Determination of particle spectrum of atmosphere aerosol by light scattering

By K. S. SHIFRIN and A. Y. PERELMAN, *Hydrometeorological Service, Moscow, U.S.S.R.*

(Manuscript received October 12, 1965)

ABSTRACT

The difficulties of determining the particle spectrum of the atmosphere aerosol are considered. The transparency and scattering pattern methods which allow one to determine the particle size distribution function of an arbitrary system are described. The requirements which these methods present to initial optical information are indicated. The examples of the inversion of the transparency and scattering pattern are given.

1. Introduction

Investigation of the atmospheric aerosol is one of the actual problems in physics of the atmosphere. The aerosol effects the important processes in the atmosphere: condensation of the water vapour, scattering of the radiation over a wide spectral interval, transfer of the radioactivity, formation of the electrical field etc. However, we know little about the atmospheric aerosol. The main reason of this is the lack of reliable and simple methods of measuring the aerosol particles. We meet difficulties as soon as we try to sample because the radii of these particles are about 0.1 μ. The particles are so small that they in fact do not deposite on the plate flowing from it together with gas. If we nevertheless deposite them it is impossible to examine the obtained sample by the optical microscope. The diffractive parameter ϱ for these particles in visual range will be

$$\varrho = \frac{2\pi r}{\lambda} = \frac{6 \cdot 0.1}{0.55} \simeq 1$$

(r = the particle radius, λ = the wavelength).

This parameter is too small to obtain the image. The light spots which particles give in the microscope field of vision are the parts of their scattering patterns. It is not clear how one can determine the true sizes and shapes of the particles by the scattering patterns. The difficulties arising from diffraction disappear when one uses very short wavelengths, in particular, when one observes the particles by an electronic microscope. Such measurements being very complicated, the assurance that the observed particles are just the same which really present in the atmosphere disappears. It is possible to avoid both difficulties (the distortion of the spectrum during the sampling and the impossibility of utilizing the optical microscope) when for the determination of the particle spectrum one uses the data on light scattering. In such cases the diffraction may help us. Note that the particles of the atmospheric aerosol relative to the visual radiation lie in the range of sizes where the maximum scattering takes place [1*a*, ch. 7].

The light scattering methods or methods of the optical sounding are reduced to analysing the peculiarities of the light scattering and to restoration of the particle spectrum by this information. This is an indirect problem. The questions which are very important for the investigators are as follows: how to carry out the optical experiment in order that the optical data should contain microphysical information and then how to treat the data of the optical measurements, how to inverse them to obtain an accurate information. Very often the scattered flux does not contain the necessary information on the material properties we search for and which cannot be found by means of the mathematical devices. For example if one uses the long wavelengths, in Rayleigh region, the data on light scattering would contain the sixth moment of distribution only. And, naturally, we are not able to restore the whole distribution according to these data. In general we often obtain only separate moments of the distribution and strictly speaking know nothing about the complete one. This must be taken into account when comparing the results of measuring the same system by the different methods. It is no wonder that in taking systems as quasi monodisperse we obtain different values for the "mean" particle size.

However, in recent years, some methods of solution of indirect problems have been developed. These methods allow one to obtain the whole spectrum of particles from the light scattering data only. The techniques considered are the small angle, spectral transparency and scattering pattern methods. We have obtained in all these methods analytical solutions and simple calculational schemes for the determination of the particle spectrum from the light scattering data. The experiments on light scattering appear to be very simple and the accuracy requirements of photometry are not high.

Thus using the optical radiation one can include the range of spherical particle radii from approximately 0.01 μ to 100 μ by means of these three methods.

The short review of all the three methods is given in [4*f*].

In the present paper we have studied in detail the transparency method [4*a*–*g*] and the scattering pattern method [4*f*–*h*]. We have not studied the method of small angle here because it does not suit for the atmosphere aerosol. The reader can find our analysis on the method of small angle in [1, 5, 6].

