

ON THE ACCURACY OF THE SPECTROPHOTOMETRIC TECHNIQUE FOR MEASURING THE OPTICAL CONSTANTS OF DISPERSE MATERIAL IN THE VISIBLE

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Some results of calculation of the extinction coefficient of immersion particles of the BS-4 glass as functions of the difference between the refractive indices of the glass and immersion liquid and the absorption coefficient of particles are presented. It is shown that when the difference between the refractive indices is small the immersion method ensures satisfactory accuracy of determining the absorption coefficient.

Further development of laser radar techniques as well as the techniques for measuring size spectra and number density of aerosol particles and gas-dust flows in the atmosphere depends strongly on the possibility of measuring optical constants of finely disperse material in the IR and, especially, in the visible.

Unfortunately, traditional methods of measuring refractive indices and absorption coefficients of monolithic materials based on the interaction between the substance and electromagnetic waves and recording the changes in the intensity or direction of propagation of radiation flux after the interaction are inapplicable in the case of finely disperse material.

In such disperse media the attenuation of radiation occurs not only due to absorption but also due to scattering which, in its turn, depends on many parameters, i.e., the ratio of refractive indices of particles and medium, number density and size spectrum of particles, and so on.

Inverse problems of retrieval of the parameters n and κ of aerosol particles from optical measurements were investigated in detail in Ref. 1. One can find a discussion of some peculiarities of light scattering by soft particles in Ref. 2. Refractive indices of disperse material can be determined, in particular, by the immersion technique. However, we believe that the capabilities of the immersion technique have not yet been exhausted. Thus in Ref. 3 we have shown that the values of refractive index of amorphous silicon oxide with the particles $0.02 - 0.03 \mu\text{m}$ in diameter (aerosil) measured in the IR using the immersion technique agree well with the spectrum of $\kappa(\nu)$ for both a film and monolithic silicon oxide.

We have proposed a spectrophotometric technique for measuring the refractive index of larger particles in the visible in Ref. 4 by measuring the intensity of light passed through the layer of suspension of the particles under study in various immersion liquids at a fixed wavelength.

In our experimental study³ we have shown that in the case of isotropic and sufficiently transparent particles of silicon oxide this method can ensure an accuracy of the refractive index measurements of the order of $5 \cdot 10^{-4}$. It is evident that this technique can also ensure satisfactory accuracy of the absorption coefficient measurements. Moreover, such measurements can be made not only at a

fixed wavelength but in a sufficiently wide spectral range, provided the refractive index of particles depends weakly on the wavelength.

In this paper we present test experiments on measuring $\kappa(\nu)$ spectra using this technique and a theoretical interpretation of the observed effects based on the calculations from Mie's formulas.

EXPERIMENT

To estimate experimentally the accuracy of the immersion technique we used the same optical media as in our previous studies of the influence of dispersion of refractive index of particles on the transmission of layer of suspension.

Based on the catalog of pigmented glasses we have chosen the BS-4 (achromatic glass with $n_D = 1.52$) and PS-7 (purple glass with $n_D = 1.53$). The values n_D were measured to an accuracy of 0.02. For a selection criterion we took the difference in absorption coefficients of these glasses. According to the catalog $\kappa_{\text{BS-4}}$ is equal to $10^{-8} - 10^{-7}$ and $\kappa_{\text{PS-7}} - 10^{-4} - 10^{-3}$. Such a great difference between absorption coefficients of the glasses makes it possible to estimate the accuracy of the immersion technique under substantially different conditions.

For making a test we measured the absorption coefficient of the PS-7 purple glass. To do this, we first ground off a glass plate to make it only 0.5 mm thick then polished it. Transmission of thus prepared plate was measured with a Specord UV-VIS spectrophotometer. An example of the $\kappa(\nu)$ spectrum measured in such a way is shown in Fig. 1.

For each type of pigmented glass we selected a proper immersion liquid from the collection of such liquids we have prepared for this purpose. In the case of the BS-4 glass we used the liquid with $n_D = 1.50$ and the liquid with $n_D = 1.53$ for the glass PS-7. Unfortunately, the absorption coefficients coincide only at $\nu = 17000 \text{ cm}^{-1}$ and, moreover, an absorption band of the PD-7 glass is centered at this frequency. However, qualitative estimate of the situation is quite reliable.

