Study of light-scattering properties of protein-containing microparticles with a small difference in refractive indices

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Abstract. The refractive indices of fodder yeast grown on oil paraffins (paprin) and natural gas (gaprin) were measured by phase microscopy. The scattering matrices of aqueous suspensions of paprin and gaprin are calculated within the framework of the model of spherically symmetric particles. The possibility of identifying the suspensions by their scattering matrices is analyzed for a small difference in the real parts of the refractive index. Experimental measurements of the light scattering matrices show that in the region of small values of the size parameter ($\approx 1$) the identification of paprin and gaprin can be based only on the difference in the shapes of the particles, and the difference in the refractive indices is manifested for the values of the size parameter greater than 3.

Keywords: Protein-containing suspensions; identifying organic compounds; light scattering matrix

1. Introduction

Information about the light-scattering properties of various substances in dispersed form is required in both fundamental and applied science. The problem of recognition (identification) of dispersed media by their scattering matrices is of great practical importance. The values of the scattering matrix elements depend on the size of the dispersed particles, the type of their size distribution, their shape and structure, orientation, degree and nature of the agglomeration, complex refractive index ($n + ik$), and scattering angle ($\theta$). Due to a large number of factors affecting the scattering matrix, the recognition is possible within a limited set of dispersed media.

The aim of this work was to determine the conditions under which differences in the microphysical parameters of protein-vitamin concentrates (PVC) such as paprin and gaprin will allow them to be identified by measuring the light scattering matrices of their aqueous suspensions. A feature of the problem under consideration is the fact that suspensions of these protein-containing substances are characterized by close to unity values of the relative refractive index [1].
When analyzing the recognition conditions, it is assumed that the sample preparation of suspensions is the same and provides approximate equality of the average sizes of the particles of the suspension with the smallest possible spread of the particle size distribution. In addition, the concentration of suspended particles is such that, on the one hand, a satisfactory signal-to-noise ratio is ensured when detecting the scattered radiation, and, on the other hand, the scattering is single.

2. Modeling the scattering matrices

The scattering matrix describes the transformation of the polarization state of the incident radiation by the medium. For a macroscopically isotropic medium containing the same number of randomly oriented scatterers and their mirror-symmetric counterparts, the scattering matrix $F$ (4x4) has a block-diagonal form [2]. In this case, the elements $F_{14}, F_{41}, F_{24}, F_{42}, F_{31}, F_{13}, F_{23}$ are zero, $F_{12} = F_{21}, F_{34} = -F_{43}$. The dependence of the element $F_{11}$ on the scattering angle $\theta$ describes the scattering indicatrix of unpolarized radiation. For spherical particles, $F_{22} = F_{11}$ and $F_{33} = F_{44}$ in the whole range of the scattering angles.

Microphotographs of the suspension particles of PVC are shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** Geometric shape of the particles in the samples of paprin (a) and gaprin (b). The size of the white frame on the images is 8x8 microns.

The micrographic data suggest that the shape of the particles is close to spherical, the ratio of the longitudinal size to the transverse for the particles falls within the range 0.5–2.

Measurements carried out using a phase microscope [3] showed that the real part of the refractive index for paprin is 1.46 and that for gaprin is 1.52, which corresponds to the relative refractive index in water $n_r = 1.1–1.14$. The imaginary part of the refractive index of proteins, depending on the light wavelength in the visible range, is limited to 0–0.1 [6].

In the course of the work, the scattering matrices for suspensions of PVC (paprin and gaprin) were theoretically simulated. The calculations were carried out using a program developed by M.I. Mishchenko according to T-matrix method [2] for an ensemble of randomly oriented spheroids (ellipsoids of revolution).

The scattering matrix of an ensemble of dispersed particles of a spheroidal shape with a random size distribution is determined mainly by the following two parameters of this distribution: effective size parameter $x_{\text{eff}} = 2\pi r_{\text{eff}}/\lambda$ and effective width $v_{\text{eff}}$:

$$r_{\text{eff}} = \frac{\int_0^{\infty} p(r) r^2 dr}{\int_0^{\infty} p(r) r^2 dr}, \quad v_{\text{eff}} = \frac{\int_0^{\infty} p(r)(r-r_{\text{eff}})^2 r^2 dr}{r_{\text{eff}}^2 \int_0^{\infty} p(r) r^2 dr}$$

(1)

where $p(r)$ is the probability density distribution. Along with these parameters, the parameter determining the shape is also important in the model of spheroidal particles $\varepsilon = ab/a$, where $a$, and $b$ are the semiaxes of the ellipsoid.
Scattering matrices were modeled for particles with a size parameter from 3 to 30. The distribution width varied in the range \( v_{\text{eff}} = 0.1 \sim 0.3 \), and the imaginary part of the refractive index (\( k \)) in the range 0–0.1. Note that for values of the relative refractive index of suspended particles close to unity, a change in the distribution width leads to small changes in the dependences \( F_{11}(\theta), f_{12}(\theta), f_{44}(\theta) \) and the values of the matrix elements. An increase in the imaginary part of the refractive index leads to a shift of the dependence of \( f_{44}(\theta) \) and the maximum of \( f_{12}(\theta) \) towards the smaller values of \( \theta \) for the size parameter \( x_{\text{eff}} \leq 30 \).