2. General statement of the problem. Full and limited problems

In the case of "dilute" systems when it is possible to restrict oneself to examining single scattering, the problem is reduced to the inversion of integral equation of the first kind:

$$\varphi(x) = \int_0^\infty F(x,r)\, f^*(r)\, dr. \tag{1}$$

Here $f^*(r)$ is the particle size distribution curve; $F(x,r)$ is the kernel of equation known from the Mie theory; $\varphi(x)$ is the function determined experimentally. The kernel $F(x,r)$ may be, for example, the scattering pattern of a monodispersed system with particle radii r; in this case $\varphi(x)$ would be the polydispersed scattering pattern, describing scattering at the angle $\beta = x$ etc. In all the cases the task of inversion theory is to find a calculational method for determining the unknown distribution function $f^*(r)$ by a function of $F(x,r)$ and $\varphi(x)$.

The inversion of equation (1) by means of substituting it by the algebraic system of equations results in difficulties characteristic of integral equations of the first kind. The resulting algebraic system is ill conditioned and small inaccuracies in determining $\varphi(x)$ and $F(x,r)$ inevitably arising due to errors of the measurement and calculation cause great errors in $f^*(r)$.

The cause of these difficulties lies in peculiarities of equation (1). For example, if the kernel is degenerating, i.e.

$$F(x,r) = \sum_{i=1}^{n} a_i(x)\, b_i(r).$$

equation (1) either has no solution or an infinite number. If, however, the kernel is of the form $\exp(ixr)$ (a Fourier kernel), a simple inversion is known. In general, if the kernel depends only upon the product of arguments

$$F(x,r) = F(xr), \tag{2}$$

the formal solution of equation (1) can be obtained with the help of Mellin's or Titchmarsh's transformations.

Errors inevitably present in $\varphi(x)$ make the inversion problem (1) incorrect. This means that the solution $f^*(r)$ is determined accurate to an arbitrary function which, for example, is of the form $\Delta f^* = C\exp(i\omega r)$.This function will add

$$\Delta\varphi = C\int_0^\infty F(x,r)\, e^{i\omega r}\, dr$$

in the left part of equation (1).

If $F(x,r)$ as function of r changes slowly, $\Delta\varphi$ being a Fourier coefficient will decrease with the enchancement of frequency ω. When ω has a large enough value, $\Delta\varphi$ varies in the limits of a fluctuation range of φ, which is defined by the errors of measurement. Thus both solutions f^* and $f^* + \Delta f^*$ appear to be indistinguishable whereas practically they can differ as much as possible by suitable choice of C. Errors in function $\varphi(x)$ cut off the Fourier spectrum of the sought answer at some critical frequency ω_0. Fourier components which frequencies are higher than ω_0 cannot be determined.

Difficulties which one meets inverting the equation (1), often cause to examine a limited problem instead of full one and be satisfied with separate characteristics of distributions obtained from (1).

If besides optical information described by equation (1) we have extra information on the nature of the unknown distribution $f^*(r)$ one can use the results of measuring $\varphi(x)$ to determine parameters of some distribution chosen beforehand. In many cases it is convenient to use an extended Γ-distribution

$$f^*(r) = Ar^{\mu} e^{-\beta r^{\gamma}} \qquad (3)$$

suggested in [1*d*] or its particular form at $\gamma = 1$

$$f^*(r) = Ar^{\mu} e^{-\beta r} \qquad (4)$$

(see in detail in [1*e*]). For the atmosphere aerosol a Junge distribution can also be used:

$$f^*(r) = \begin{cases} 0 & r < r_0 \\ Ar^{-n} & r \geqslant r_0 \quad n = 4 \end{cases} \qquad (5)$$

or Junge types ($n = 3, 5, 6 \ldots$) or a logarithmic normal distribution etc. In all the cases the amount of necessary experimental data must not be less than the number of parameters.

