DETERMINATION OF THE REFRACTIVE INDEX OF CERAMIC MATERIALS

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1. INTRODUCTION

A key aspect of ceramic floor and wall tiles is their design. Indeed, the latest innovations in the ceramic sector (inkjet decoration, thin tile bodies, etc.) have focused on fostering this feature, creating new aesthetic concepts and applications with high added value. Thus, in design, colour constitutes a fundamental tool.

From a scientific viewpoint, colour may be considered the result of an optical response generated from the interaction between visible radiation and the material that contributes the coloration (essentially ceramic pigments in the case of ceramic materials). In particular, one of the characteristic parameters in the study of a material's optical behaviour is the refractive index.

When a beam of light travelling in a medium, n_1, enters a different medium, n_2, part of the beam is reflected, remaining in the initial medium, while the other part undergoes refraction, i.e. it interacts with the second medium and the beam changes direction.

This change in direction of the beam is explained by a variation in the speed of travel of the light. The ratio between the speed of light in a vacuum and in a material is defined as the refractive index and is represented by n, in accordance with the following equation:

$$n = \frac{c_0}{v} \qquad [1]$$

where c_0 is the speed of light in a vacuum ($3x10^8$ m/s) and v is the speed of light in the material.

Furthermore, the relationship between the incident angle (Θ_1) and the refraction angle (Θ_2) of a beam of light when it crosses two mediums with a different refractive index is expressed by Snell's Law:

$$n_1 \cdot \sin\theta_1 = n_2 \cdot \sin\theta_2 \qquad [2]$$

Strictly speaking, equation [2] is only valid for perfectly transparent materials. In materials that display a certain absorption, such as ceramic pigments, a complex equation is used that draws together the change in speed of light in the medium (real part) and the absorption (or reflectance) of the material (imaginary part):

$$\tilde{n} = n + ik \qquad [3]$$

where k is the extinction coefficient (also called index of absorption).

As a result, the refractive index may be considered an intrinsic property of a material, which is expressed as the result both of the interaction phenomena of light with matter (absorption–reflectance) and of changes in light travelling speed. Owing to that relationship between the absorption–reflectance characteristics of a material and the refractive index, the value of n can be calculated from the reflectance measurement and subsequent application of the Fresnel equation:

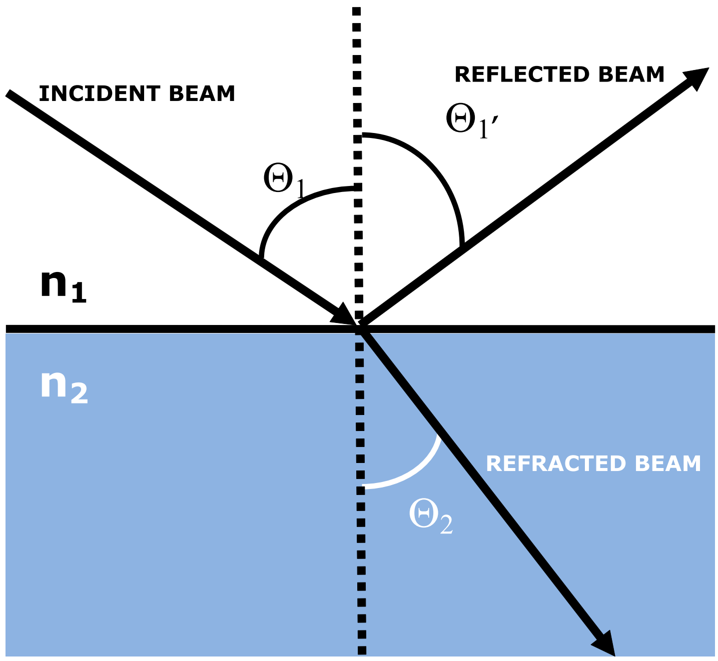

Figure 1. Representation of the refraction phenomenon

The measurement of n is widely used in such wide-ranging industrial sectors as hydrocarbons, wines, plastics, paper, textile, and lenses. However, despite the importance that optical properties have in ceramic pigments, to date it has not been common practice to characterise these by measuring the refractive index. In effect, although there are different methods of measuring the refractive index as a function of type of material, physical state (generally liquid or gas), and detection limit, these methods display two constraints that make it difficult to apply them to ceramic pigments, such as the possibility of using solid and dark samples.

2. OBJECTIVE

The objective of this study was to evaluate the validity of the method of determining the refractive index of powdered ceramic pigments based on spectrophotometric measurements. The refractive index of different ceramic pigments was therefore measured, determining the reproducibility and sensitivity of the method, and the influence that different synthesis parameters (synthesis temperature, variation of Co moles, type of Co precursor, and particle size) had on this property was studied.

3. EXPERIMENTAL AND RESULTS

3.1. Study of the refractive index in ceramic pigments

With a view to evaluating the possibility of measuring the refractive index in ceramic pigments customarily used in the ceramic sector, three commercial ceramic pigments were selected: a brown pigment (Cr-Fe-Mn spinel), a black pigment (Cr-Fe mixed oxide), and a blue pigment (Co spinel, $CoAl_2O_4$). In the three cases, the refractive index was measured in the wavelength range from 220nm to 2500nm, based on the method set out in the paper: *Method of determining the optical properties of ceramics and ceramic pigments: measurement of the refractive index*, developed by A. Tolosa and N. Alcón, also presented at Qualicer 2012.

