Talanta 81 (2010) 1322–1324

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A method for the detection of the refractive index of irregular shape solid pigments in light absorbing liquid matrix

Ilpo Niskanen [a,*], Jukka Räty [a], Kai-Erik Peiponen [b]

[a] Measurement and Sensor Laboratory, University of Oulu, Technology Park 127, FI-87400 Kajaani, Finland
[b] Department of Physics and Mathematics, University of Eastern Finland, P.O. Box 111, FI-80101 Joensuu, Finland

ARTICLE INFO

Article history:
Received 8 December 2009
Received in revised form 3 February 2010
Accepted 7 February 2010
Available online 16 February 2010

Keywords:
Mineral pigments
Complex refractive index
Immersion method
Colored liquid

ABSTRACT

The immersion liquid method is powerful for the measurement of the refractive index of solid particles in a liquid matrix. However, this method applies best for cases when the liquid matrix is transparent. A problem is usually how to assess the refractive index of a pigment when it is in a colored host liquid. In this article we introduce a method, and show that by combining so-called multifunction spectrophotometer, immersion liquid method and detection of light transmission and reflection we can assess the refractive index of a pigment in a colored liquid, and also the extinction or absorption coefficient of the host liquid.

1. Introduction

The immersion liquid method [1] is very useful for the measurement of the refractive index of a pigment whose shape is irregular and size may range from a nanoparticle to a macroscopic object [2–8]. The idea of immersion technique is to find a perfect refractive index match between the solid medium and the immersion liquid. The immersion method involves measurement of light transmission with a conventional spectrophotometer and preparation of a set of immersion liquids with variable refractive index. The refractive index of an immersion liquid is typically measured at a fixed wavelength of sodium light using an Abbe refractometer. We have studied measurement of the refractive index of a pigment using a protocol different from the conventional measurement technique. Firstly, the refractive index of the immersion liquid itself at any wavelength in the visible spectral range is obtained with a multifunction spectrophotometer (MFS). Also transmittance from a mixture of pigments and the immersion liquid is measured with the MFS [9]. So far, we have replaced the conventional spectrophotometer and the Abbe refractometer with one single device namely the MFS. Secondly, with the MFS we are able to measure in addition to the transmission of light also light scattering to detect index matching or mismatching between the pigment and the immersion liquid [10]. The studies [8–10] involved index matching using a fixed wavelength of light but chosen freely in the UV–visible range. Unfortunately, a conventional Abbe refractometer suffers from the requirement of a non-absorbing liquid sample. However, it is a fact that there are lots of samples that have a color, e.g. industrial and biomedical. As an example of the importance of the immersion liquid method we mention the photo clearing of tissues and blood samples [11]. Turbidity of a colored liquid can be monitored with the aid of a sensor that detects dynamic speckle pattern using total internal reflection of a laser beam in a prism–turbid liquid interface [12]. Theoretical studies on apparent optical properties of particles in absorbing media have been considered, but for the simple case of spherical particles [13]. Unfortunately, the traditional immersion method which is used for the assessment of the refractive index of solid pigments embedded in a colored liquid, and exploits the transmission-measurement mode is quite problematic due to light absorption at the probing wavelength. To overcome this shortcoming, we report here advances on how to assess the refractive index of a pigment in a colored two-phase system. To show how it works in practice we demonstrate a case where water and glycerol are mixed to obtain immersion liquids with different refractive indices. In addition we mixed red food-coloring stuff into the immersion liquid, and finally mixed CaF_2 pigment with the colored immersion liquid.

2. Experimental and discussion

In Fig. 1 is shown a schematic diagram of the MFS. The user may choose any wavelength from 270 to 800 nm. Monochromatic light is guided into a bifurcated optical fiber. Part of the light beam is going to a reference detector, which monitors the intensity variations of

* Corresponding author. Tel.: +358 44 353 3690; fax: +358 8 614 9615.
E-mail address: ilpo.niskanen@oulu.fi (I. Niskanen).

