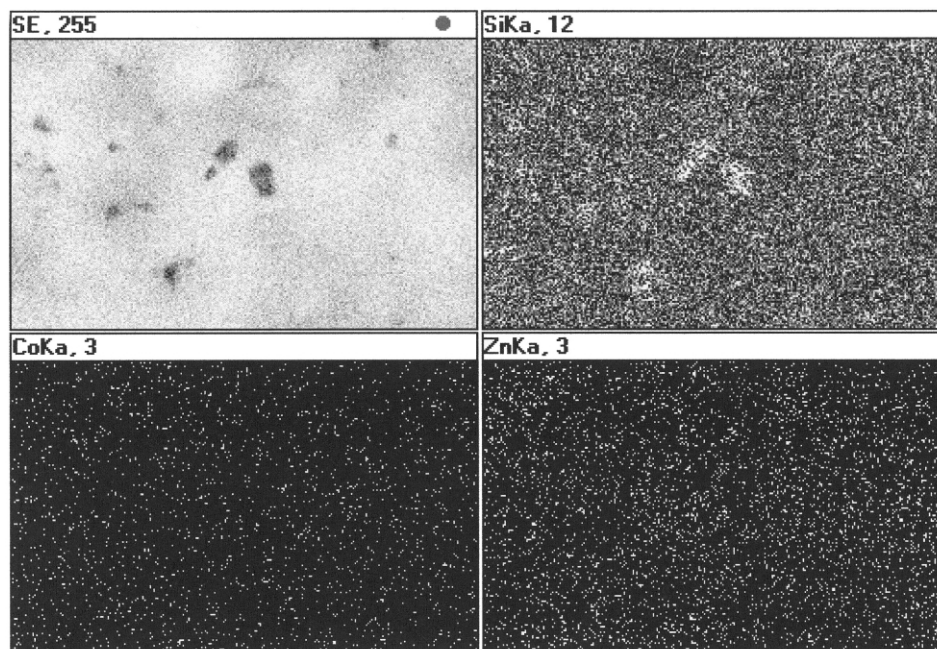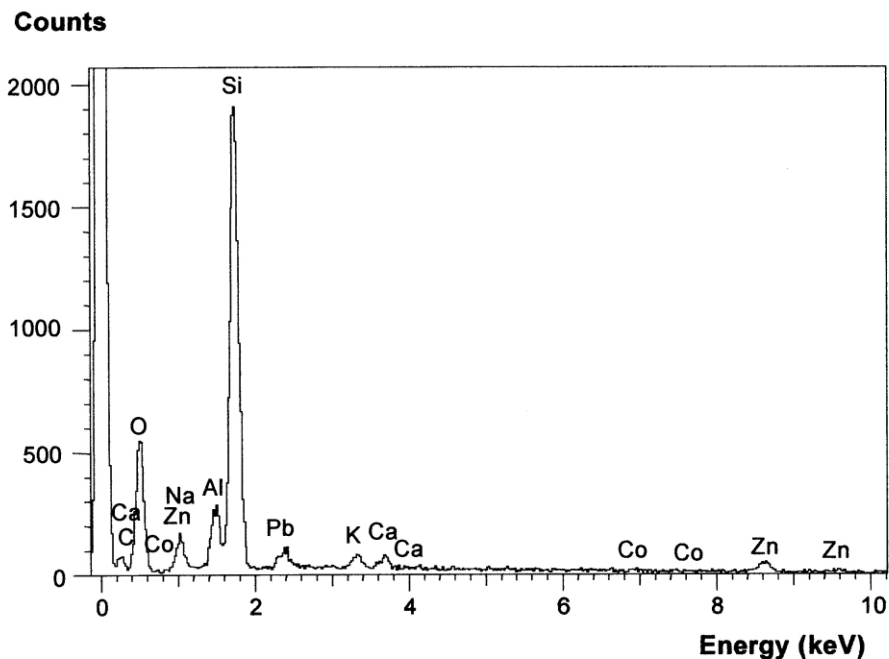

Fig. 3. EDX mapping of a detail of O fired pigment enameled with porcelainized glaze (a), and EDX spectra corresponding to two spot analyses performed on a Co-poor region (b) and on a Co-rich region (c).

