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Measurements of the Size and Refractive Index of Fe_3O_4 Nanoparticles

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Abstract—Optical methods and electron microscopy have been used to determine the size distribution and complex refractive index of magnetite (Fe_3O_4) particles. The particles were synthesized as a component of magnetically controlled pills. The proposed algorithm for experimental data processing is intended for nanoparticle sizes from 1 to 100 nm.

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INTRODUCTION

The ability to measure the size of small particles in emulsions, suspensions, gas flows, etc. is a problem that has long faced researchers and has been addressed using a wide variety of techniques. The key approaches to this problem have been the subject of monographs and many reports, but it has not yet been fully solved, so reports addressing this issue continue to appear in the literature.

One obvious approach is to observe particles and measure their size under a microscope. This approach has the advantages of clarity and simplicity but is time-consuming and difficult to automate. To measure the size of nanoparticles, one has to use electron microscopes—unwieldy and expensive instruments. Moreover, this method is inapplicable in many instances, for example, when the size of particles is to be measured in a gas flow.

Optical methods are widely used for the purpose in question [1–8]. They are based on measurements of characteristics of light scattered or absorbed by a medium containing particles. These methods are relatively easy to implement, are readily amenable to automation, allow one to rapidly obtain results, and can be used not only in the laboratory but also under industrial and field conditions.

The development of these methods is, however, far from completed, even though they have long been dealt with. One principal reason for this is the necessity to solve the inverse problem: to assess the properties of particles from the characteristics of their interaction with radiation. This involves the following difficulties:

1. Inverse problems are, as a rule, ill-conditioned. Small errors in input data lead to large errors in results, and input data are never free of errors because they result from experiments.

2. To reduce errors, statistical data processing is commonly used, which requires lengthy calculations.

The wide use of computers and application programs for mathematical signal processing has allowed new approaches to the problem in hand to be applied. In this paper, we examine algorithms for determining not only the size of particles but also their optical properties: indices of refraction and absorption.

Optical methods can be divided into two groups. The methods of one group determine the shape of the light scattering indicatrix of particles and the polarization of the scattered light. The methods of the other group examine the spectral dependence of light extinction by a system of particles.

The studies described below belong to the latter group. Using a spectrophotometer, we measured transmittance as a function of wavelength for a cuvette containing a suspension of particles. Analysis of the data thus obtained allowed us to find the size distribution and complex refractive index of the particles. The proposed algorithm for experimental data processing is intended for nanoparticle sizes from 1 to 100 nm.

THEORETICAL BACKGROUND

Light extinction in a medium containing absorbing and scattering particles is represented by the relation

$$I = I_0 e^{-\alpha l}, \quad (1)$$

where I_0 and I are the incident and transmitted light intensities, respectively; l is the thickness of the layer containing the particles; and α is the extinction coefficient. If the medium contains N identical particles per unit volume, the extinction coefficient can be found as

$$\alpha(N, r, m, \lambda) = N\pi r^2 Q(r, m, \lambda), \tag{2}$$

where r is the particle radius, $m = n - i\kappa$, n is the index of refraction, κ is the index of absorption, λ is the wavelength of the light in the surrounding medium, and Q is the extinction efficiency factor. The last parameter specifies what part of the energy of an incident beam is removed (scattered and absorbed) by a single particle.

If a medium contains particles of various sizes, relation (2) takes the form

$$\alpha(N, r, m, \lambda) = N\int_0^\infty Q(r, m, \lambda)\pi r^2 f(r)dr, \tag{3}$$

where the function $f(r)$ represents the particle size distribution.

In solving such problems, the particles are commonly taken to be spherical. In many instances, this is indeed so, for example, in emulsions. If the particles are irregularly shaped, the characteristics of the light scattered by a large number of randomly oriented particles differ not much from those of the light scattered by spherical particles.

The extinction efficiency factor of spherical particles can be evaluated using formulas known from diffraction theory [9, 10]:

$$Q = \frac{2}{\rho^2}\sum_{l=1}^{\infty}(2l+1)\operatorname{Re}(a_l + b_l), \tag{4}$$

where

$$a_l = \frac{m\psi_l(m\rho)\psi_l'(\rho) - \psi_l'(m\rho)\psi_l(\rho)}{m\psi_l(m\rho)\zeta_l'(\rho) - \psi_l'(m\rho)\zeta_l(\rho)}, \tag{5}$$

$$b_l = \frac{m\psi_l'(m\rho)\psi_l(\rho) - \psi_l(m\rho)\psi_l'(\rho)}{m\psi_l'(m\rho)\zeta_l(\rho) - \psi_l(m\rho)\zeta_l'(\rho)}, \tag{6}$$

$\psi_l(z)$ and $\zeta_l(z)$ are Bessel–Riccati functions, and $\rho = \frac{2\pi r}{\lambda}$.