The simulation results showed that for wavelengths, which are characterized by the absence of radiation absorption or weak absorption by PVC particles (\( k < 0.1 \)), the identification of fine particles is possible by the dependences \( F_{11}(\theta), f_{12}(\theta), f_{44}(\theta) \). For the particles of the large fraction in the absence of absorption, identification can be realized by the dependences \( F_{11}(\theta), f_{12}(\theta), f_{44}(\theta), f_{34}(\theta) \). In the case of absorption of the probe radiation by particles of both suspensions (\( k \approx 0.1 \)), identification is possible only by the dependences \( F_{11}(\theta) \). On the basis of model representations, the measurements of the dependences \( F_{11}(\theta), f_{12}(\theta), f_{44}(\theta) \) will enable identification.

### 3. Results of experimental measurements

Experimental studies have also been conducted. The scattering matrices were measured using a laser polarimeter [5], in which a single-mode He-Ne laser with a wavelength of 0.63 μm and a power of 7 mW was used as a radiation source. The scattering matrices were measured in the range of scattering angles of 25°–150°. At scattering angles greater than 150°, measurements could not be carried out due to the fact that the photoreceiving part of the setup blocked the laser radiation. The suspension obtained after mixing the powders with water was filtered through a paper filter.

The experimental dependences of the matrix elements on the scattering angle for suspensions of paprin and gaprin are shown in Fig. 2. By \( f_{ij} \), we mean the matrix elements \( F_{ij} \) normalized to \( F_{11} \) (\( f_{ij} = F_{ij}/F_{11} \)). The measurement error of \( F_{11}(\theta) \) does not exceed the size of the experimental point in Fig. 2, and the error in determining the normalized matrix elements \( f_{ij} \) is 0.03.

**Figure 2.** Dependence of the matrix elements \( F_{11}(\theta), f_{12}(\theta), f_{44}(\theta) \) on the scattering angle for the aqueous suspensions: paprin (blue dots), gaprin (black dots)

Using the obtained data (Fig. 2) and modeling the particles of PVC by elongated ellipsoids of revolution (with \( \varepsilon = 0.7 \)), the size distributions of the particles of the medium were restored. For this purpose, the possible size range (0.05 - 1.1 μm) of the particles was divided into 12 subranges, for each of which scattering matrices were calculated. The experimentally measured scattering matrix was approximated by a weighted sum of theoretically calculated scattering matrices of model particles of various sizes (grades):
where $\theta_k$ is the scattering angle, $a_p$ is the contribution of the corresponding type of particles to the scattering matrix, $C_p$ is the scattering cross section, and $f_{ij}^{(\theta_k)}$ are the matrix elements of the $p$-th type of particles calculated in the framework of the model of spheroidal scatterers. The values of the corresponding weights, providing a minimum of the mean square deviation of the theoretical and experimental data, determined the particle size distribution. In solving the optimization problem, the Levenberg - Marquardt algorithm was used. The resulting distributions are shown in Fig. 3. Most of the particles are in the size range $0.05$–$0.12$ μm, a small fraction of particles with a relative contribution of $10^{-4}$–$10^{-5}$ is in the range $0.35$–$1.0$ μm (not shown in the figure). The data (Fig. 3) indicate the practical identity of these distributions for both suspensions studied.

Figure 3. Histograms of particle size distribution for the aqueous suspensions: papin (blue bars), gaprin (black bars)

Nevertheless, even for suspensions characterized by a size parameter $x_{eff} \approx 1$, differences in the values of $f_{12}(\theta)$ take place. Such differences can be explained by the difference of particle shape from spheroidal one. These differences include the presence of flat faces, edges, sharp edges, surface roughness, and asymmetry of shape. The data [6] show that the presence of small ($<< \lambda$) surface irregularities does not lead to noticeable changes in the matrix elements.

The scattering matrices of polyhedral straight prisms with the number of side faces $4$–$7$ [7] are largely similar: a change in the number of prism faces and the ratio of height to length of the base side weakly affects the dependencies of the matrix elements on the scattering angle. Moreover, the scattering properties of an aerosol of irregular feldspar particles, which have flat faces and sharp edges, are better described in the spheroidal scatterer model than in the model of regular prisms [7]. Therefore, the mere presence of flat faces and edges does not explain the differences between the experimental and calculated data.

For non-absorbing dispersed media, models of asymmetric scatterers (asymmetric hexahedrons [8], Gaussian spheres [9]) describe experimentally measured scattering matrices better than the model of spheroids, mainly because they give lower values of the elements $f_{34}(\theta)$ and $|f_{12}(\theta)|$ for the same size parameter. In this case, the dependences $f_{34}(\theta)$, $f_{44}(\theta)$ for asymmetric and symmetric scatterers (spheroids) are close, but slightly shifted relative to each other, and the dependences $f_{22}(\theta)$ are similar, but differ by a small shift of the minima (by $\approx 10^0$) and, in the cases Gaussian spheres, by a smaller value of $f_{22}(\theta)$ at the minimum. All this allows us to consider the asymmetry of particles of a dispersed medium
as the main reason for the difference between the experimental dependences $f_{ij}(\theta)$ and those calculated for spheroids.

According to [10], the asymmetry of the dispersed particles does not affect the values of the matrix elements at $x_{\text{eff}} = 0.1$ or less. In the case considered, the difference in the values of $f_{12}(\theta)$ for the studied suspensions within the framework of the Gaussian sphere model [9] is explained by a large value of the particle deformation parameter for gaprin.

4. Conclusion
It has been shown that it is possible, in principle, to identify aqueous suspensions of protein-vitamin concentrates (paprin and gaprin) by measuring their dispersion matrices. For values of the size parameter $x_{\text{eff}} \geq 3$, the difference in the matrix elements is due to the difference in the real parts of the refractive index. For values of the size parameter $\approx 1$, identification results from a difference in the shape of the particles of paprin and gaprin.

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