3. The transparency method

The main idea of the method is the determination of the particle spectrum according to the spectral transparency $g^*(\nu)$ associated with diffraction. This is possible if the variation of the transparency (in the investigated interval of wavenumbers $\nu = \lambda^{-1}$) associated with the change of the refractive coefficient m is small or can be separated from the diffraction band of attenuation.

The transparency method for soft particles is developed in [4*a*–*d*] (see also [4*e*–*g*]). We call the particles soft if their scattering cross section $2K(\delta)$ is determined by Van de Hulst formula [2]

$$K(\delta) = 1 - \frac{\sin 2\delta}{\delta} + \frac{1 - \cos 2\delta}{2\delta^2}, \qquad \delta = (m-1)\varrho. \qquad (1)$$

The basis of the transparency method is the utilization of Mellin's transformation [3] to obtained integral equation

$$g^*(\nu) = \int_0^{\infty} 2\pi r^2 K(\delta) f^*(r)\, dr. \qquad (2)$$

The accurate inversion formula (2) has been obtained in [4*a*].

In the case of the tabulated transparency the approximate inversion formula (2) has been found in [4*c*]. It has been shown that the inversion is quite possible when a sufficient amount of the transparency values of $g^*(\nu)$ in the range $(0, \tau^*)$ of its essential variation and asymptotic behaviour of $g^*(\nu)$ in the field of the geometric optics [4*f*, *g*] are known.

The inversion formula of the tabulated transparency contains the following functions (fig. 1) as factors

$$\begin{aligned} \omega(y) &= y \sin y + \cos y - 1, \\ \omega_0(y) &= \cos y - 2\frac{\sin y}{y} + 1, \\ \omega_2(y) &= \cos y - 1. \end{aligned} \qquad (3)$$

If the particle spectrum $f^*(r)$ has been found in the range $(0, r^*)$, then y from (3) varies in the range $(0, Y)$, where

$$Y = 4\pi(m-1) r^* \tau^*. \qquad (4)$$

It is proved in [4*d*] that the inversion of the tabulated transparency can be made as accurate as possible if simultaneously one would increase the spectral interval τ^*, the number of samples n and rise the accuracy of calculations. Besides, the amplitudes of oscillation $\omega(y)$ increase rapidly and when $Y \simeq 10-20$ they become (on an average) several orders greater than the results of calculations. All these force to increase the accuracy of optical measurements that results in sufficient difficulties.

It has been shown in [4*g*] that the enhancement of τ^* must be accompanied by simultaneous increase in n. It is evident from the point of view of physics. If τ^* increases and n is constant (or even increases insignificantly) then almost all values of wavenumbers ν for which the transparency is measured, fall in the field of the geometric optics. This field contains little information about the disperse system. At the same time it is shown in [4*f*, *g*] that the inversion formulas of the tabulated transparency gives a satisfactory result if $g^*(\nu)$ is measured accurate to 1–2 %, the number of samples $n \simeq 10-20$ and

