METHOD OF DETERMINING THE OPTICAL PROPERTIES OF CERAMICS AND CERAMIC PIGMENTS: MEASUREMENT OF THE REFRACTIVE INDEX

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ABSTRACT

The knowledge of the optical properties of materials, such as pigments or the ceramics that contain these, is a key feature in modelling the behaviour of light when it impinges upon them.

This paper presents a method of obtaining the refractive index of ceramics from diffuse reflectance measurements made with a spectrophotometer equipped with an integrating sphere. The method has been demonstrated to be applicable to opaque ceramics, independently of whether the surface is polished or not, thus avoiding the need to use different methods to measure the refractive index according to the surface characteristics of the material. This method allows the Fresnel equations to be directly used to calculate the refractive index with the measured diffuse reflectance, without needing to measure just the specular reflectance. Alternatively, the method could also be used to measure the refractive index in transparent and translucent samples.

The technique can be adapted to determine the complex refractive index of pigments. The reflectance measurement would be based on the method proposed in this paper, but for the calculation of the real part of the refractive index, related to the change in velocity that light undergoes when it reaches the material, and the imaginary part, related to light absorption by the material, the Kramers-Kronig relations would be used.

1. INTRODUCTION

The refractive index of a material medium is one of its main optical parameters. Knowing this completely explains all the optical properties of the medium and, based on these, it is possible to extract a great deal of information on its molecular structure, composition, and behaviour[1]. The refractive index is, therefore, a basic parameter in generating models, qualitative interpretations, and quantitative evaluations of a material's characteristics.

As examples of the importance of this parameter for the design of different devices and structures or for materials characterisation, the following may be cited: the design of waveguides, where the refractive index of the material mediums that make up the guide, for example those making up an optic fibre, determine which modes will be propagated and their scatter along this fibre; or the design of solid-state lasers, among others. Another application of this parameter is in the study of the adulteration of liquids or of the presence in liquids of certain compounds, such as sugar in juices or wine, which is customarily done with refractometers.

The optical properties of a pigment can also be predicted from the refractive index. This determines its opacity, such that the greater the refractive index of the pigment with relation to the refractive index of the medium or vehicle in which it is immersed, the greater will the opacity be. In this context, models are available that are capable of simulating and predicting the colouring properties of a pigment, using the Mie theory[2] to predict the absorption and scattering. These models require the refractive index, among other parameters, such as particle size, for their application[3].

However, one of the problems that arise when it comes to measuring the refractive index is how to measure this. In itself, this is not terribly complicated, but the techniques and apparatuses that exist to measure it are highly conditioned by the nature of the medium that it is sought to characterise: gas, liquid, or solid; by the optical characteristics: transparent, opaque, translucent; by the surface morphology: rough or smooth; etc.[4] For that reason, a technique that allows the refractive index to be measured in the greatest range of material mediums, which only needs a single instrument without requiring additional investment in new apparatuses as a function of the type of material involved, becomes necessary when the group of materials to be characterised is of different nature.

This paper presents a technique that allows the refractive index to be measured in a simple way, using a spectrophotometer equipped with an integrating sphere. The technique uses the diffuse reflectance measurements made with this instrument.

2. THEORETICAL FRAMEWORK

Light, or any other radiation of the electromagnetic spectrum, is an energy form that in the absence of any material medium, i.e. in a vacuum, travels at a speed of $2.998 \cdot 10^8$ m/s. This is the highest speed at which a wave can travel and is a universal constant that is represented by the letter c . When light crosses a transparent material medium it interacts with this, reducing its speed by a certain quantity with relation to the speed that it would have if it propagated in a vacuum. The refractive index is a dimensionless parameter that indicates how much greater the speed of light is in a vacuum than in the medium in which it is propagating, v . This is expressed as the quotient of the former and the latter:

$$n = \frac{c}{v} \qquad (1)$$

It is important to note that the refractive index is not same for all wavelengths that make up electromagnetic radiation: it depends on the electromagnetic radiation. This phenomenon is known as scattering.

Since no radiation can travel faster than the speed of light in a vacuum, from Eq.(2) one deduces that the refractive index of a material medium is always a positive quantity that is larger than one, being one in a vacuum. In this sense it may be noted that recent studies and advances in nanotechnology have demonstrated that it is possible to fabricate 'new matter', which does not exist in nature, which can give rise to negative refractive indices[5]. These new materials do not follow the known laws of optics and the propagation of light, but they can give rise, for example, to coatings that make objects invisible. These new materials are called *metamaterials*[6].

As mentioned above, the refractive index of a material medium explains its optical properties. Thus, if light propagates through the air ($n \cong 1$) and it impinges upon another medium, for example glass ($n_v \cong 1,5$), this jump in index will therefore lead to transmission, reflection, and absorption.