0039-9140/$ – see front matter
doi:10.1016/j.talanta.2010.02.027

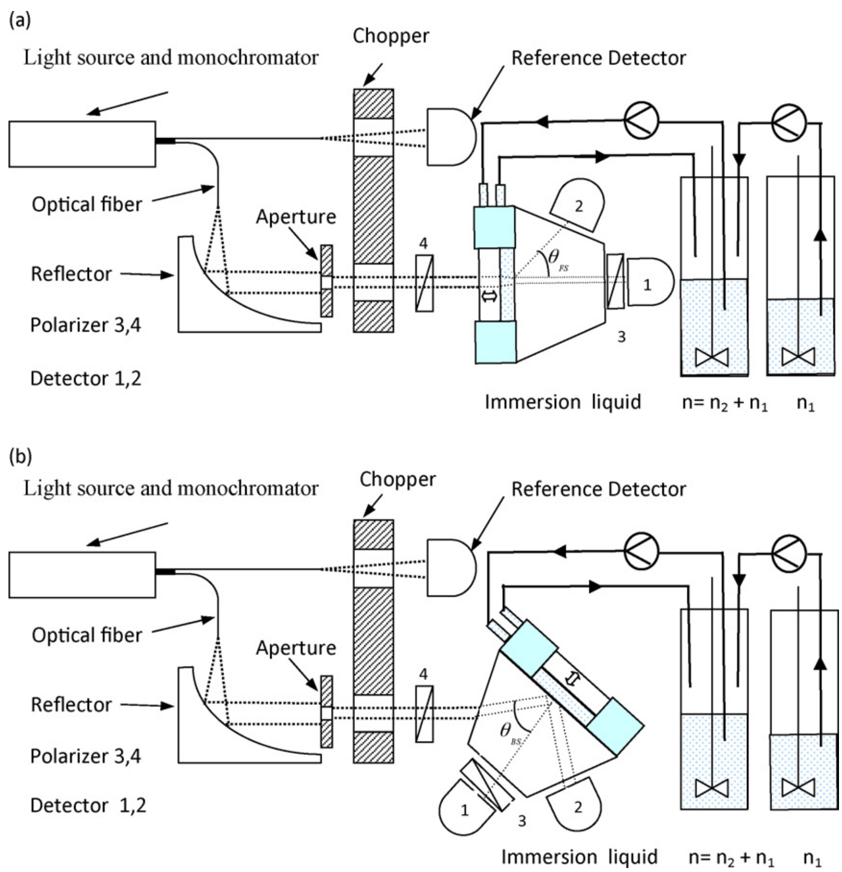

Fig. 1. Schematic diagram of the MFS. (a) Transmission and scattering measurement modes, and (b) reflection and scattering measurement modes.

the light source. The remaining part of the light is guided to the parabolic reflector, aperture, chopper and polarizer. The polarized light beam propagates to the prism–sample interface and finally on a detector. The angle of light incidence can be varied using a step motor. Pumps are used for suspension circulation between the containers and the sample compartment, and changing the refractive index of the mixture. Fig. 1a illustrates the principle of light transmission and scattering measurement. In the event of light scattering we get information on the color (color coordinates) of the liquid and also the concentration of the pigments. However, in this paper we concentrate on studying the refractive index (n) of the pigment and the extinction coefficient (k) of the liquid. The extinction coefficient describes the absorption of light in a medium in the absence of light scattering. In Fig. 1b is a schematic diagram of the measurement principle of light reflection and also scattering. The reflectance and scattering signals can be recorded as a function of wavelength, angle of incidence and state of polarization of the light.

The pigment we used is CaF_2, which is a product of Merck and it has 97% purity. According to the manufacturer the particle size is less than 15 μm. The red food-coloring dye was bought from a drug store. Transmission spectra (350–770 nm) were measured with the MFS at 1.0 nm intervals with sample path length 10 mm.

In Fig. 2 is shown transmittance of different water/glycerol/red food-coloring-mixture samples all in a total volume of 100 ml. In all cases the refractive index of the immersion liquid is 1.434 which according to Palik [14] is supposed approximately to match with the refractive index of CaF_2 at the wavelength 589 nm, which represents the wavelength of the well-known sodium light that is used in many standardized optical measurement devices. The data of Fig. 2 was measured using the configuration of Fig. 1a. We observe from Fig. 2 that once the amount of the pigment is constant but the amount of the coloring stuff is increased the transmittance is decreasing in the measured spectral range. Such a behavior of transmittance is what one can expect. Fig. 2, there is a transmittance curve for a sample without pigments.