The reflectance measurements were made with a Perkin-Elmer model Lambda 19 spectrophotometer equipped with an integrating sphere for measuring specular and diffuse reflectance, which allows analysis from the Ultraviolet to the Near Infrared regions (180nm – 2000nm).

The variation of the refractive index as a function of the wavelength (λ) for each pigment is shown in Figure 2. As may be observed, n exhibits a different spectrum for each pigment, owing to its coloration and, therefore, also different optical behaviour.

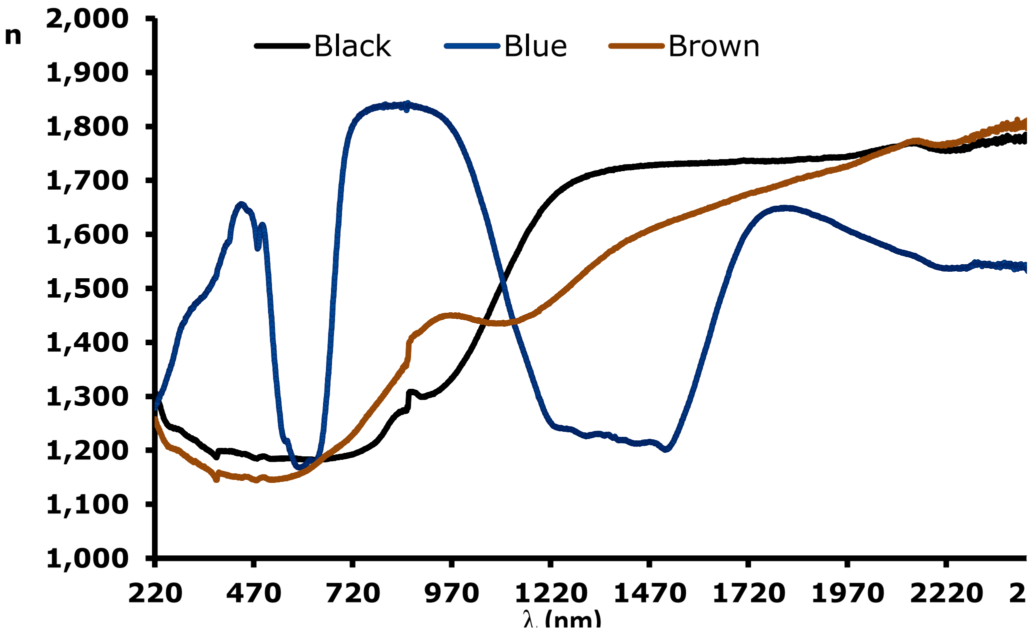

Figure 2. Evolution of the refractive index of the three ceramic pigments.

In order to evaluate the reproducibility and sensitivity of the method in ceramic pigments, the measurement of n was repeated 10 times in each pigment. In the three cases, very high reproducibility was obtained, with a maximum standard deviation of ±0.003.

In addition, 5 different samples were also taken of each pigment and the value of n was measured. In the three pigments, good reproducibility of the method was similarly obtained with a standard deviation, in the worst case, of ±0.004.

Once the possibility of measuring the refractive index in the ceramic pigments had been demonstrated, it was decided to carry out more detailed studies of different variables related to the synthesis of the cobalt blue spinel, because this is one of the most widely used pigments in the ceramic sector. Four variables were studied: synthesis temperature, chromophore (Co) moles, chromophore precursor, and synthesised pigment particle size. Moreover, as these materials have a fundamentally aesthetic function in the ceramic sector, the measurement of n focused on the visible range (350nm–780nm). As may be observed, a peak occurred at 490nm, proper to the blue coloration of this pigment, so that it was decided also to study its evolution with the different synthesis variables.

3.2. Study of the influence of temperature on the refractive index

3.2.1. Experimental

The industrial synthesis of the $CoAl_2O_4$ pigment was performed by the ceramic method. For this, a stoichiometric Co:Al mole ratio of 1:2 was used, in which the precursors were cobalt oxide (Co_3O_4) and aluminium oxide (Al_2O_3), the usual synthesis temperature being 1295ºC.

With a view to studying the influence of synthesis temperature on the refractive index, the blue pigment was synthesised at different temperatures, keeping the other variables (Co:Al mole ratio, Co and Al precursors, and particle size) constant. The pigment was synthesised at four different temperatures: 1295ºC, 1150ºC, 1050ºC, and 900ºC.

Once all pigments had been synthesised, the refractive index was measured. A crystallographic characterisation was also performed at each temperature by X-ray diffraction (XRD).

3.2.2. Results

The XRD analysis at each temperature gave rise to the diffractograms shown in Figure 3. As may be observed, at the optimum synthesis temperature used in industrial practice (1295ºC), the spinel phase was completely developed. However, as temperature decreases, more peaks of Al_2O_3 and Co_3O_4 were gradually detected, indicating the presence of residual reagent phases, so that the synthesis reaction of the Co spinel was incomplete. It may be noted that at a temperature of 900ºC, no spinel had formed and only the Al (Al_2O_3) and Co (Co_3O_4) precursors were detected.

