A SPECTROPHOTOMETRIC METHOD FOR DETERMINING THE REFRACTIVE INDEX OF DISPERSE MATERIAL IN THE VISIBLE

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Some results of theoretical and experimental studies of the immersion technique for determining the refractive index of disperse material are presented. Certain prospects of this method are demonstrated by measuring the spectral behavior of a suspension layer using the BS–4 glass filter.

INTRODUCTION

The refractive index of particles in the visible is one of the most important physical parameters of disperse materials which is used in many areas of applied science ranging from the methods of laser sounding to the problems on constructing devices for quality control of product. However, the information on the refractive indices of disperse materials compiled so far is yet insufficient. It is connected with the laborious and complicated measurements and the lack of universal techniques and criteria for assessing measurement accuracy.

The refractive index of bulky, transparent and homogeneous samples is usually determined by a refractometric method.[1] However, this method fails in the case of finely disperse particles. In practice, especially in mineralogy, the high–contrast method based on the use of an optical microscope and a set of immersion liquids is being employed.[1] This method consists of placing a suspension droplet composed of an immersion liquid and particles of the material to be analyzed on the microscope slide and then determining visually the contrast grade of particles. The refractive index of particles n is assumed to be equal to the refractive index of liquid when the contrast disappears, i.e., the particles become invisible against the liquid background. Although, these measurements are sufficiently accurate ($\Delta n \sim 0.001$) but it is practically impossible to determine the variance of the refractive index n_D using this technique. It is also impossible to study n of absorbing substances ($\kappa \geq 10^{-5}$).

Ryzhkov[2] proposed the method which makes it possible to obtain the optical constants from measurements of light extinction by two layers of suspensions composed of the particles under study and two transparent immersion liquids with different refractive indices. In this case very small particles are used to satisfy the condition of the Rayleigh scattering ($2\pi a/\lambda \ll 1$). Then the system of two equations derived from the Rayleigh theory is solved with respect to n and κ. Unfortunately, it is practically impossible to select such immersion liquids for the visible and to grind the particles to such an extent.

Several papers are available[3] where the inverse problem of light scattering is solved based on the Mie theory. The values to be measured are the extinction coefficient and the intensity of light scattering at a certain angle. The method is rather complicated from the point of view of both experimental performance and mathematical processing though sometimes a fairly good accuracy in determining the optical constants can be obtained.

Moreover, there is the immersion method which is based on the Christiansen effect, i.e., the closer in value are the refractive indices of the particles and the immersion liquid, the weaker is the scattering and the higher is the transmission of the suspension layer.[4] Just this method combining the advantages of immersion method and simplicity of spectrophotometric measurements has been chosen for further studies and development.

EXPERIMENTAL TECHNIQUE AND MEASUREMENT RESULTS

It is convenient to study and develop the aforementioned method using the substances whose dispersion is known in a wide spectral region. Unfortunately, the class of such materials is greatly limited: first by the complexity of studies of the optical properties of disperse materials in the visible. As is well known the optical constants found for monocrystals cannot be compared with the measurement data obtained in studies of the disperse systems. Thus, from the very beginning our choice is limited by the condition that the material under study is to be isotropic. The achromatic glass BS–4 turned out to be most useful for our studies. The spectral behavior of the BS–4 glass dispersion measured by the refractometric method is plotted in Fig. 1.

The optical characteristics of glasses were taken from the catalog of the pigmented glasses.[5] It was found in the test measurements of glasses that the data on n from catalog were not always in good agreement with the experimentally measured refractive indices n_D of disperse materials. The maximum difference between the measured values and those taken from the catalog was about 0.02. It can be explained by violations of the glass production technology and by poor control of the glass quality.

To develop the immersion method we selected a set of immersion liquids meeting the requirements of sufficient viscosity, chemical inertia, weak light absorption, etc. Depicted in Fig. 1 are the spectral behaviors of dispersion of the refractive indices for some liquids. As can be seen from this figure, such a set of liquids makes it possible to study the effect of the difference between the refractive indices of particles and those of the immersion medium in a wide spectral interval.