$$Y \simeq 20 - 25. \qquad (5)$$

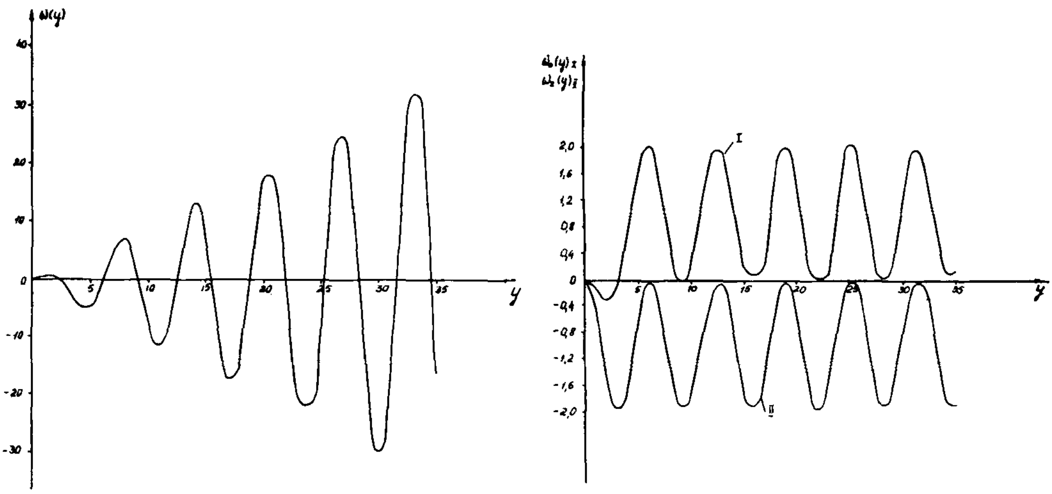

FIG. 1. Functions used in the transparency method.

The length of the interval of wavenumbers τ^* depends on the concrete physical system. However in all the calculated examples (both for the inversion of experimental transparency and for the inversion of different models) it appeared that practically the distribution curve $f^*(r)$ completely falls inside the limits of the interval $(0, r^*)$, where r^* is determined by the equations (4) and (5). When the last condition is broken it is necessary to increase essentially the accuracy of the measurements and calculations and to improve the precision of the calculation formula [4*b*, *c*, *g*]. All these are illustrated by the calculations and graphs given in [4*e*, *f*, *g*].

Experimental check of the transparency method was carried out on two plane models: 1, microcrystals of AgBr in gelatine (particle radius is about 0.3 μ) and 2, Spores of Calvatia (particle radius is about 2.5 μ). In spite of great values of m ($m \simeq 1.5$) and roughly spherical form of the particles the agreement is satisfactory (see in detail [4*f*]).

4. The scattering pattern method

The relation between the light scattering pattern of a single particle $J(\beta, r)$ the particle size distribution function $f^*(r)$ and the polidisperse scattering pattern $\bar{J}(\beta)$ is of the form

$$\bar{J}(\beta) = \int_0^\infty J(\beta, r) f^*(r)\, dr. \tag{1}$$

Let us consider the particle system optical properties of which differ very little from that of their environment and at any rate

$$\varrho(m-1) < 1, \quad |\alpha| < 1. \tag{2}$$

In such a case the monodisperse scattering pattern $J(\beta, r)$ is expressed by a simple formula [1*a*] (Rayleigh-Gans approximation)

$$J(\beta, r) = I_0 \psi(\beta) K(q) r^2, \quad q = 2\varrho \sin\frac{\beta}{2}, \tag{3}$$

$$K(q) = \left(\frac{\sin q - q\cos q}{q}\right)^2; \tag{4}$$

here β = scattering angle

I_0 = intensity of incident light,

$$\alpha = \frac{3}{4\pi}\frac{m+1}{m^2+2}(m-1), \quad \psi(\beta) = 2\pi^2 |\alpha|^2 \frac{1+\cos^2\beta}{(1-\cos\beta)^2}. \tag{5}$$

The scattering pattern method for such "very soft" particles is developed in [4*h*] (See also [4*f*]). The solution of the integral equation (1) is analogous to the solution (1) from § 3. The accurate inversion formula (1) has been obtained. The equation good for approximate calculation of the distribution function $f^*(r)$ in case of tabulated scattering pattern $\bar{J}(\beta)$ has been found,

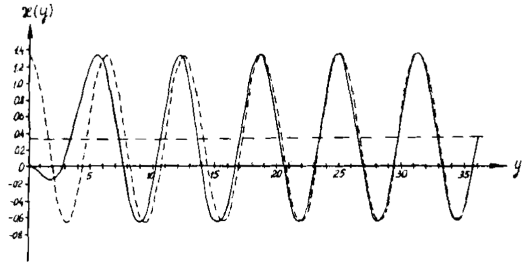

FIG. 2*a*. Functions used in the scattering pattern method.