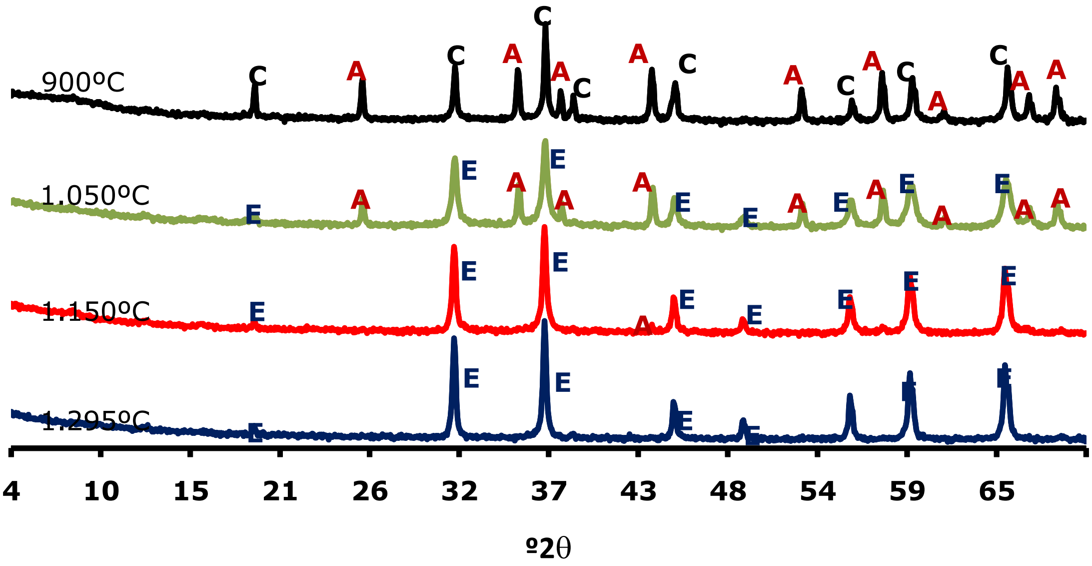

Figure 3. XRD at different temperatures. **E: Spinel $CoAl_2O_4$**. **A: Alumina Al_2O_3**. **C: Cobalt oxide Co_3O_4**.

The n spectra at each synthesis temperature are shown in Figure 4. Except at 900ºC, at which as noted previously, the Co spinel had not formed, the other temperatures display similar graphs albeit with different values in certain zones. Specifically, two types of behaviours may be distinguished. On the one hand, in the 500nm–675nm range, corresponding to the absorption zone, all the graphs exhibited a similar value of n. On the other hand, in both the 350nm–500nm and the 675nm–780nm ranges, the values of the refractive index decreased as the synthesis temperature was reduced, the difference being most pronounced at 490nm. Focusing on this peak and making a plot of n at each temperature, one obtains the graph shown in Figure 5, in which the value of n is observed to decrease as synthesis temperature dropped. The fact that the refractive index decreased with temperature was because the unreacted residual phase displayed a lower refractive index than the spinel phase, as shown by the measurement at 900ºC in which the structure had not formed. This behaviour means that the measurement of this parameter could constitute a rapid and reliable way of determining whether ceramic pigment synthesis had been performed at the optimum temperature.

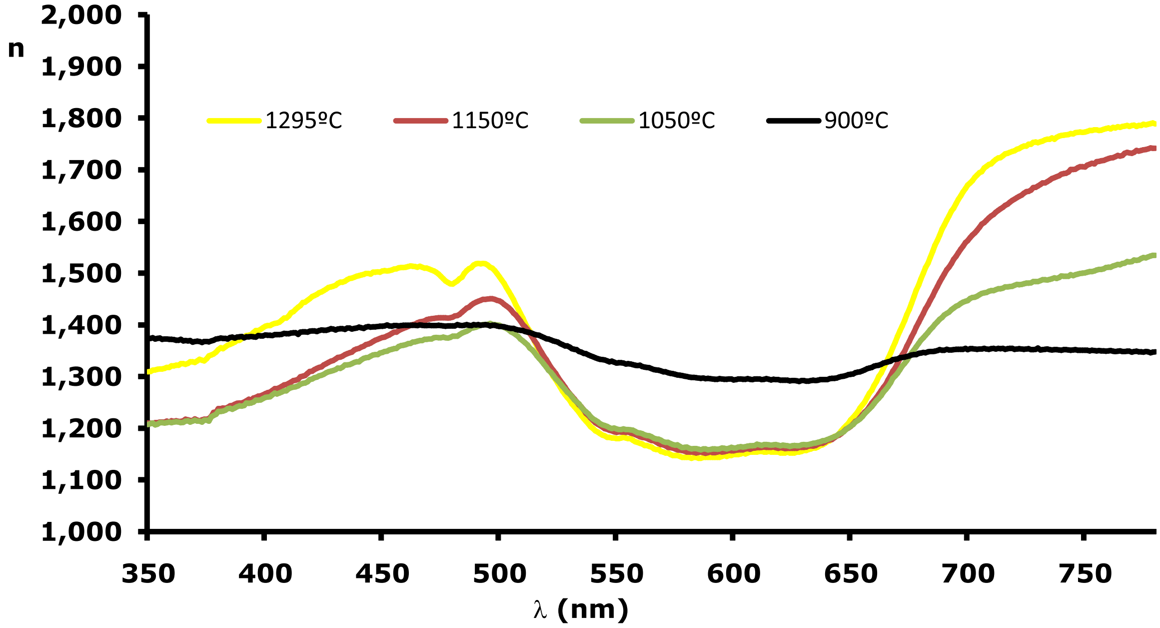

Figure 4. Variation of n with temperature.