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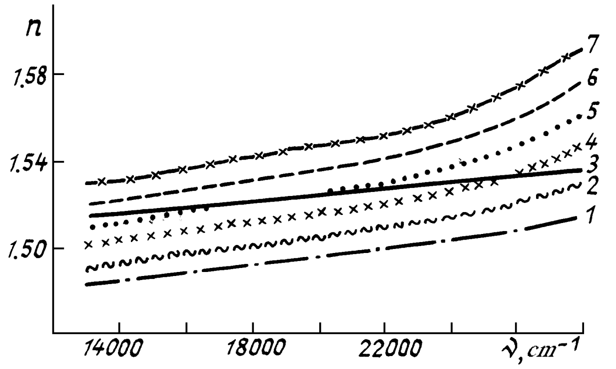

FIG. 1. Dispersion of the refractive indexes of the BS–4 glass (curve 1) and immersion liquids with n_D = 1.49 (*2*), 1.50 (*3*), 1.51 (*4*), 1.52 (*5*), 1.53 (*6*), *and* 1.54 (*7*).

The same set of liquids was used in our previous studies for determining n_D of some salts and minerals. The experimentally obtained plots of the transmission of suspension of some materials with known refractive indices at the frequency ν = 17000 cm^{-1} vs the refractive indices of immersion liquids are shown in Fig. 2. The curves have a typical dome–shaped configuration. Maximum transmission was observed when the values of refractive indices of particles and the immersion liquid coincide. The arrows denote the values of n determined for monolithic samples. The mean experimental error in determining the value of n_D of these particles by the proposed method is approximately 0.0005 for the transparent isotropic particles.

The experiment was performed in the following way. The refractive index of a monolithic glass plate was measured by the refractometric method. Then the glass has been ground in a jewel mortar to obtain particles with size from 1 to 20 μm which were tested using an optical microscope.

The powder obtained was sifted through a 20 μm sieve. The larger particles were separated out and the aggregate formed during grinding the glass were broken. The prepared powder was then used for making suspensions.

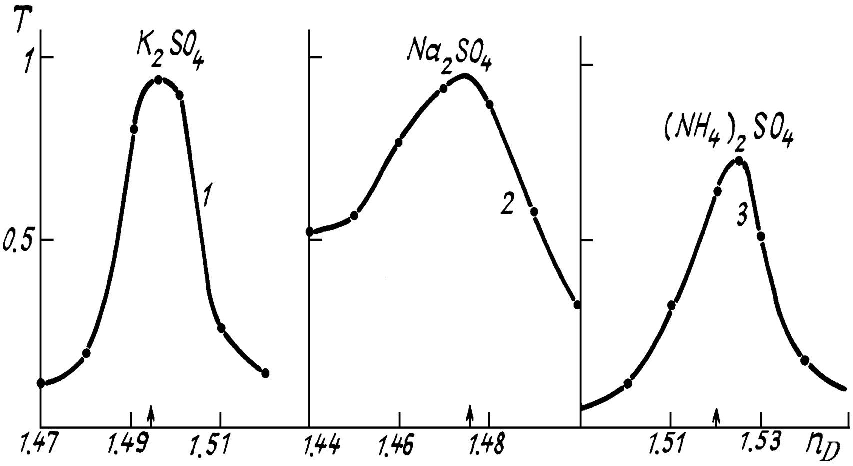

FIG. 2. Experimental curves of the transmission of the layer of suspension (d = 5 mm) as functions of the refractive index of immersion liquid: 1) K_2SO_4; *2)* Na_2SO_4; *3)* $(NH_4)_2SO_4$.

To do this, the weighted portion of the powder was mixed with a weighted portion of immersion liquid in a 1 : 20 ratio. Viscosity of the immersion medium was chosen so that the particles could not settle and coagulate during the measurements. The transmission suspensions of was measured with a "Specord UV–VIS" spectrophotometer using standard cells which were of 1, 3, 5, and 10 mm thick.

Figure 3 shows the transmission spectra of suspensions (BS–4 and liquids) in the thickness d = 1 mm. As can be distinctly seen from the figure, the behavior of the curves are quite similar to that of the dispersion curves (see Fig. 1), i.e., the closer in value are the refractive indices of the glass and a liquid, the higher is the transmission of the suspension. These figures allow one to qualitatively determine the spectral region where the refractive indices of particles and liquid become close in value.

The absorption coefficient of achromatic glass is very small. Therefore it is possible to assume that all changes in transmission of the suspensions are solely caused by the difference between the refractive indices of particles and immersion media.