XRD. Fig. 3 also presents the EDX spectra of two spot analyses performed in a dark, Co-poor region (3b) and in a white, Co-rich region (3c). Regarding the W pigment ($Co_{0.05}Zn_{1.95}SiO_4$), although willemite crystals were detected by XRD in the sample enameled with the double firing glaze, it was not possible to identify by SEM characterization stable willemite particles dispersed in this molten glaze. In the representative SEM detail of this sample shown in Fig. 2b, only dark crystals could be seen in the glassy matrix, which also presented homogeneously spread white spots. The EDX mapping obtained at a higher magnification (Fig. 4a), let us associate the dark crystals to Si containing crystals (either quartz or cristobalite, according to XRD), while the bright spots would be indicative of a significant diffusion of Zn and Co ions in the molten glaze. The cor-

Fig. 4. EDX mapping of a detail of W fired pigment enameled with double firing glaze (a), and the corresponding EDX spectrum (b).

responding EDX spectrum (Fig. 4b) evidenced a very low Zn content, while the Co signal was not detected, which can be explained by the very low cobalt content of this sample (1.3 wt.% in the fired pigment and 1.3/5 wt.% in the glaze).

In contrast to the O and W samples, in the case of the Co aluminate sample (O), an appreciable quantity of individual pigment particles (bright particles in the backscattering image of Fig. 2c) could be seen dispersed in the molten glaze; the occurrence of a partial dissolution of the pigment in the glassy matrix also was evidenced by the less intense white spots surrounding the particles and spread throughout. The corresponding EDX mapping and spectra of Fig. 5 confirmed that the bright crystals corresponded to Mg–$CoAl_2O_4$ pigment particles (EDX spectrum 1) and that cobalt ions had also diffused to the glaze (EDX spectrum 2).

In conclusion, XRD and SEM/EDX analyses performed on enameled samples confirmed that the olivine (O) and willemite (W) pigments dissolved to a higher extent in the molten glazes than the cobalt aluminate (especially in the glazes fired at higher temperatures, SF and PO), being Co^{2+} ions incorporated to some extent in the glassy matrix in all cases.