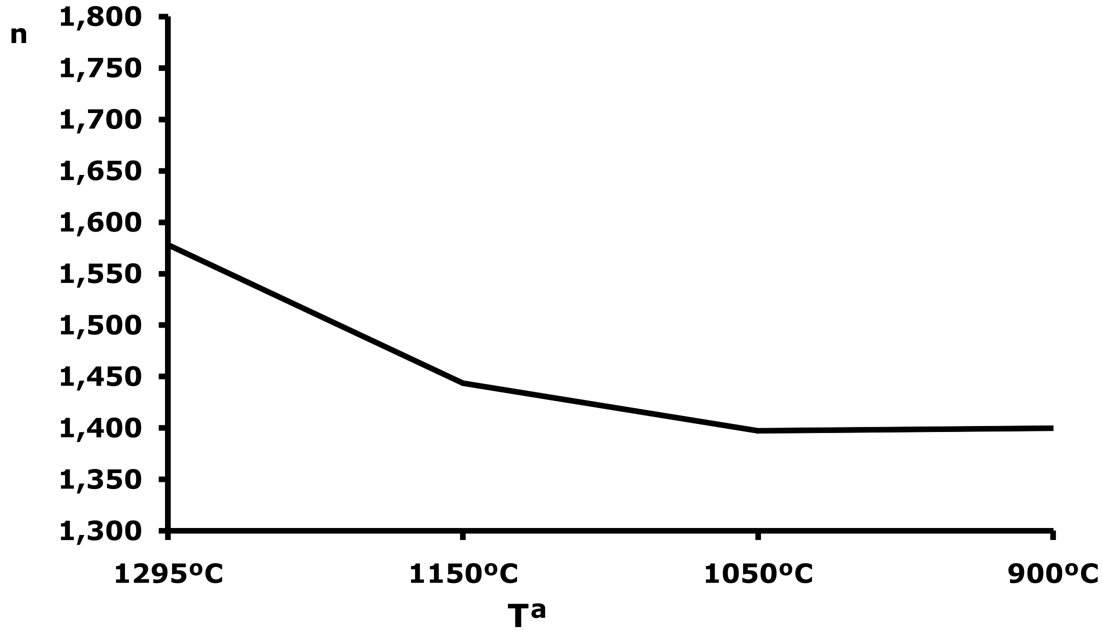

*Figure 5. Variat*ion of the peak at 490nm with temperature.

3.3. Study of the influence of the Co moles on the refractive index

3.3.1. Experimental

As mentioned previously, industrial synthesis is performed using the Co:Al stoichiometric ratio proper to the spinel structure, i.e. 1 mole of Co and 2 moles of Al. In order to evaluate the influence that the variation in the moles of the chromophore (Co) might have on the refractive index measurements, 3 pigments were synthesised with a lower cobalt mole content in the stoichiometric formula (0.9, 0.75, and 0.6) and three other pigments with surplus cobalt moles (1.1, 1.25, and 1.4). In every case, the synthesis temperature was 1295ºC.

3.3.2. Results

- Decrease in Co moles

The XRD analysis shows that when the stoichiometric composition (1 mole of Co and 2 moles of Al) was used, the only crystalline phase obtained was the spinel, without any presence of residual reactive phases, while the progressive decrease in the cobalt moles led to a smaller quantity of the spinel phase, as well as the presence of unreacted Al_2O_3 as a result of the lack of cobalt.