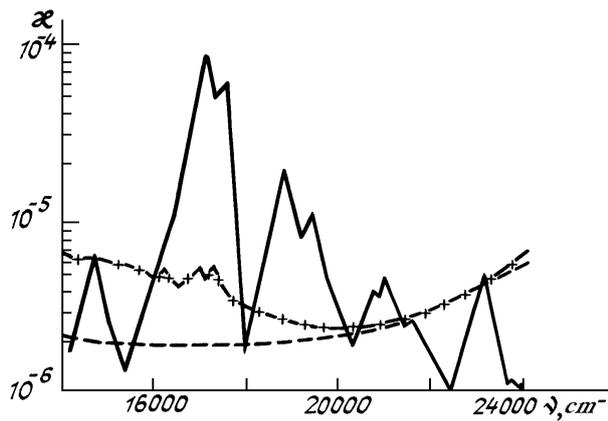


FIG. 1. Absorption spectra (experiment) of glasses. Solid line represents the spectrum of the PS-7 glass in the form of monolithic sample; dashed line and crosses are the absorption spectra of the BS-4 glass and the PS-7 glass measured using the immersion technique.

To prepare suspensions for making the transmission measurements we first grind glass particles in an agate mortar to obtain particles 1–10 μm in diameter. Weighed quantity of the particles in powder form were shaken with liquid to produce uniform suspensions. Then the transmission of a cell containing the suspension was measured with the Specord UV-VIS spectrophotometer. Assuming the decrease of the cell transmissions to be only due to the light absorption by particles the absorption coefficient of particles is calculated using the Bouguer-Beer formula

$$\kappa(\nu) = \frac{1}{4\pi d C_v} \ln \frac{1}{T(\nu)},$$

where $T(\nu)$ is the transmission of the suspension layer of thickness d and C_v is the number density of particles. In these measurements we used a reference cell filled with the pure immersion liquid. Thus calculated spectra $\kappa(\nu)$ of both glasses are shown in Fig. 2.