3.2. UV-vis-NIR and color characterization

The oxidation state and location of cobalt ions in the fired powders and in enameled samples were determined by UV-vis-NIR absorption spectra (see spectra of representative samples in Fig. 6). The energy-level diagram for Co(II) ($3d^7$ configuration), in both octahedral and tetrahedral ligand field, presents three spin-allowed transitions. The transitions for Co(II) ions in an octahedral ligand field are: $v_1[^4T_1(F) \rightarrow {}^4T_2(F)]$, $v_2[^4T_1(F) \rightarrow {}^4A_1(F)]$, and $v_3 [^4T_1 (F) \rightarrow {}^4T_1 (P)]$. For the olivine pigment (Co_2SiO_4), Corma and Lambies[11] assigned the first band (v_1) at 1350 nm, the second (v_2) at 570 nm and the third (v_3) at 490 nm (commonly, a multiple band around 510 nm is seen due to a rhombic distortion of the octahedral coordination caused by Jahn-Teller effect). Regarding to Co(II) in a tetrahedral ligand field, the three spin-allowed transitions are: $v_1[^4A_2(F) \rightarrow {}^4]_2 (F))$, $v_2[^4A_2 (F) \rightarrow {}^4 T_1(F)]$, and $v_3[^4A_2(F) \rightarrow {}^4 T_1(P)]$. According to the literature, in the case of tetrahedral $[Co^{II}O_4]$ groups, the two first spin-allowed bands fall in the infrared region (around 1400 and 1600 nm), and only the third one is present in the visible region, usually as a triple band around 540 (green region), 590 (yellow–
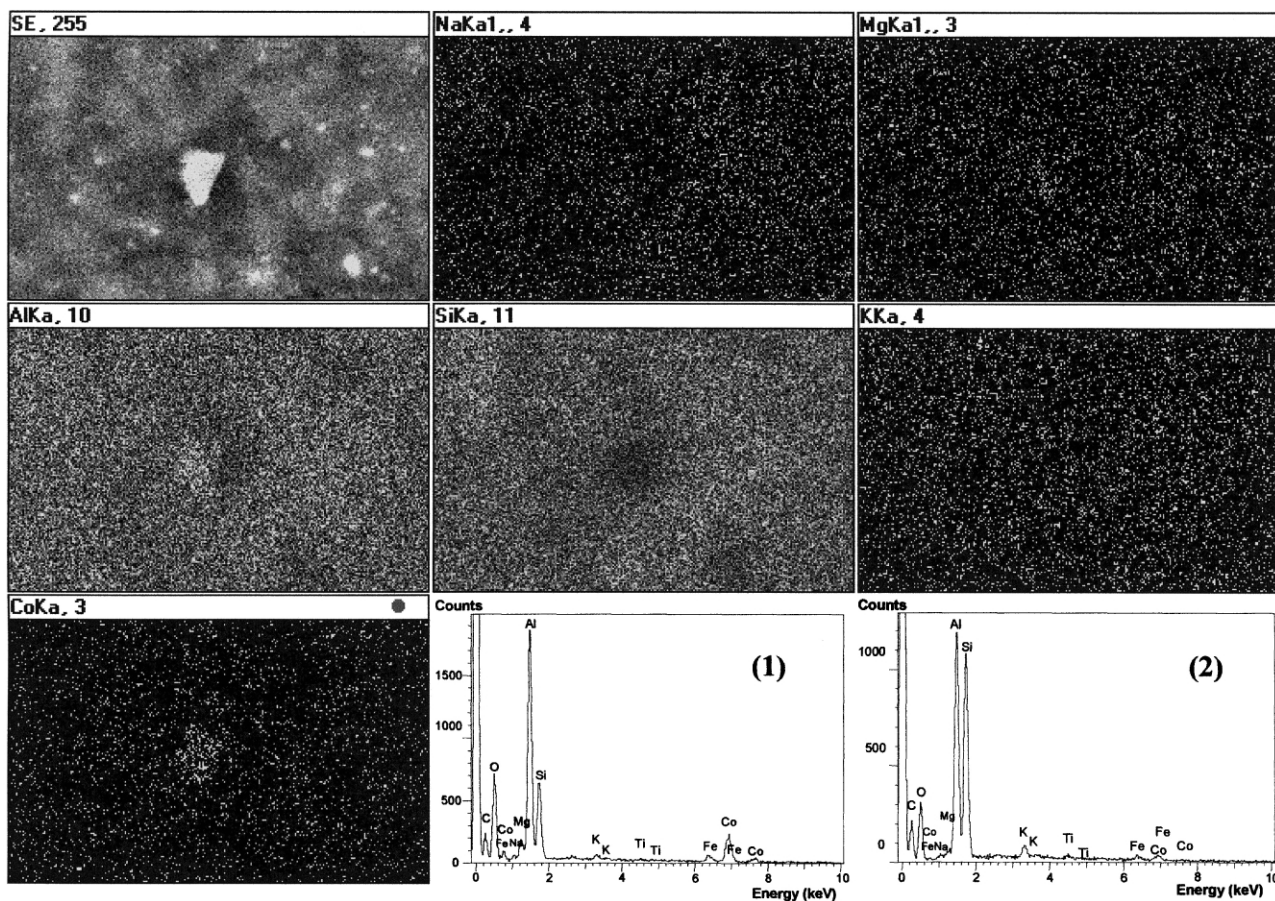

Fig. 5. EDX mapping of a detail of S fired pigment enameled with porcelainized glaze, including the EDX spectra of two spot analyses performed on a Mg–$CoAl_2O_4$ pigment particle (**1**) and on the glassy matrix surrounding this particle (**2**).

orange region), and 640 nm (red region), which gives rise to the blue coloration. This triple band can be attributed to a Jahn-Teller distortion of the tetrahedral structure, according to Bamford,[12] or to an interaction

Fig. 6. UV-vis-NIR absorption spectra of representative fired powders and enameled samples (**1**: fired powders, **2**: double-firing glaze, **3**: single firing glaze, and **4**: porcelainized glaze): (a) O (Co_2SiO_4), (b) W ($Co_{0.05}Zn_{1.95}SiO_4$), and (c) S ($Co_{0.8}Mg_{0.2}Al_2O_4$).

between L and S quantic numbers, according to Bates.[13] Therefore, the general form of the spectra, the shift of the third spin-allowed transition to higher wavelengths (540–640 nm), along with the presence of a single band (octahedral) or a multiple band (tetrahedral) in the infrared region, can be used to distinguish both octahedral and tetrahedral Co(II) coordinations.