$$f^*(r) \simeq \frac{4}{\pi r_0^4 a^2} \times \left\{ \sum_{j=1}^{n} g\left(\frac{x_j}{2}\right) \varkappa(ax_j)\, \Delta x_j + C_0 \tau \varkappa_0(a\tau) + C_2 \frac{\varkappa_2(a\tau)}{\tau} \right\}. \tag{6}$$

Function $\varkappa(y)$, $\varkappa_0(y)$ and $\varkappa_2(y)$ (fig. 2)[1] represent functions

$$\varkappa(y) = \left(1 - \frac{8}{y^2}\right) \cos y + \left(\frac{8}{y^3} - \frac{4}{y}\right) \sin y + \frac{1}{3},$$

$$\left.\begin{aligned} \varkappa_0(y) &= \frac{\varkappa(y) - \omega_0(y)}{2} \\ \varkappa_2(y) &= \frac{\varkappa(y) - \omega_2(y)}{4}. \end{aligned}\right\} \tag{7}$$

It is highly essential that all these functions have limited amplitudes of oscillation. Thus in distinction from the transparency method the enhancement of y here does not result in rapid growth of errors.

In formula (6) the following designations are introduced:

$$x = \gamma \sin \frac{\beta}{2}, \quad \gamma = 4\varrho_0, \quad \varrho_0 = \frac{2\pi r_0}{\lambda}, \quad \tau = \gamma \sin \frac{\beta_{\max}}{2}, \tag{8}$$

$$r = ar_0, \quad g\left(\frac{x}{2}\right) = \frac{r_0}{\psi(\beta)} \frac{\bar{J}(\beta)}{I_0}, \tag{9}$$

where r_0 = (arbitrary) linear scale of the problem. Values of x_j correspond to scattering angles β_j, for which the scattering pattern $\bar{J}(\beta)$ was measured, $\beta = \beta_{\max}$ is the largest of such angles. We have

$$0 \leqslant x_j \leqslant \tau, \quad \sum_{j=1}^{n} \Delta x_j = \tau, \quad 0 < \beta_{\max} \leqslant \pi. \tag{10}$$

The coefficients C_0 and C_2 are determined from the relationship

$$g(\tfrac{1}{2}x) \simeq C_0 + \frac{C_2}{x^2}, \tag{11}$$

which approximates "the tail" of the function $g(\frac{1}{2}x)$ when $x > \tau$. But on the basis of the physical content of the problem the function $g(\frac{1}{2}x)$ can

[1] In Fig. 2*a* the dashed curve represent the function $\cos y + \frac{1}{3}$.

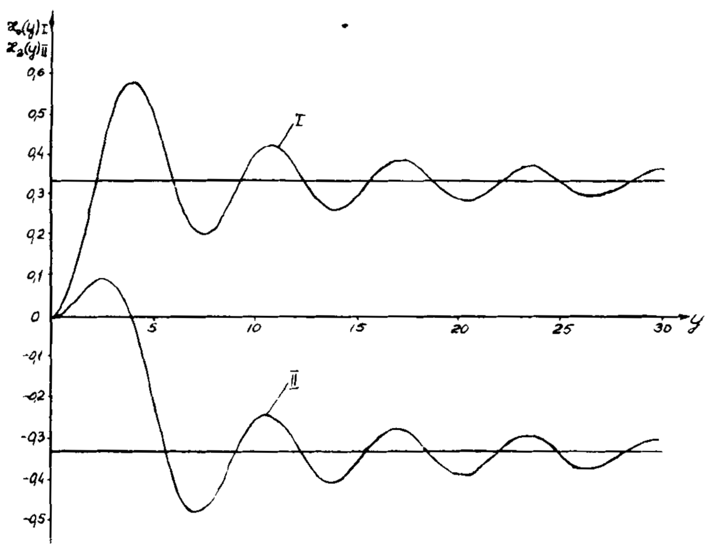

FIG. 2*b*

be measured when $x < \tau$. Thus the formula (6) can be used when the following main condition is fulfilled: the extrapolation of the expression (11) from the interval $(1,\tau)$ to the interval (τ,∞) is correct.