The issue is how to obtain reliable estimate, using the MFS and a chosen wavelength, for a refractive index of a pigment embedded in a colored liquid? This is possible by a two-stage process. First we detect maximum transmission of light exploiting a set of colored liquid samples with different refractive indices. Hence, we find an immersion liquid that provides the best index match. In

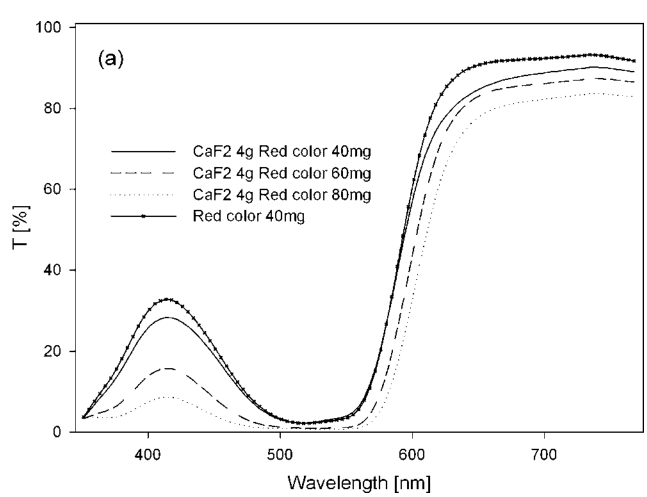

Fig. 2. Transmittance as function of wavelength for samples with constant pigment (4 g) amount but variable coloring into immersion liquid (100 ml). The refractive index of immersion liquid was 1.434.

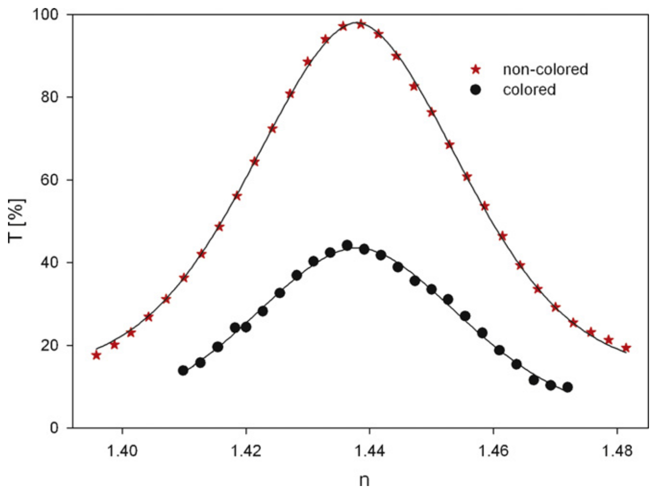

Fig. 3. Transmittance of non-colored and colored sample as a function of the refractive index of the immersion liquid at 589 nm. The immersion liquid is mixture of water ($n = 1.333$) and glycerol ($n = 1.482$). The solid line is a Gaussian line for fitting the experimental data.

other words we prepare a set of immersion liquids which are also measured by the MFS. The refractive index of the set of immersion liquids is measured by the MFS too. In Fig. 3 we show transmittance data for non-colored and colored mixtures containing CaF_2 pigments. In the case of the colored sample, i.e., in the presence of light absorption we get a maximum transmittance just like in the more conventional case of transparent (non-colored) mixture. The data of Fig. 3 was measured using the wavelength 589 nm. The refractive index that yields the maximum is the same for colored and non-colored samples namely $n = 1.434$. Hence, the coloration stuff has a negligible effect on the refractive index of the mixture. The second stage is to measure the reflectance from the colored liquid with pigments embedded in an immersion liquid with refractive index $n = 1.434$ that provides the maximum transmission, i.e. the best index match between the immersion liquid and the pigment. In such a case we can assume no or negligible scattering of light. The reduction of light scattering can be detected using the scattering measurement mode of the MFS. For the purpose of measuring the reflectance in the index match condition we used s-polarized light, the wavelength was once again 589 nm, and changed the angle of the light incidence. Thereafter, the reflectance data was fitted by minimizing the least square sum

$$S = \sum_{i=1}^{J} (R_{mi} - R_s(\theta_i, N_{21}))^2, \quad (1)$$

where R_s is reflectance obtained from Fresnel's theory, R_{mi} is the measured reflectance at a certain range of incidence angle θ_i, $N_{21} = N_1/n_2$ is the relative complex refractive index, where N_1 is the complex refractive index of the liquid, and n_2 is the refractive index of the prism of the MFS. In Fig. 4 is shown the measured reflectance (discrete points) and the one obtained from the theory (solid line) both for water and a colored liquid with pigments. It is interesting that one can distinguish the location of critical angle for the colored liquid. This results from the fact that the wavelength used for measurement of the light reflection with the MFS corresponds to orange light, which is in the vicinity of the red light which is transmitted without loss in the present red sample. In Table 1 are shown the data obtained from the reflectance signal and calculated with the aid of Eq. (1). The refractive index is close to the one obtained with the aid of the transmission-measurement technique (Fig. 3), and the extinction coefficient of the liquid is subject to change due