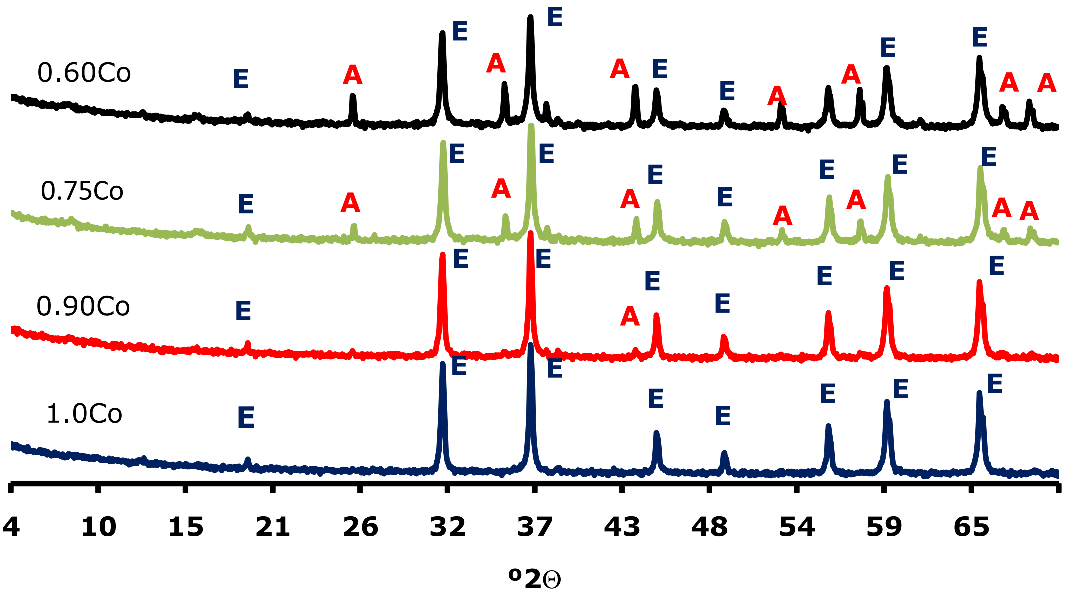

Figure 6. XRD of pigments with a decrease in Co moles **E: Spinel $CoAl_2O_4$**.
A: Alumina Al_2O_3.

The evolution of n of the different synthesised pigments, together with the Al_2O_3 spectrum, is depicted in Figure 7. It shows that, as the Co moles decreased, the refractive index increased. In addition, the value of n of Al_2O_3 was higher than that of the stoichiometric spinel (1.0Co). Taking into account that, on the one hand, as shown in the XRD analysis, the decrease in the cobalt moles led to the progressive presence of unreacted alumina (Al_2O_3) and that, on the other, its value of n was higher, the increase in the refractive index with the decrease in cobalt moles was due to the presence of alumina and its greater refractive index.

Taking the values at 490nm of the different synthesised pigments, a linear trend was obtained (R=0.9989) of the increase in n with the decrease in cobalt moles. This result thus evidenced that a measurement of n at this wavelength would allow it to be determined whether pigment synthesis had been performed under stoichiometric conditions.

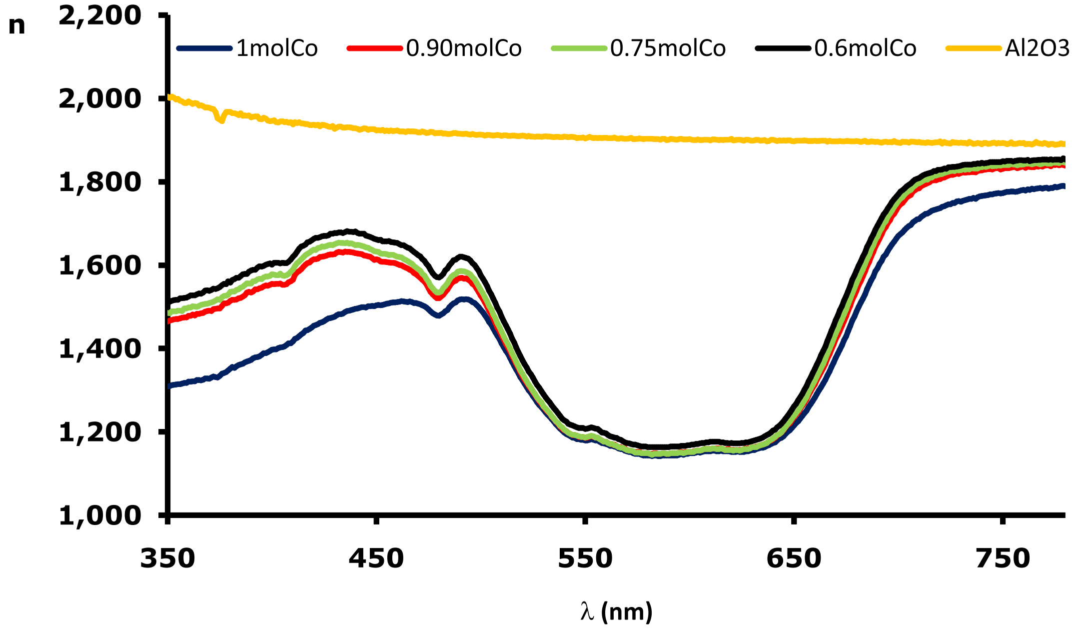

Figure 7. Measurement of n at decreasing Co moles.