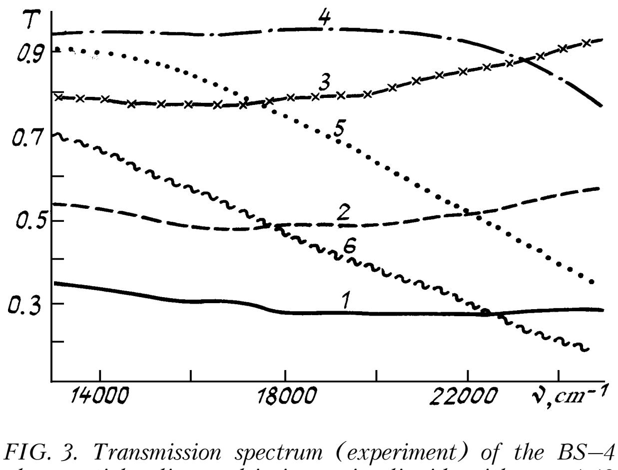

FIG. 3. Transmission spectrum (experiment) of the BS–4 glass particles dispersed in immersion liquids with n_D = 1.49 *(1)*, 1.50 *(2)*, 1.51 *(3)*, 1.52 *(4)*, 1.53 (*5*), *and* 1.54 *(6)*.

Thus, all changes of the transmission are due to variations in the fraction of scattered light. This is distinctly illustrated by the curves representing the spectral behaviors of the extinction coefficient of the BS–4 glass particles (see Fig. 4). The spread of $\alpha(\nu)$ values at the variations of layer thicknesses is obviously caused by variations of the multiple scattering contribution rather then by the experimental error since the significant portion of the scattered light is rescattered in thick layers thereby decreasing the extinction coefficient.

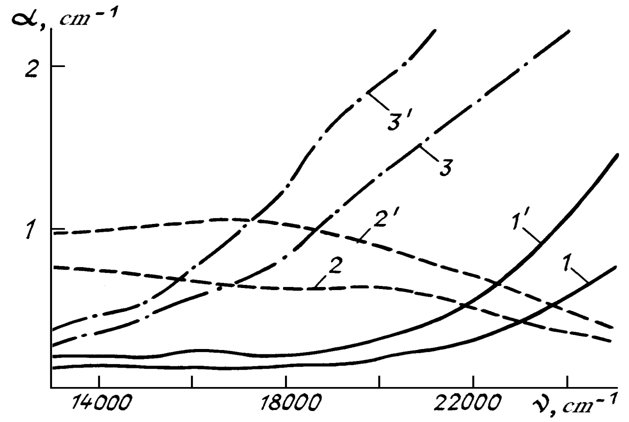

FIG. 4. Extinction coefficients of the layer of suspension of the BS–4 glass particles. The thickness of the layer was equal to 0. 1 and 1 cm. n_D = 1.52 *(1 and 1')*, 1.51 *(2 and 2')*, 1.53 *(3 and 3')*, *1, 2, 3)* d = 0.1 cm; *1', 2', 3')* d = 1 cm.

The spectral behavior of $\alpha(\nu)$ for different immersion liquids differs markedly. This difference increases with increase of the difference in the refractive indices of liquid and particles. As could expected, the smallest extinction coefficient was observed at the smallest values Δn. It should also be noted that for small Δn the value of α_{ext} remained practically constant. This is indicative of the fact that insignificant variations in Δn weakly affect the extinction of "soft" particles, hence the main contribution is due to the absorption by particles. The contribution from multiple scattering in this case is also negligible.

The Mie theory was used in the model calculations to make clear the dependence of transmittance on the parameters of the problem.

THE USE OF THE MIE THEORY IN CALCULATIONS OF A SUSPENSION LAYER TRANSMISSION

To determine the mechanism and characteristic features of the immersion method for measuring the optical constants, we have numerically simulated the problem based on the Mie theory describing light scattering and absorption by an individual spherical particle. Calculations by the Mie theory were made on a routine basis. First, the particle size a, the wavelength λ, and the relative refractive index of particles $\hat{n}_{rel} = \hat{n}_{part}/\hat{n}_{liq}$ were specified and the diffraction parameter $\rho = 2\pi a/\lambda$ was calculated. The cross sections of scattering σ_s and extinction σ_{ext} were then calculated using the well – known algorithm.[6] These quantities were used in our calculations. After simple transformations of the extinction cross section one can obtain the efficient extinction coefficient

$$\alpha_{ext} = \frac{3\sigma(\hat{n}_{rel}, \rho)}{4\pi a^3} .$$

The value α_{ext} is similar to the absorption coefficient used in spectroscopy. Hence, it is possible to estimate theoretically the transmission of a suspension layer of the particles using the formula

$$T = T_1 = \exp(-C_V \cdot d \cdot \alpha_{ext}),$$

where C_v is the volume number density of particles in the suspension, d is the thickness of the suspension layer (d = 5 mm).

When the immersion medium has a noticeable absorption, the formula can be modified as follows

$$T = T_1 \cdot T_2,$$

$$T = \exp(-(1 - C_V)\, d\, \alpha_{liq}).$$

This approximation is similar to that used in calculations of the absorption coefficient of particles in the IR by the transmission method.[7] Of course, multiple scattering of light and the interference effects are not taken into account here. Moreover, this information is not needed for qualitative analysis of the problem.