In Fig. 6a, the absorption spectra of the olivine fired pigment (O fired powder) may be seen to present the typical bands of octahedrally coordinated cobalt: a single, very wide band in the infrared region around 1350–1400 nm, which could be associated with the ν_1 transition, along with a second multiple band between 502 and 592 nm, which would include the ν_3 and ν_2 transitions, according to McClure.[14] Moreover, the absorption curve of the fired powder also presents two shoulders at 660 and 770 nm, that could be attributed to the presence of unreacted cobalt spinel accompanying the cobalt olivine (as detected by XRD). In the absorption spectra corresponding to O enameled samples (referenced as O-DF, O-SF, and O-PO), however, an evolution from octahedral to tetrahedral coordination is observed, which is indicative of a different degree of olivine dissolution in the three glazes: O-DF exhibits a wide multiple band between 500 and 650 nm which would include both octahedral and tetrahedral Co(II) bands (a shift to higher wavelengths is observed, appearing as a new band at 640 nm), along with two shoulders around 660 and 770 nm due to unreacted cobalt spinel which have not been dissolved by the glaze. The wide band in the visible (500–650 nm) also may be seen in the O-SF sample, and it is observed to be narrower and more shifted to higher wavelengths in the series O-DF < O-SF < O-PO. The later (O-PO) only presents the characteristic spectrum of Co(II) in tetrahedral coordination, with a triple band in the visible around 540, 590 and 640 nm, and with a multiple band in the infrared region. From these spectra, therefore, it appears clear that olivine decomposes by reacting with the three glazes, being Co^{2+} ions accommodated in tetrahedral sites of the glaze. Dissolution of olivine (and also of residual CoO and Co_3O_4) in molten glazes appears to be greater, the higher the firing temperature (PO > SF > DF) of the glaze, this interaction being softer in the double-firing glaze (DF), in agreement with XRD and SEM/EDX observations.

On the other hand, the absorption spectra of willemite (Fig. 6b) and spinel (Fig. 6c) fired powders and enameled samples, may be seen to present in all cases similar features, with typical bands of Co in tetrahedral coordination. Taking into account XRD and SEM/EDX characterization, these tetrahedral bands observed in the W and S enameled samples are due to both Co^{2+} ions accommodated in the glassy matrix (especially in W sample), and to cobalt ions in tetrahedral coordination in the pigment lattice (to a higher extent in S sample).
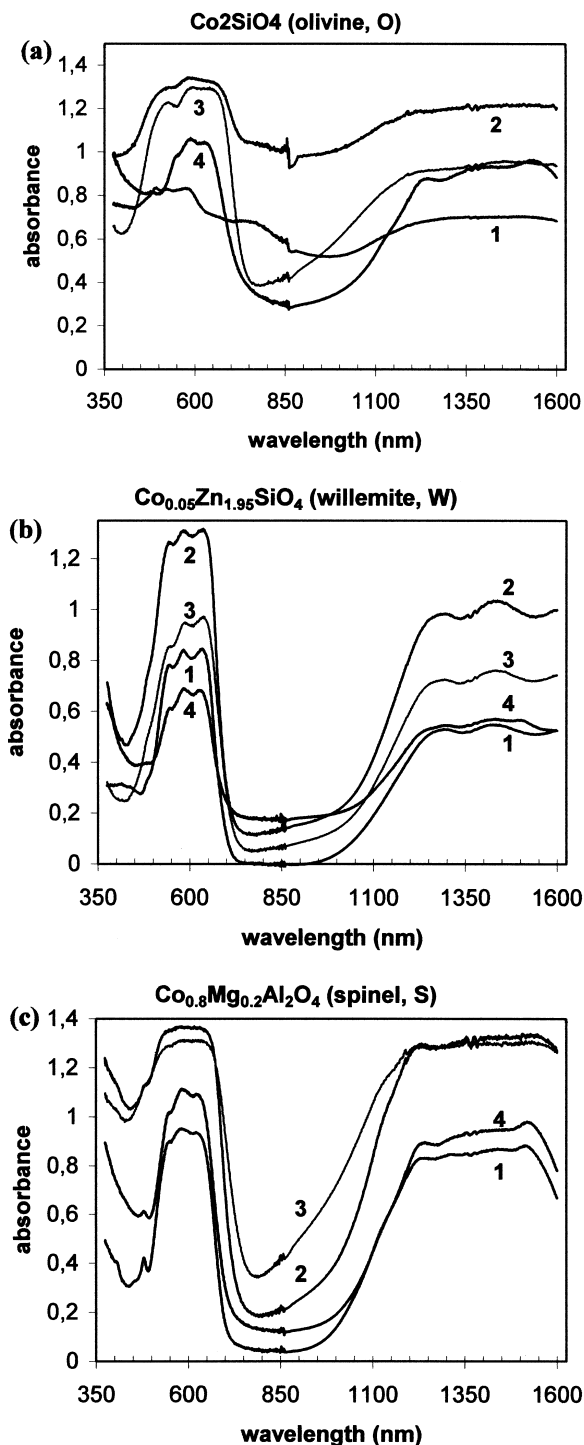
As a relevant observation, in the same way as the pigment dissolution in the molten glazes was observed to be triggered by increased firing temperatures in the series DF < SF < PO (especially in olivine and willemite samples), the absorption intensity of enameled samples also was observed to decrease in the same direction (DF > SF > PO), which very probably results in obtaining less bright and intense colorations. Accordingly, color measurements of the fired powders and of enameled samples also were performed to compare their color efficiency (color hue and strength) in the three different glazes.