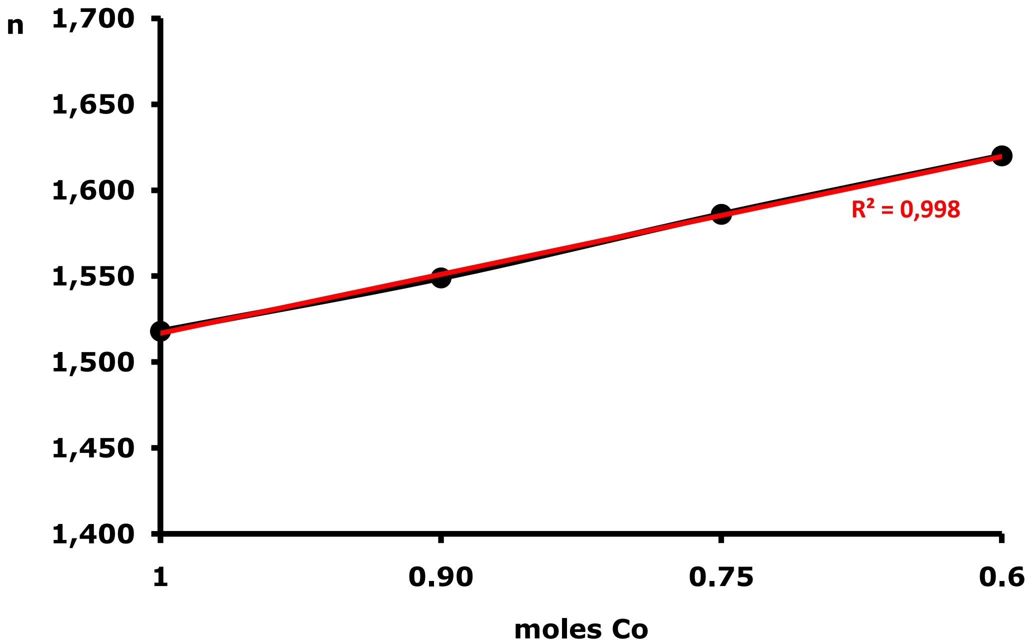

*Figure 8. Varia*tion of n at 490nm at decreasing Co moles.

- Increase in Co moles

The XRD analysis shows that the increase in cobalt moles led to a smaller spinel phase and the presence of unreacted cobalt oxide (Co_3O_4). Since the diffraction peaks of the spinel and of Co_3O_4 appeared at the same º2Θ, except for a peak at about 38º2Θ proper to Co_3O_4, the presence of the oxide and the decrease in the spinel were evidenced by the reduction in peak intensity, as well as by the presence of the peak mentioned at 38º2Θ.

The refractive index measurements as a function of the cobalt moles indicated that, as the cobalt moles increased, the value of n decreased. The following figure presents the spectra obtained together with the Co_3O_4 spectrum. As may be observed, as the cobalt moles increased with respect to the stoichiometric composition, the refractive index decreased. The figure also shows that the value of n of Co_3O_4 was lower than that of the stoichiometric spinel (1 mole of Co). Therefore, taking into account that, as indicated in the XRD analysis, the increase in the Co moles raised the presence of Co_3O_4 and lowered its value of n, the greater the surplus of cobalt moles that are introduced, the lower will the value of the refractive index be.

Taking the values at 490nm of the different synthesised pigments, a linear trend of the increase in n with the decrease in cobalt moles was obtained. Therefore, this result again demonstrates that a measurement of n at this wavelength would allow it to be determined whether pigment synthesis had been performed under stoichiometric conditions.

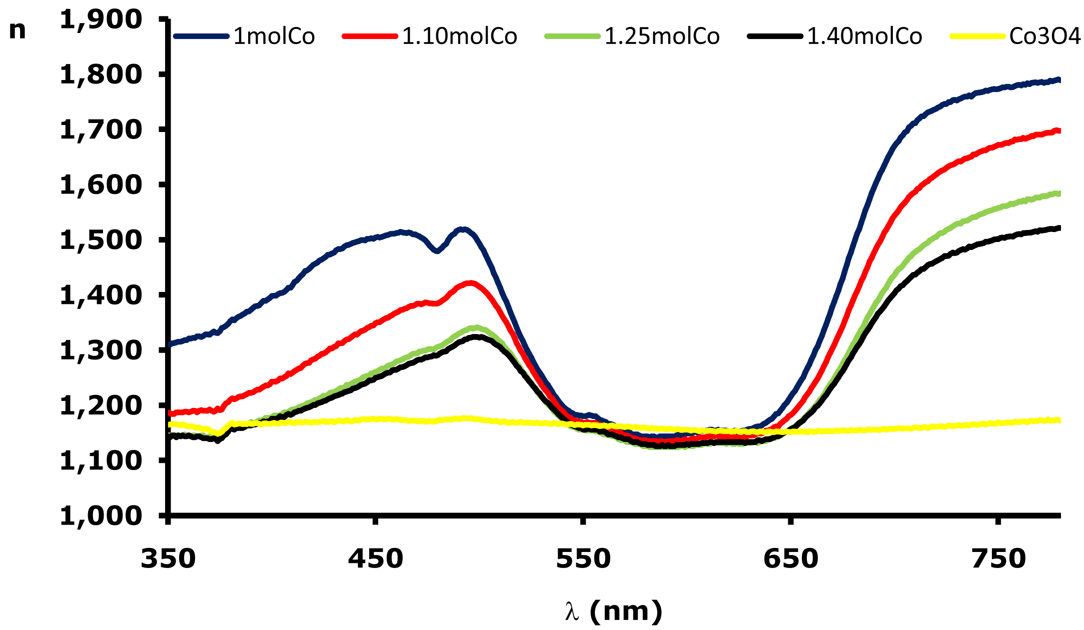

Figure 9. Measurement of n at increasing Co moles.