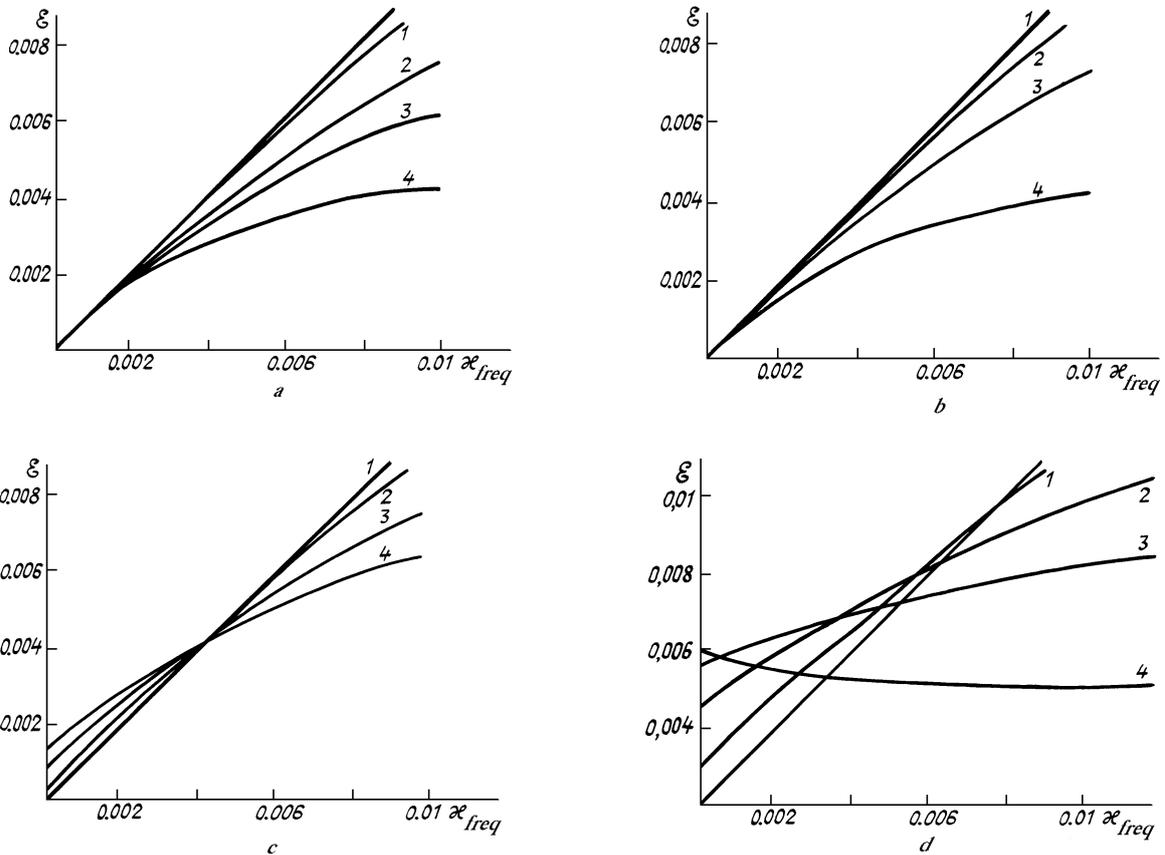


FIG. 2. Extinction coefficients of absorbing particles suspended in liquids with different refractive indices. Figures a, b, c, and d represent the data obtained for $\Delta n = 0, 0.001, 0.005,$ and $0.01,$ respectively. Curves 1, 2, 3, and 4 were obtained for $\rho = 21, 64, 106,$ and $213,$ respectively.

The experiment has shown that the value of absorption coefficient of the BS-4 glass measured using the immersion technique is smaller than its true value, the largest discrepancy is about an order of magnitude. To understand the nature of such a disagreement we undertook numerical simulation.

NUMERICAL SIMULATION

Since the process of light extinction in a suspension depends on many factors the interpretation of the experimental data is a complicated problem. Among these factors the shape and size of particles should be mentioned

along with the degree of their "softness" which is defined as the ratio $\hat{n}_{\text{part}}/\hat{n}_{\text{liq}}$. In addition, such factors as nonuniformity of particles, nonuniform size distribution, multiple scattering and others also affect the extinction process.

In our numerical simulations we took into account only the effects of light scattering by an individual particle. In this case we could use Mie's formulas. Neglecting all statistical effects one can assume that in the first approximation it is quite sufficient to consider only light scattering by spherical particles. In the case of sufficiently rarefied media one can also neglect the effects of multiple light scattering.

The scheme of numerical simulations included calculation from Mie's formulas of the extinction cross section $\sigma(n_{\text{rel}}, a, \lambda)$ at the given frequency of light ν , of the particle radius a , and of the relative complex refractive index $\hat{n}_{\text{rel}} = n_{\text{rel}} - ik_{\text{rel}}$, where

$$\hat{n}_{\text{rel}} = (n - i\kappa)/(n_{\text{liq}} - ik_{\text{liq}}).$$

The value of the effective extinction coefficient was calculated using the formula

$$\varepsilon(\nu) = \frac{\sigma(n_{\text{rel}}, a, \lambda)}{\frac{16}{3} \pi^2 a^3 \nu}.$$

Calculations were made for the yellow sodium line at $\nu = 17000 \text{ cm}^{-1}$. The value of refractive index of particles varied in calculations from $n_{\text{part}} = n_{\text{liq}}$ to $n_{\text{part}} = n_{\text{liq}} \pm 0.01$. The size of particles and absorption coefficient of particles also varied. Some calculated results are shown in Fig. 2.

DISCUSSION

To estimate the influence of the size of particles and of the difference between the refractive index of particles and the refractive index of immersion liquid on the extinction process we have plotted the functions $\varepsilon(\kappa, n, \rho)$. Here the effective extinction coefficient ε plays the role of the experimental parameter, namely, the extinction coefficient of the particles. The magnitude ε incorporates not only the fraction of the energy absorbed by the material of the particle but also the fraction of the scattered light energy since in the single scattering approximation it is assumed that scattered light does not enter the receiving aperture. Deviations of ε from the actual value of the absorption coefficient characterize the systematic error of the experiment because in the technique described above it is assumed that light attenuation is entirely caused by absorption of particles. In this case the linear dependence of the function $\varepsilon(\nu)$ would indicate that contributions of any factors caused by scattering are negligible compared to the absorption. Therefore, the closer the curve $\varepsilon(\nu)$ to the linear dependence $\varepsilon = \kappa$ the higher is the accuracy of the immersion technique.

As can be seen from Fig. 2a for $n_{\text{part}} = n_{\text{liq}}$ the curves are close to straight lines and when $\kappa \leq 0.01$ a high accuracy can be achieved for any size of particles available in the experiment. Moreover, the error rapidly decreases as $\kappa \rightarrow 0$.