It should be noted that the dispersions of immersion liquids and of the glass BS–4 were taken in calculations to be close to those of actual materials. However, the size spectra of glass particles were unknown, therefore we carried out the calculations for particles of different size.

The numerical simulation was performed once but already taking into account the actual experimental conditions. The plots of the suspension layer transmissions vs Δn for different size of particles at ν = 17000 cm^{-1} are shown in Fig. 5.

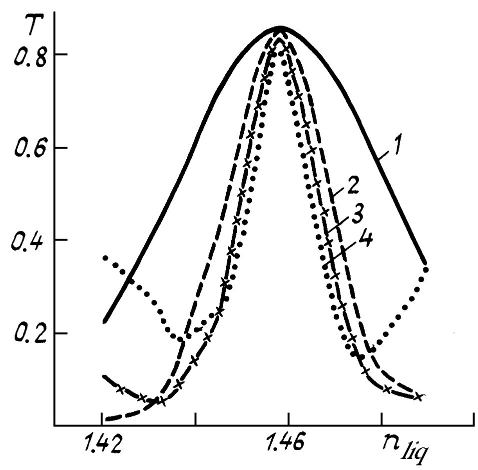

FIG. 5. Transmission of the layer of suspension of particles dispersed in immersion liquids (ν = 1700 cm, d = 5 mm*) for the particles with radii a* = 1 *(1)*, 5 *(2)*, 10 *(3)*, *and* 15 *(4)* mm. *Dots denote the results of calculations.*

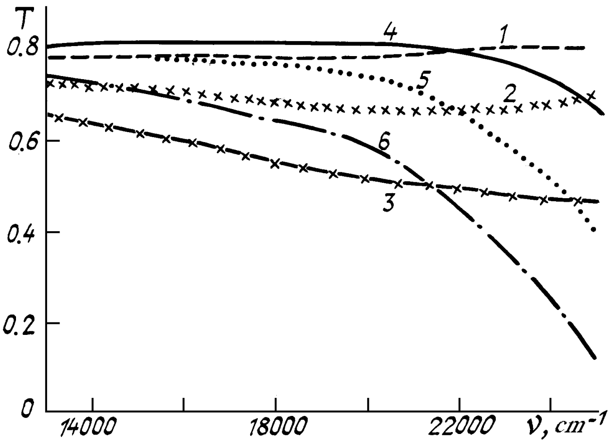

FIG. 6. Transmission of the layer of suspension of the BS–4 glass particles of radius 1 mm dispersed in immersion liquid with n = 1.49 *(1),* 1.52 *(2),* 1.51 *(3),* 1.52 *(4),* 1.53 *(5),* 1.54 *(6). The thickness of the layer was 1 mm. Dots denote the results of calculations.*

By comparing the data presented in Figs. 5 and 2 one can come to a conclusion that typical dome–shaped curves are satisfactorily described within the approximation used. The maximum transmission was observed when the refractive indices of particles and liquid are equal irrespectively of the particle size. However, in the case of relatively large particles, the interference oscillation become noticeable that can essentially hamper the determination of the refractive index by the immersion technique. In the experiment it was really difficult to determine the maximum of the curve $T(n)$ for some materials. However, the anisotropy of the optical properties of different materials (salts, minerals, etc.) also plays an important role in this process and leads to smearing and splitting of the maximum of curves. One more peculiarity is that the maximum decreases with increasing refractive index of particles. This results from the Bouguer law which, in the case of absorbing immersion media, can lead to the negative absorption coefficient of the particles (when the particle transmission is larger than unity).

The calculated curves of the transmission spectrum of the particle in the visible and UV are given in Fig. 6. As can be seen from the figure, there exists similarity between the experimental and theoretical curves. It becomes more pronounced if we take into account actual size of the particles.

CONCLUSION

The studies of light extinction by suspension layers have shown that it is mainly caused by scattering. The larger is the difference between the absorption coefficients of particles and immersion liquid, the larger is this extinction. The comparison between the experiment and the numerical simulations of this phenomenon allows one to conclude that the model used describes well the actual situation. This means that in the experiment the single scattering predominates and the largest portion of scattered light is attenuated. The assumption on the particle sphericity made in calculations seems to be justified.

All the above said enables us to hope that the inverse problem can be solved using the immersion method. In the subsequent publication the effect of other factors on the accuracy of the absorption coefficient determination by the immersion method will be discussed.

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