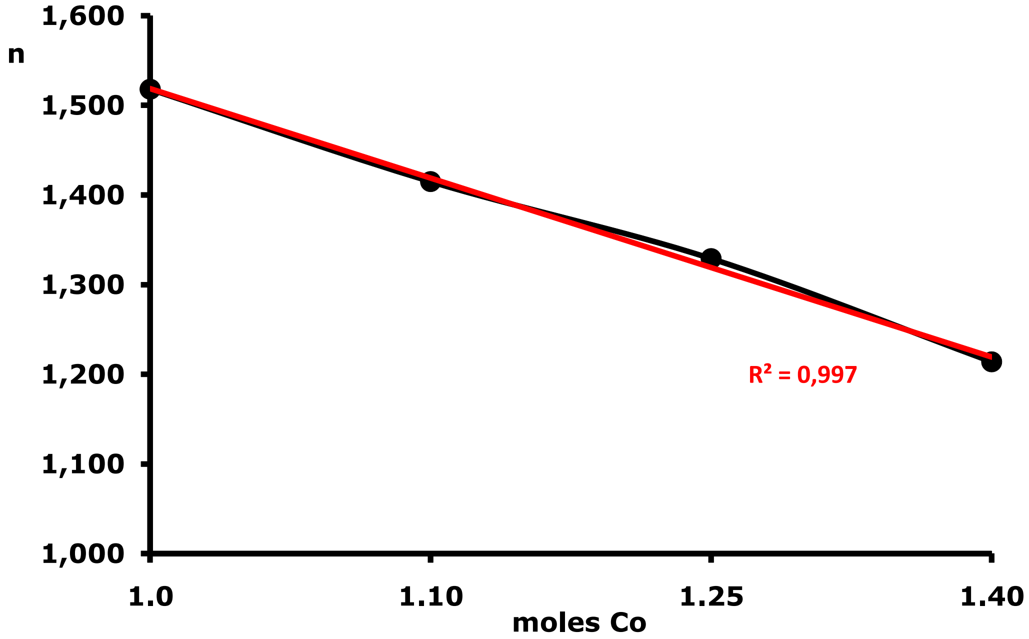

Figure 10. Variation of n at 490nm at increasing Co moles.

3.4. Study of the influence of the Co precursor on the refractive index

3.4.1. Experimental

In industrial synthesis of the cobalt spinel, cobalt oxide (Co_3O_4) is used owing to raw material availability. However, other raw materials could also contribute the chromophore cation, so that it was decided to compare the refractive index when cobalt hydroxide ($Co(OH)_2$) was used as cobalt precursor instead of the usual Co_3O_4. The pigment was, therefore, synthesised with the 1:2 stoichiometric mole ratio of cobalt to aluminium, at a temperature of 1295ºC, so that the only variable that could influence the value of n was the cobalt precursor.

3.4.2. Results

No difference was detected in the XRD analysis and in both cases the spinel was completely formed.

In regard to the analysis of the refractive index, Figure 11 shows the spectra obtained. It shows that, though in most of the spectrum no significant differences were to be observed, in the zone between 400nm and 500nm, corresponding to the visible zone where this colour is perceived, a variation occurred in the value of n. It deserves to be noted that this variation, just as it was not detected by XRD, was not noted visually either once the pigment had been applied and fired in a standard porcelain tile firing cycle at a peak temperature of 1200ºC

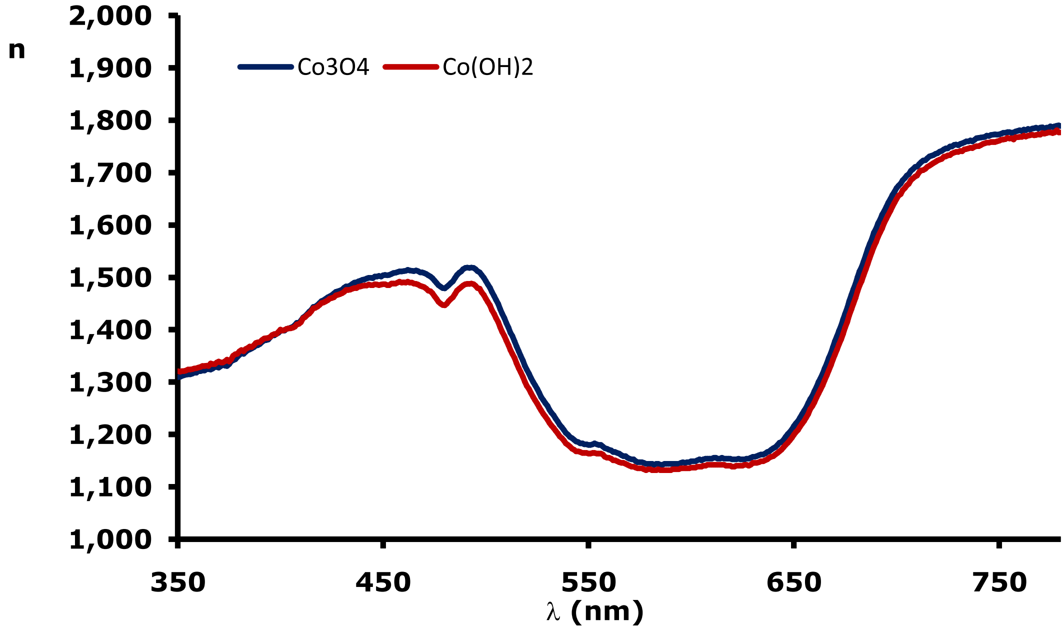

Figure 11. Variation of n with different Co precursors.