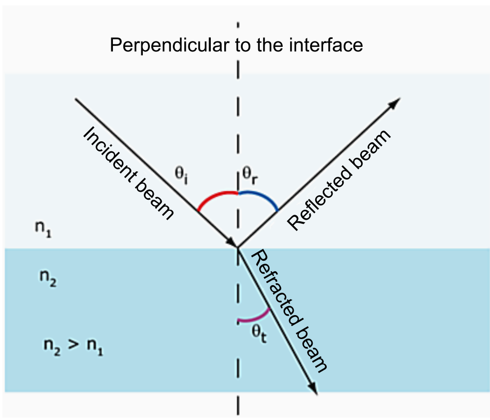

Figure 1. Specular reflection and regular transmission of a beam that impinges upon a medium of greater refractive index. Under these conditions the transmitted beam refracts, approaching the vertical of the interface.

In the foregoing case, when the light is transmitted from the air to the glass it undergoes refraction, which is no more than a departure with relation to the path that it followed in its travel through the air. The departure that it undergoes is explained by Snell's Law:

$$n_1 \sin \theta_i = n_2 \sin \theta_t \tag{2}$$

where θ_i and θ_t are, respectively, the angles that the incident beam and the refracted transmitted beam form with respect to the vertical of the interface that separates both mediums, as illustrated in Figure 1.

From the previous equation it can be immediately deduced that if the refractive index of the medium from which the light comes (in Figure 1, n_1) is lower than the refractive index of the medium to which it is transmitted (n_2), the transmitted beam approaches the vertical: i.e. θ_i is larger than θ_t. In contrast, when the refractive index of the medium from which the light comes is larger than that of the medium to which it is transmitted, the transmitted beam moves away from the normal. In this case, as the incident angle increases, the transmitted beam can move so far away from the vertical that a situation can develop in which transmission does not really occur and all the impinging light is reflected. The angle beyond which this occurs is termed the limit angle or critical angle. When this situation occurs, at which the impinging beams have a larger angle than that of the limit angle, all the impinging light is entirely reflected. The condition of total internal reflection is then met. This is the foundation of different instruments and techniques for the calculation of the refractive index, such as the Abbé refractometer.

Specular reflection and regular transmission, the respective causes of the gloss and transparency of materials, are related to the refractive index by means of the Fresnel equations[7]. Both meet a fundamental condition, which is that the impinging beam, the specularly reflected beam, and the regularly transmitted beam are in the same plane. With relation to specular reflection it may readily be deduced from Eq. (2) that the incident angle and the reflected angle have the same angle.

The reflection can be measured and evaluated by means of the reflectance, which is no more than the ratio between the intensity of the reflected radiation and the incident radiation. The Fresnel equations enable reflectance to be related to the refractive index according to:

$$R = \left(\frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t}\right)^2 \tag{3}$$

When the incidence is perpendicular (θ_i =0) and the medium from which the radiation impinges is air, Eq. (3) can be simplified to:

$$R = \left(\frac{1 - n_2}{1 + n_2}\right)^2 \tag{4}$$

The two forgoing ratios are important and quantify, for example, the specular reflection of a glass or a ceramic material in air.

Transmission can be measured and quantified by means of transmittance as the ratio between the intensity of the transmitted radiation and the incident radiation. When there are no losses of intensity owing to radiation absorption, transmittance is related to reflectance as follows:

$$1 = R + T \tag{5}$$

where T is the transmittance of the medium. This equation responds to the law of conservation of energy, and it assumes that all the energy intensity of the incident radiation,, is reflected and/or transmitted.

When absorption occurs in the medium, it is necessary to consider the energy losses with relation to the impinging energy, incorporating this portion of absorbed energy into the foregoing expression:

$$1 = R + T + A \tag{6}$$

where A is the absorption of the medium.

The absorption of a medium can also be explained by means of the refractive index. In this case, it is necessary to consider that this parameter is a complex number:

$$\tilde{n} = n + ik \tag{7}$$

where i is the imaginary unit given by $i = \sqrt{-1}$. The real part, n, corresponds to the change of speed that light undergoes when it travels through a medium: i.e. the refractive index as defined above. The imaginary part, k, designated the coefficient of extinction, is linked to the absorption of the material. It is related to this by means of its coefficient of absorption according to:

$$k = \frac{\alpha\lambda}{4\pi} \tag{8}$$

Just as occurs with the real part, the imaginary part also depends on the wavelength.

3. METHOD

Since our objective was to establish a reasonable and relatively simple method of calculating n_i, an initial analysis was performed of the techniques or strategies that could be used for this purpose.