The color parameters ($L^*a^*b^*$) of the fired powders and of enameled samples can be seen in Table 3, along with the value of the Kubelka–Munk absorption function [$F(R)$] measured at 600 nm. The yield of blue color is mainly governed by the parameter b^*: the more negative the b^* value, the bluer the color hue. On the other hand, the coordinate L^* gives us the lightness of the pigment (the higher L^*, the lighter), also being an indirect measurement of the brightness or intensity of the pigment (the lower L^*, the brighter or more intense the color). The color intensity of the pigments also can be compared with the $F(R)$ value, with the blue color being more intense, the higher this value (at the wavelength having a higher absorption in the yellow-red region, around 600 nm). Comparing first the color developed by the fired powders, olivine (O) exhibited an achromatic (very low a^* and b^* values) violet or indigo color, while the willemite and spinel samples (W and S) produced much bluer color hues (b^* values around −36 for willemite and around −39 for spinels), due to the presence in the later of cobalt (II) ions in tetrahedral coordination. Both

willemite and spinel formulations contained a significantly lower cobalt amount than olivine (especially W sample, with only a 1.3 wt.% of cobalt), yet both fired powders gave rise to much bluer colors than olivine and with a similar intensity (compare L^* and A_{KM} values), which is remarkable from an environmental point of view.

Regarding the enameled samples, the olivine sample also produced darker violet colors in all glazes, being considerably bluer in the single firing glaze ($b^* = −26$) than in double firing ($b^* = −11$) or in porcelainized ($b^* = −9$) glazes. On the other hand, the willemite sample (W) showed the bluest color hues of all pigments in both double and single firing glazes ($b^* = −44$), and also exhibited an interesting blue coloration in the porcelainized glaze ($b^* = −17$), though the blue color was very light (high L^*) or less intense [low $F(R)$] in this case. As for the spinel sample (S), it produced the most intense and bluest color in the porcelainized glaze ($b^* = −22$), but the color was darker and less blue in the other glazes (b^* around −12 and −14).

As previously suggested, in all cases the color intensity of enameled samples was found to diminish [higher L^* and/or lower F(R)] in the series DF > SF > PO, as a result of the higher amount of cobalt ions incorporated in the glassy matrix once released from their coordination sites in the pigment crystals. This change in the color intensity, and also in the blue hue, was observed to be much higher in the olivine and willemite samples than in the spinel sample, which also accounts for a lower dissolution of the Co–Al spinel in the molten glazes, in agreement with XRD and SEM/EDX characterization.