Experimentally determining the light extinction spectrum of a medium containing particles and solving the integral equation (3), we can find the size distribution $f(r)$, complex refractive index m, and concentration N of the particles.

EXPERIMENTAL PROCEDURE AND DATA PROCESSING

We studied a suspension of magnetite (Fe_3O_4) particles in a transparent gel with a refractive index of 1.45. Such suspensions are used in the pharmaceutical industry in the preparation of some ointments. A cuvette containing the suspension was placed in a SPEKOL 11 spectrophotometer, and the transmittance of the medium was measured as a function of wavelength in the range 0.4 to 0.8 μm. The extinction coefficient was calculated by a formula derived from relation (1):

$$\alpha = -\frac{\ln T}{l},$$

where T is transmittance and $l = 1$ cm is the thickness of the cuvette.

Numerical mathematical methods allow one to solve the integral equation (3) and find the function $f(r)$ and the parameters r, n, κ, and N. To this end, however, one has to minimize a function of four variables. Since such a function may have many minima, a totally incorrect result may be obtained. Moreover, the extinction efficiency factor is described by the cumbersome formulas (4)–(6), so that a very long computation time (tens of minutes) is needed to solve Eq. (3), even with state-of-the-art computers. This led us to use some simplifications in formulating and solving the problem.

1. The particle size distribution was taken in the form

$$f(r) = \frac{\beta^\mu}{\Gamma(\mu+1)} r^\mu e^{-\beta r},$$

where $\Gamma(z)$ is the gamma function, and μ and β are parameters of the distribution.

As shown previously [5–7], this formula adequately describes the size distribution of micro- and nanoparticles in emulsions and suspensions. The parameters μ and β determine the position of the maximum of the function (r_{max}) and its full width at half maximum (Δr):

$$\mu = \left(\frac{2.48 r_{max}}{\Delta r}\right)^2, \quad \beta = \left(\frac{2.48}{\Delta r}\right)^2 r_{max}.$$

The problem then reduces to finding μ and β values at which Eq. (3) is satisfied.

2. To reduce the computation time, we used an approximate expression for the extinction efficiency factor. There are quite a few such expressions, each valid for particular conditions: for very large or very small particle sizes (compared to the wavelength), perfectly reflective particles, or particles with a low refractive index. In the case of nanoparticles ($\rho \ll 1$), it is expedient to use expansion of (4) into a power series in ρ [9, 11]:

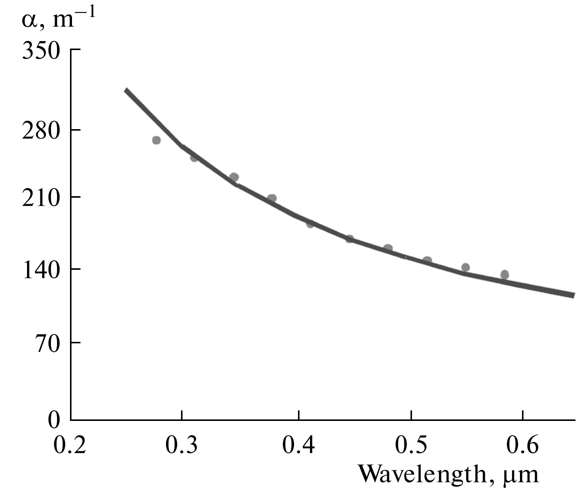

Fig. 1. Spectral dependence of the extinction coefficient.

$$Q = -\mathrm{Im}\left[4\rho\frac{m^2-1}{m^2+2} + \frac{4}{15}\rho^3\left(\frac{m^2-1}{m^2+2}\right)^2 \times \frac{m^4+27m^2+38}{2m^2+3}\right] + \mathrm{Re}\left[\frac{8}{3}\rho^4\left(\frac{m^2-1}{m^2+2}\right)^2\right].$$

For $\rho < 0.6$, $n = 1.2$–2, and $\kappa < 0.75$, the error of this series is within 2%.

3. Integral (3) is replaced by the sum

$$\alpha(N, m, r, \lambda) = N\pi\delta r \sum_j Q(r, m, \lambda) r_j^2 f(r_j).$$

In this expression, j goes from zero to $j_{\max}$, which determines the number of node points in the integration range. The spacing between the node points is

$$\delta r = \frac{r_{\max} - r_{\min}}{j_{\max}},$$

where $r_{\min} = 0$ and $r_{\max} = 0.05$ μm define the range of possible nanoparticle radii in experiments. This also considerably reduces the computation time.

Experimental data processing comprised two steps.