The Fresnel equation (3) is known to be highly suited for obtaining the refractive index from the reflectance measurement of materials that reflect specularly: i.e. glossy materials. Therefore, its application is generally restricted to more or less polished surfaces, as is the case of many ceramics. In ceramics that exhibit a certain gloss, other techniques can be used to measure n_i, such as ellipsometry, which even allows the complex part of the refractive index to be measured; techniques that involve measurement of the limit angle; or techniques that involve measurement of the Brewster angle[7], which is related to the polarisation of reflected light. In this last case, the ceramic must be highly reflecting.

However, the surface is not always polished, and the foregoing techniques are then inapplicable. Therein lies the interest in having a technique that allows the refractive index to be measured in the greatest possible range of materials, without the materials surface characteristics being a constraint.

When the surface of a material medium displays irregularities and light impinges on this, at macroscopic level the reflection that occurs is no longer specular, since the incident beam and the reflected beam are neither in the same plane nor have the same angle. In this case the incident radiation energy is distributed across all the surface of the material once it is reflected (Fig. 2, right). This distribution need not be uniform. The reflected radiation in the foregoing conditions is termed diffuse radiation and is characterised by diffuse reflectance. This type of reflectance is the cause, among other things, of the matt appearance of surfaces that have a certain roughness. In these types of surfaces, diffuse reflectance can be measured with spectrophotometer equipped with an integrating sphere. A simplified scheme of an integrating sphere is shown in Figure 3.

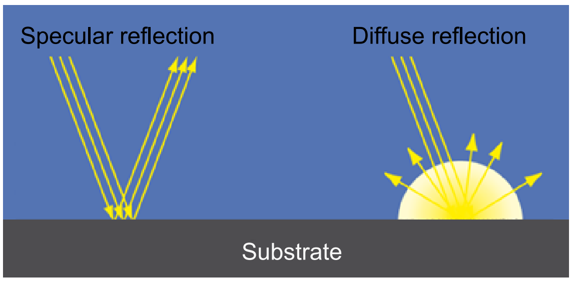

Figure 2. Specular reflection and diffuse reflection. In the first case the beams are reflected at the same angle at which they struck. In addition, the incident beam and the reflected beam are in the same plane. In the second case, owing to surface irregularities, the energy of the reflected beam is not concentrated in the specular direction, but is distributed across the substrate surface.

In our case, in order to measure the refractive index of rough matt surfaces, the starting assumption was made that as a result of their surface irregularity, the specular radiation energy that would be observed if the surface was perfectly polished, which would obey Snell's Law and the Fresnel equations, is distributed across all the material surface, since the impinging light is reflected in every direction and plane perpendicular to that surface. Since an integrating sphere enables the total energy spread over the entire surface, reflected by this, to be measured, the total of this diffuse radiation energy may be assumed to be very similar to the energy reflected specularly if the material was polished, since the refractive index is an intrinsic property of the material and not of its surface.

Making this assumption would allow the refractive index of a rough material to be calculated, by measuring the diffuse reflectance of the surface with a spectrophotometer equipped with an integrating sphere, and introducing this information into the Fresnel equation as if the diffuse radiation were specular.

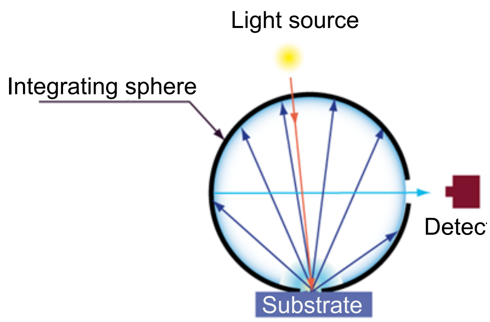

Figure 3. Scheme of an integrating sphere for diffuse reflectance measurements with a geometry of 8º/d. Light enters the integrating sphere forming an angle of 8º with relation to the vertical of the substrate to be measured. The light diffused by this substrate is collected inside the sphere, which has a highly reflecting white lining. After multiple reflections the light exits the sphere and reaches the detector.

In order to verify the goodness of the hypothesis and to verify that it is possible to obtain the refractive index of a rough surface from diffuse reflectance measurements, the diffuse reflectance of a perfectly polished black ceramic with a known refractive index was measured. The ceramic was then subjected to two different abrasion processes in order to obtain a semi-matt surface with the first process, and totally matt surface with the second one. Diffuse spectral reflectance, including the specular component, was measured in the range between 400 nm and 800 nm at the end of each abrasion process using a Perkin Elmer Lambda 800 spectrophotometer equipped with an integrating sphere. Reflectance was measured for each nanometre in the range indicated. The obtained reflectance results were used to calculate the refractive index, and the value obtained in each case was compared with the reference value of the ceramic refractive index.

In order to obtain the reference refractive index, a conventional technique was applied that is used to measure the refractive index of highly glossy materials. This consists of measuring the Brewster angle (which is the angle at which the parallel component (polarisation during reflection) of the reflected light is cancelled).