To better compare and visualize the coloring performance of the different pigments in the porcelainized glaze, the Kubelka–Munk remission function spectra of samples enameled with the porcelainized glaze (PO) are

Table 3
Color parameters (L^*, a^*, b^*) and Kubelka–Munk remission function value, $F(R)$[a], corresponding to fired pigments (powders) and enameled samples

Samples	L^*	a^*	b^*	$F(R)$[a]
Fired powders				
O	45.7	5.1	−3.2	2.3
W	54.1	0.1	−36.3	2.3
S	49.6	2.2	−39.4	3.4
Double-firing enameled sample				
O	26.0	3.8	−11.4	9.9
W	33.6	15.4	−44.0	9.1
S	26.1	2.3	−14.2	10.6
Single-firing enameled sample				
O	29.0	11.2	−25.6	8.8
W	47.9	11.3	−43.8	3.4
S	27.5	3.3	−14.2	9.2
Porcelainized glaze enameled sample				
O	39.7	−5.7	−9.0	4.6
W	58.7	−5.6	−16.9	1.4
S	42.1	−7.9	−22.4	5.3

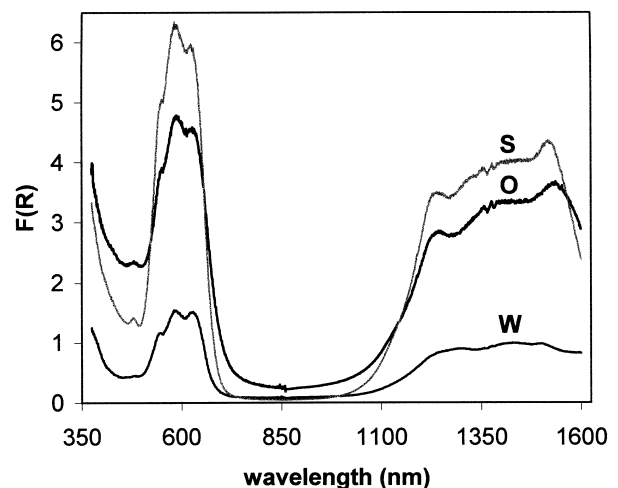[a] Value presented at 600 nm (maximum absorption region).

Fig. 7. Kubelka–Munk remission function spectra, $F(R)$, of samples (O, W, and S) enameled with the porcelainized glaze.

presented in Fig. 7. As may be seen, the spinel sample (S) exhibited the highest value of the Kubelka-Munk absorption function at the region of maximum absorption (500–650 nm), confirming the higher color intensity accomplished in this sample. The less intense $(F(R))$ spectrum of W sample also accounts for the poor intensity of the blue color developed in this sample, while the olivine sample presented an intermediate intensity. Therefore, the Co–Al spinel proved to be the most appropriate blue pigment in the bulk coloration of fast-fired porcelainized stoneware, considering both its lower reaction with the glaze and its best color yield (hue and intensity).

4. Conclusions

The coloring efficiency in different glazes of the classical Co-olivine blue pigment (Co_2SiO_4) has been compared with those obtained with a Co-doped willemite ($Co_{0.05}Zn_{1.95}SiO_4$), and with a magnesium-doped Co–Al spinel ($Mg_{0.2}Co_{0.8}Al_2O_4$), in which the Co content has been reduced to minimize both costs and environmental impact. The following points can be made:

1. All the studied pigments reacted with the ceramic glazes selected (representative of double firing, single firing and porcelainized stoneware industrial sectors), diffusing Co^{2+} ions from their coordination sites in the pigment (either octahedral or tetrahedral) to be preferentially accommodated in tetrahedral sites of the glassy matrix.
2. The cobalt olivine and willemite pigments reacted to a higher extent in the molten glazes than the magnesium doped Co–Al spinel, and this interaction was found to be triggered by increased firing temperatures of the glazes (DF < SF < PO), resulting in less intense blue colors.
3. The darker blue indigo color of the Co-olivine was found mostly due to Co^{2+} ions incorporated in the glassy matrix. The Co-willemite composition, though it contained an extremely low cobalt amount (1.3 wt.%), produced the bluest color hues of all

pigments in both double and single firing glazes, while the magnesium doped Co–Al spinel was found the most appropriate blue pigment in the bulk coloration of fast-fired porcelainized stoneware.

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