3.5. Study of the influence of particle size on the refractive index

3.5.1. Experimental

The last variable to be studied was the refractive index as a function of cobalt spinel particle size, holding the other variables according to the usual industrial synthesis conditions (1:2 moles of Co:moles de Al, 1295ºC, and using Co_3O_4 and Al_2O_3 as precursors). Four different particle sizes were studied. The largest, with a D90 of 9.61 micrometres, corresponded to that obtained in the synthesis. The other three, with D90 values of 4.19 micrometres, 2.17 micrometres, and 1.28 micrometres, were obtained by grinding the first.

3.5.2. Results

The XRD analysis showed no difference when particle size was reduced, only the Co spinel being detected.

With regard to the refractive index measurement, as the following figure shows, two different behaviours were observed as a function of the spectrum zone. Thus, in the range between 350nm and 500nm, corresponding to the pigment reflection zone and proper to this colour, as particle size decreased, the value of n increased. In the absorption zone, however, between 500nm and 780nm, no significant differences were noted. Taking into account this difference in the reflection zone of the material and the XRD results, the change in the value of n did not occur as a result of variations in the material, but was assignable to a usual phenomenon, known as dispersion or scattering, in optical measurements of solid materials. As particle size decreased, the beam that impinged upon the pigment was scattered, raising the detector response. This result highlights the fact that the comparative refractive index measurements of a given pigment should be made at the same particle size.

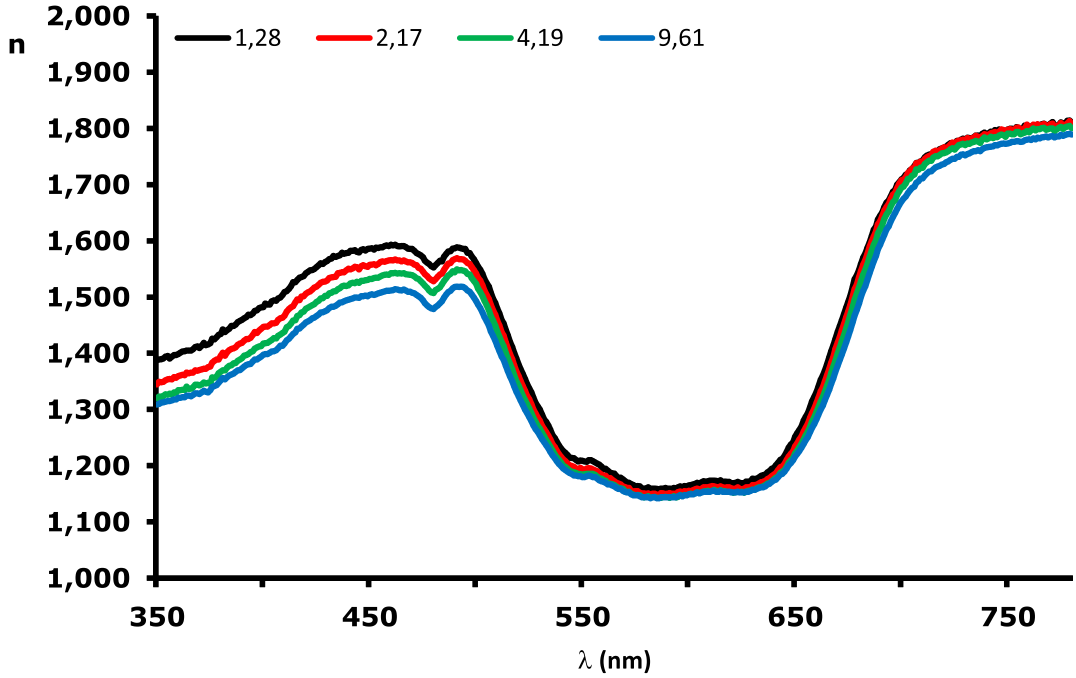

Figure 12. Evolution of n with particle size.

4. CONCLUSIONS

The results of the study allow the following conclusions to be drawn:

- The validity of the method of determining the refractive index of powdered ceramic pigments based on spectrophotometric measurements was demonstrated.
- The value of n at 490nm of the cobalt spinel pigment decreased as the synthesis temperature was lowered.
- The decrease in cobalt moles with relation to the stoichiometric composition led to an increase in the value of n at 490nm owing to the presence of residual Al_2O_3.
- The increase in cobalt moles with relation to the stoichiometric composition led to a decrease in the value of n at 490nm owing to the presence of residual Co_3O_4.
- The measurement of n at 490nm could constitute a rapid and reliable way of determining whether pigment synthesis had been performed at the appropriate temperature and with the optimum molar ratio.
- The replacement of Co_3O_4 with $Co(OH)_2$ in the cobalt spinel led to changes in the value of n in the pigment reflection zone. However, this variation was not detected either by XRD or visually.
- The reduction in particle size raised the value of the refractive index as a result of beam scattering phenomena during the measurement.

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