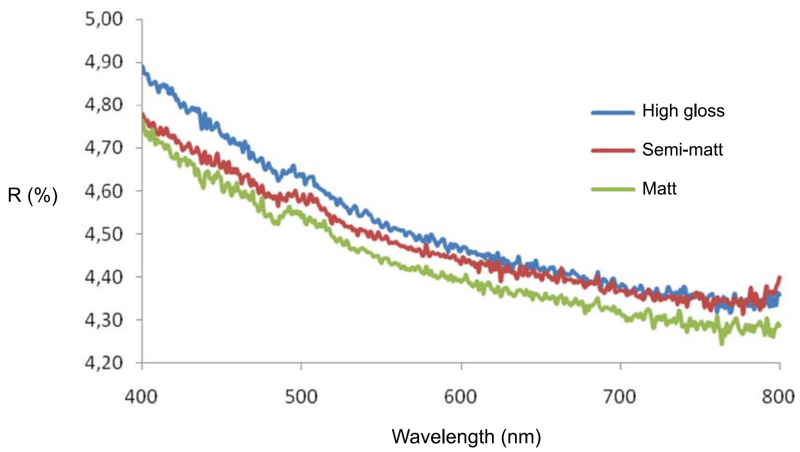

Figure 4. Diffuse reflectance, including the specular component, of a black ceramic. The high-gloss sample corresponds to the polished ceramic. The semi-matt and matt samples correspond, respectively, to the same foregoing sample subjected to two different abrasion processes.

4. RESULTS

Figure 4 shows the reflectance values obtained for each polished, semi-matt, and matt ceramic, measured in the conditions indicated previously. As may be observed, there was a small difference between the reflectance of the high-gloss ceramic and the reflectance of this ceramic when it had been completely matted. For semi-matt, the differences were smaller towards the longest wavelengths. This was basically due to an increase in absorption as a result of the generated roughness. The losses by light diffusion were not taken into account in the reflectance calculations of the semi-matt and matt surfaces, though models are available for quantifying this absorption. This allows the reflectance to be corrected, enhancing the subsequent accuracy in the calculation of the refractive index.

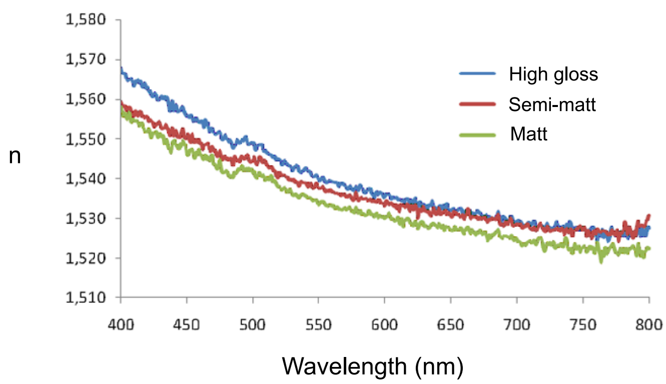

Figure 5. Refractive index calculated from the diffuse reflectance measurements on the ceramic with different surface treatments.

Using the reflectance values, the refractive index was obtained. Figure 5 presents graphically the value of the refractive index for each wavelength in the visible range. As in the previous case, the difference between the matted and the polished samples was also noted. In order to compare the goodness of the results, the refractive index of the polished ceramic was measured at a wavelength of 589 nm using the Brewster angle technique. The resulting index value was 1.536 nm and it served as a reference for comparison with the value obtained by the technique proposed in this paper. The results of this comparison are detailed in Table I. The relative variation is very small, so that the proposed method offers a similar accuracy to that obtained with the classical Brewster angle measurement technique.

Refractive index in 589 nm			
Reference	High gloss	Semi-matt	Matt
1.536	1.538	1.535	1.531
Relative variation with respect to the standard (%)			
	1.001	0.999	0.997

Table I. Values of the refractive, reference, and calculated indices for the ceramic with different surface treatments and the relative variation of these values with respect to the reference value.

5. CONCLUSIONS

The refractive index is a fundamental parameter in the characterisation of material mediums, because their main optical properties depend on it. However, there is no single technique that allows this to be evaluated in all of these, independently of their nature or surface characteristics: gas, liquid, solid, rough, polished, turbid, etc.

This paper presents a valid technique for measuring the refractive index of solid materials that display great absorption, independently of whether the surface is very polished, high gloss, or displays roughnesses and a matted appearance. The technique uses a spectrophotometer with an integrating sphere to measure diffuse reflectance. Based on this reflectance measurement, using the Fresnel equations, it is possible to obtain the material's refractive index. The results obtained show that the method offers results with a similar accuracy to that obtained in the measurement of the refractive index of the same ceramic when this was highly polished from measurements of the Brewster angle. This technique is customarily used to measure the refractive index, the real part, of highly glossy materials. The technique described therefore entails an improvement, since it can be applied to rough surfaces.

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