1. Using Eq. (2), we determined the average particle radius r and the parameters n, κ, and N. To this end, we set up the function

$$S(r, n, \kappa, N) = \sum_{i=0}^{i_{\max}} \left[N\pi r^2 Q(r, n, \kappa, \lambda_i) - \alpha_i\right]^2,$$

where λ_i is the wavelength at which the extinction coefficient α_i was measured, and, using least squares fitting, determined the parameters r, n, κ, and N at which $S(r, n, \kappa, N)$ had a minimum.

The parameters thus found were highly dependent on the input approximations used in seeking the minimum. Because of this, we additionally checked the shape of the plots with α_i data points and that of the $\alpha(r, n, \kappa, N, \lambda)$ curve, which should pass near the data points (Fig. 1). We checked the value of the function $S(r, n, \kappa, N)$ as well, which also depends on the input approximations and should be minimized.

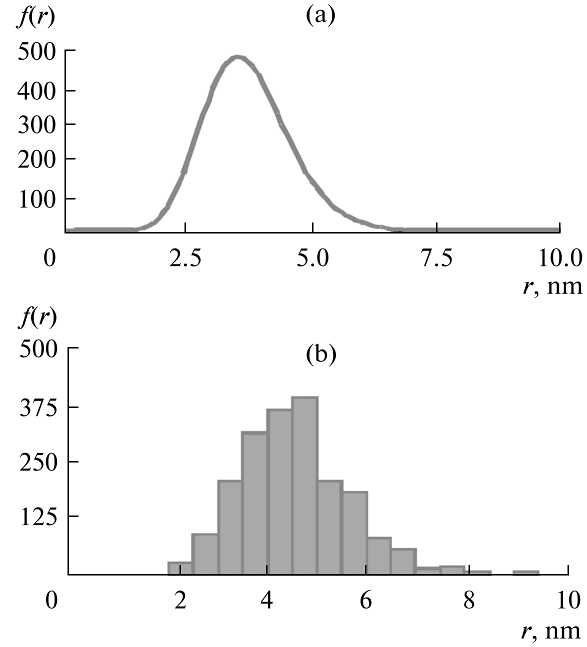

Fig. 2. Particle size distribution of magnetite: (a) optical data, (b) electron microscopy data.

For the suspension of magnetite particles under consideration, we obtained

$r = 12$ nm, $n = 1.41$, $\kappa = 0.01$, and $N = 7.96 \times 10^{11}$ m^{-3}.

The indices of refraction and absorption are in reasonable agreement with reference data for magnetite: in the wavelength range 0.4 to 0.8 μm, its index of refraction varies from 1.9 to 1.7, and its index of absorption, from 0.1 to 0.01.

2. The data obtained were used in a program for determining the parameters β and μ in the particle size distribution. We examined the function

$$S(r_{\max}, \Delta r) = \sum_{i=0}^{i_{\max}}\left[N\pi\delta r\sum_j Q(r, m, \lambda_i) r_j^2 f(r_{\max}, \Delta r, r_j) - \alpha_i\right]^2$$

and determined the parameters $r_{\max}$ and r at which it had a minimum.

Figure 2a shows the function $f(r)$. For comparison, Fig. 2b shows the particle size distribution derived from electron microscopy data for the magnetite. It is seen that the results obtained by the two methods agree well. Figure 3 shows an electron micrograph of the magnetite particles.

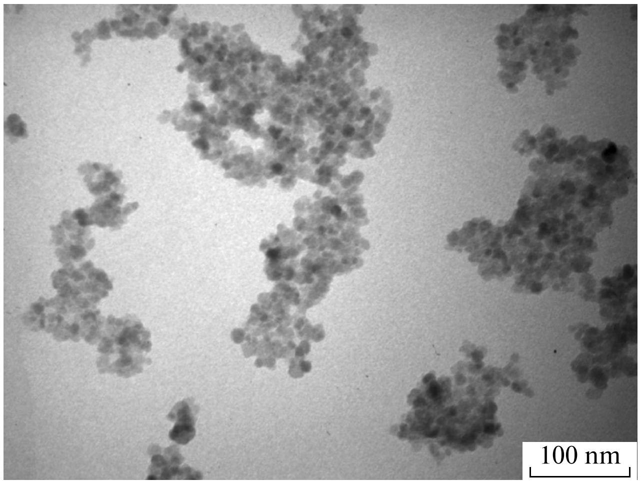

Fig. 3. Electron micrograph of magnetite particles.

CONCLUSIONS

A method has been described for determining the size and optical properties of nanoparticles from the spectral dependence of light extinction in the nanoparticles. The particle size obtained by this method agrees with that evaluated by electron microscopy.

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