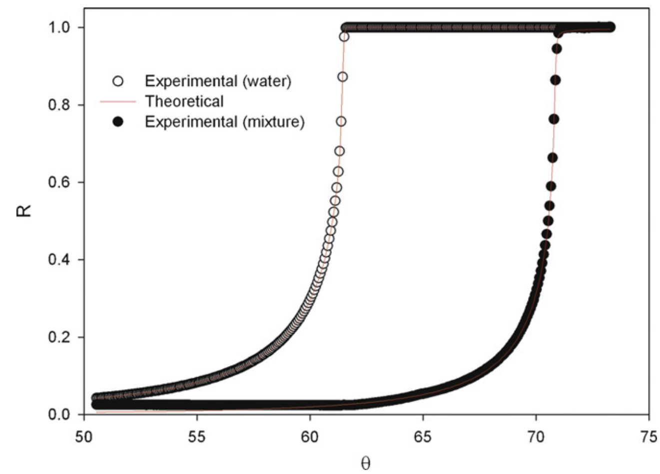

Fig. 4. Reflectance as a function of the angle of incidence for water and water/glycerol/red food-coloring-mixture (80 mg) sample with CaF_2 pigments (4 g/100 ml).

Table 1
Refractive index and extinction coefficient data for colored samples with pigments.

Liquid	Fresnel method	
	n (589 nm)	k (589 nm)
CaF_2 (4 g) Red color (40 mg)	1.432	0.000055
CaF_2 (4 g) Red color (60 mg)	1.432	0.000074
CaF_2 (4 g) Red color (80 mg)	1.433	0.000101

to the degree of the coloration of the liquid. Under the assumption that the pigments and liquids do not react chemically with each other we suggest that the procedure described above is useful if the issue is the detection of the refractive index of pigments embedded in a liquid, and furthermore measurement of the extinction or absorption coefficient of the liquid. Naturally introduction of an immersion liquid will change the color of the mixture but this is usually inessential if the major problem is to find out the refractive index of the embedded pigment.

For some illegal purposes one may try to conceal hazardous solid material in colored liquid i.e. making solid material "invisible" by using index matching technique. Fortunately, the cloaking of such material can be revealed by introducing liquid which has index different from the index of the host liquid, and by performing measurement of the light scattering from small, nano-sized objects with the MFS.

References

[1] E.E. El-Hinnawi, Methods in Chemical and Mineral Microscopy, Elsevier, Amsterdam, 1966.
[2] F. Allen, P. Sennett, in: D. Pevear (Ed.), Clay Minerals Society, 28th Annual Meeting, Program and Abstracts, Houston, TX, 1991.
[3] P.G. Weidler, F. Friedrich, Am. Mineral. 92 (2007) 1130–1132.
[4] R.J. Nussbaumer, M. Halter, T. Trevoort, W.R. Caser, P. Smith, J. Mater. Sci. 40 (2005) 575–582.
[5] G. Smith, Appl. Opt. 21 (1982) 755–757.
[6] R.E. Marquis, J. Bacteriol. 116 (1973) 1273–1279.
[7] M. Jonasz, G. Fournier, D. Stramski, Appl. Opt. 36 (1997) 4114–4225.
[8] K. Koivunen, I. Niskanen, K.-E. Peiponen, H. Paulapuro, J. Mater. Sci. 44 (2009) 477–482.
[9] I. Niskanen, J. Räty, K.-E. Peiponen, Appl. Opt. 46 (2007) 5404–5407.
[10] I. Niskanen, J. Räty, K.-E. Peiponen, Appl. Spectrosc. 62 (2008) 399–401.
[11] V.V. Tuchin, J. Phys. D: Appl. Phys. 38 (2005) 2497–2518.
[12] V. Kontturi, P. Turunen, J. Uozumi, K.-E. Peiponen, Opt. Lett. 34 (2009) 3743–3745.
[13] Q. Fu, W. Sun, J. Quant. Spectrosc. Rad. Trans. 100 (2006) 415.
[14] E.D. Palik, Handbook of Optical Constants of Solids, vol. III, Academic, San Diego, 1998.