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Refractive index retrieval from transmittance measurements

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ABSTRACT

This study focuses on the development of an analytical method for simultaneous retrieval of the refractive index and the concentration of particles by measuring suspensions in industrial applications. The proposed method is based on the wavelength-matching method, where the idea is to find the maximum value of light transmittance of the suspension by scanning the irradiation wavelength. The samples were calcium fluoride (CaF_2) powders manufactured by different global producers. The wavelength-matching method is suggested to be a relatively easy, economic and fast modality to retrieve the refractive index of particles. The wavelength-matching method is also considered to be independent on particle size and morphology. The refractive index is of high importance, for instance, if the opacity of products, such as paper or sunscreens, is sought to be increased for product quality improvement.

1. Introduction

Calcium fluoride (CaF_2) has a wide variety of applications in metallurgical, ceramics, chemical and optical material industries [1]. Therefore, the raw material quality is an essential part of the process control. Refractive index is one of the most important parameters in quality inspection of liquids and solids and is widely used in material science to characterize minerals [2]. The refractive index of a material is associated with its electric and magnetic susceptibilities. Information on the refractive index of particles as constituents of a variety of pigments, such as calcium carbonate ($CaCO_3$) and clay pigments used at paper mills, is very important, since the pigments strongly affect optical properties of paper such as brightness, gloss, smoothness, whiteness, opacity and enhance printing surface properties [3]. An emerging trend in the pigment technology is to exploit nanotechnology (nanocoating, nanodoping, etc.) for tailoring optical properties of host pigments for different applications. It is possible to tune the refractive index of the pigment by embedding a small amount of different nanostructures into micron-sized particles such as precipitated calcium carbonate (PCC) used in paper industry as a raw material [4]. Thus, the accurate measurement of the refractive index of particles is of high importance.

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The refractive index of materials (n) has been investigated using a number of tools [5]. Conventionally, the refractive index of a transparent liquid is measured using an Abbe refractometer [6]. Ellipsometry and interferometry are also useful optical techniques for retrieving the refractive index of solid materials, but the utilized devices are rather expensive and require good sample quality [7]. The transmittance measurement technique also provides information on the refractive index of particles. A particle population changes the propagation of a light beam by scattering and absorbing light. The transmittance of light depends on a number of parameters such as the complex refractive index of the host medium and the particles, the concentration, the shape, impurity, size, distribution, arrangement, and color of the particles, sample thickness, and the wavelength of the incident light. The intensity of light is reduced exponentially according to the Beer–Lambert law: $\exp(-\alpha d)$, where α is the extinction coefficient and d is the sample thickness. When dealing with non-absorbing particles, α can also be referred to as the scattering coefficient. If N spherical particles in a unit volume with the radius r are considered, the scattering coefficient can be calculated by $\alpha = N\pi r^2 Q_{sca}$ where Q_{sca} is the scattering efficiency for one particle depending on the refractive indices of the particle and the surrounding medium, the particle size and the wavelength [8]. The Mie scattering theory gives an exact solution for Q_{sca} when the scattering particles are spherical, isotropic and homogeneous. Such a theory is useful in practical applications when the wavelength of light is comparable to the particle diameter and scattering is dominated by a single scattering process. Unfortunately, currently there is no rigorous theory available providing accurate Q_{sca} of a particle with an irregular shape and volume in a suspension. However, in the immersion liquid the method can be applied to the special case of scattering where the refractive index of particles is probed with the surrounding liquid. In the ideal case of refractive index matching, the light scattering in a suspension would be zero and thus the light transmittance through the suspension would be 100%. Consequently, the immersion method is independent on the shape and size of the particles, and the measurement of the refractive index is relatively easy and fast to perform and the quantity of the material is less than required for tests by any other method [7,9]. The refractive index can be measured by a number of different immersion techniques including liquid-, temperature- and wavelength-variation methods [10]. Recently, we have developed optical measurement methods, devices and analysis of refractive index of micro- and nanoparticles using the idea of light dispersion in a suspension, where solid particles are submerged in an immersion liquid [8,11]. The wavelength-matching technique is based on the fact that immersion liquid and the particles have different intrinsic dispersion $n(\lambda)$ characteristics. The refractive indices of the immersion liquid and the particles may be equal at a certain wavelength λ. This can be revealed from the transmittance spectrum and particularly from the spectral location of the maximal transmittance. The intersection of the wavelength-dependent refractive index curves of the particle and the immersion liquid is a crucial feature in the wavelength-matching method because at this particular wavelength the maximum light transmittance of the suspension is achieved. Presence of particle impurities shifts the intersection point to longer or shorter wavelengths depending on the range of the refractive index of the impurities to the refractive index of the host particle. In addition, the impurity decreases the maximal transmittance.

In this paper, the wavelength-matching method was used to retrieve the refractive indices of commercial calcium fluoride (CaF_2) powders. The information on the refractive index and the spectral position of the maximal transmittance can be used for the assessment of the particle concentration and for the purity estimation.

2. Materials and methods

This study deals with three samples of CaF_2 powders produced by Merck, Prolabo and Alfa Aesar. According to the product description, the purity of CaF_2 is >97% (Merck), >98% (Prolabo), and >99% (Alfa Aesar). Various physical and spectroscopic properties of CaF_2 are described in Reference [12]. The liquids used in this study were purified water and glycerol (Sigma–Aldrich), mixed to obtain appropriate immersion mixtures. The measurements were performed using a commercial spectrophotometer (Shimadzu UV-1800). The transmittance of the suspensions was recorded from a 10-mm thick quartz cuvette at the wavelength range 220–550 nm at room temperature (22 °C).

X-ray data were obtained with PANalytical MiniPal 4 EDXRF Spectrometer comprising of an energy dispersive microprocessor controlled with the Minipal software. The main instrument features are silicon drift detector, rhodium X-ray tube and He gas system. The use of He allows for detection of chemical elements with small atomic number, such as Na. In general, the system is capable for screening elements from Na to U.

3. Results and discussion

Initially, the wavelength-dependent refractive index (a dispersion curve) of a glycerol–water mixture [66:34 vol.%] was calculated using data from literature [13,14] and the refractive index data of CaF_2 were obtained from Reference [15]. The results are graphically shown in Fig. 1. In this case, the refractive indices of CaF_2 and glycerol–water mixture match at the 294-nm wavelength, where the refractive index of CaF_2 is 1.4553.

Then, a glycerol–water mixture (liquid mixture) with a ratio of 66:34 vol.% was prepared and used in all measurements with CaF_2. Six different particle and liquid mixture suspensions were used to study the effect of particle–liquid concentration on the light transmittance. The concentrations were 0.5, 2.5, 4.5, 6.5, 8.5 g per 100 ml (the total glycerol–water mixture volume). First, the CaF_2 powder produced by Merck was dealt with. Transmittance curves from 220 to 550 nm were recorded with the spectrophotometer at 22 °C and the results are plotted in Fig. 2(a). From the transmittance curves in Fig. 2(a) it is seen that the maximum point of transmittance is located at 311-nm wavelength for all particle–liquid concentrations.