With the increase of Δn (Figs. 2b and 2c) the error rapidly increases, in addition, the rate of increase is higher for larger particles. It can be also seen from Fig. 2 that for

large κ the experiment underestimates the absorption coefficient, i.e., we have $\kappa > \varepsilon$, while as $\kappa \rightarrow 0$ nonzero error results in overestimation of the absorption coefficient. Thus, only in the region of values κ near $\kappa = 10^{-4}$, where $\varepsilon \approx \kappa$, the experiment can ensure satisfactory accuracy.

The analysis of data shown in Fig. 2d indicates that for $\Delta n = 0.01$ the errors become inacceptably gross. It is even impossible to say whether the measured values are overestimated or underestimated because of very rapid changes in the shape of curves vs the particle size. At the same time it is very hard to control the size distribution of particles in the experiment. In addition, the contribution of light scattering to the extinction of light increases and, as a consequence, an increase in the multiple scattering intensity takes place that leads to the increase of the measurement errors. The analysis made allowed us to determine experimental conditions under which some prescribed accuracy of measurements can be obtained. So, the size of particles should satisfy the condition $\rho \leq 10$, and $\Delta n \leq 0.001$. Unfortunately, in the visible range these conditions can hardly be satisfied. It is obvious that the measurement error increases if the light extinction is measured in air but not in an immersion liquid. This fact makes the accuracy of determination of the absorption coefficient of the particles from measurements of the transmission of the layer of the particles settled on a substrate doubtful.⁵

The calculations make it possible to understand the reason of that or other discrepancies between the data obtained using the immersion technique and actual spectra of the absorption coefficient. Thus, for example, the increase of the values $\varepsilon(\nu)$ at the ends of the spectral interval is a common feature of the obtained results. It is evident that this circumstance occurs because the absorption coefficients of the particles and immersion liquid coincide only at $\nu = 17000 \text{ cm}^{-1}$, while their different spectral behaviors result in the increase of the value Δn towards the ends of the spectral interval (see Fig. 2c).

In the case of the transparent BS-4 glass the value κ_{imm} exceeds the actual one by about an order of magnitude. As calculations showed the contribution of light scattering to the light extinction is predominant when $\rho \geq 20$ even in the case of soft particles ($\Delta n \leq 0.001$), what results in a strong overestimation of the absorption coefficient in measurements using the immersion technique. Nevertheless, the value $\kappa_{\text{imm}}(\nu)$ is several times lower than $\varepsilon(\nu)$ calculated from the Mie's formulas. This is caused by the fact that scattering phase functions of soft particles are strongly elongated in the forward direction and, therefore, a significant portion of the scattered light enter the receiver, thereby, resulting in underestimation of the absorption coefficient.

In the case of the absorbing PS-7 glass ($\kappa \approx 10^{-4}$) the situation with $\kappa_{\text{imm}}(\nu)$ and $\varepsilon(\nu)$ is the same (i.e., $\kappa_{\text{imm}}(\nu) < \varepsilon(\nu)$), but the ratio of these values is different. The values $\kappa(\nu)$ obtained using the immersion technique are much smaller than the actual values of the absorption coefficient ($\kappa_{\text{imm}} \leq \kappa$). Moreover, many absorption bands are not seen in the measured spectra while those which are recorded are strongly smoothed. It is possible that rapid changes in $n(\nu)$ and $\kappa(\nu)$ of the particles under study cause, in particular, certain modifications of the scattering phase function shape. For example, for $\rho \geq 20$ small changes in these values can cause the changes in the degree of elongation of the scattering phase function by several orders of magnitude. Accordingly, the intensity of scattered light

changes and, hence, the portion of light entering the receiver changes too.

The calculations also show that underestimation of the absorption coefficient in the immersion measurements is quite probable and is determined by the combination of optical parameters of the problem.

In conclusion, we confirmed the fact that not always one can determine the absorption coefficient of particles from the measurements of light extinction, even in the case of soft and weakly absorbing particles. At the same time, at $\Delta n = 0$ the immersion technique ensures satisfactory accuracy of determination of the absorption coefficient of particles even for large ρ up to $\kappa = 0.01$. In our further studies we intend to search for a possibility of correcting the results obtained with the use of the immersion technique.

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