It has been shown in [4h][1] that in the case of the $\beta_{\max} = \pi$ monomodal scattering pattern $g(\frac{1}{2}x)$ formula (6) gives a satisfactory result if the condition

$$\tau = 4\varrho_0 \sin \frac{\beta_{\max}}{2} > (1.6 - 2.0)\, x_M \qquad (12)$$

is fulfilled.

Here the mode x_M of the function $g(\frac{1}{2}x)$ is taken in the scale r_0 (λ is fixed).

The necessity for the extrapolation (11) arises in connection with the utilization of apparatus of integral transformation for inversion (1). However there are reasons to suppose that this requirement is conditioned by the essence of the problem. In fact it is equivalent to the requirement that all peculiarities of the behaviour of the function $g(\frac{1}{2}x)$ must be concentrated in the interval $(0,\tau)$ beyond which $g(\frac{1}{2}x)$ is a decreasing function. Physically it can be accounted for the fact that the scattering pattern differs from a Rayleigh one when ϱ is large enough and only then the inversion is possible. Thus, on the one hand ϱ must be large enough (for the sake of inversion, otherwise optical information is not complete), on the other hand condition (2) must be fulfilled (only then the monodisperse scattering pattern is of the form (3), (4)). All these operations can be carried out for "very soft" particles, for which $m - 1$ is little.

Let us rewrite formula (12) as an equality, supposing that the coefficient of x_M is equal to 2 and $r_0 = \bar{r}$ ($\bar{r}$ is mean radius of particles). We have

$$\sin \frac{\beta_{\max}}{2} = \frac{\lambda x_M}{4\pi \bar{r}} \quad (x_M \text{ is the scale of } \bar{r}). \qquad (13)$$

Let us consider, for example, Γ-distribution (N is the volume concentration of particles)

$$f_\mu^*(r) = N \frac{\varepsilon^{\mu+1}}{\Gamma(\mu+1)} r^\mu e^{-\varepsilon r}. \qquad (14)$$

[1] Formulae in [4h] are written for the case $\beta_{\max} = \pi$.

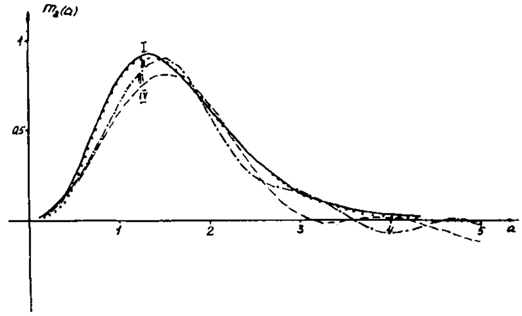

FIG. 3. Inversion of scattering pattern ($\mu = 2$). I, an exact curve; II, III, IV, curves obtained when $\tau = 8, 5, 3$ respectively.

Fig. 3 gives the inversion for $\mu = 2$ (when $\tau = 8, 5, 3$). It is quite possible to show, that $x_M \leq 4$ (in the scale $r_0 = \bar{r}$), if $\mu = 0, 2, 4, 6$. The equality (13) in this case gives

$$\sin \frac{\beta_{\max}}{2} = \frac{\lambda}{\pi} \frac{1}{\bar{r}}. \qquad (15)$$

For the specified λ the relationship (15) determines the upper limit of the angle $\beta_{\max}$ up to which one must measure the scattering pattern in order that the reliable inversion should be obtained. For example, $\lambda = 0.55\ \mu$. In this case we shall obtain the dependence between $\beta_{\max}$ and $\bar{r}$ which is illustrated in Table 1.

TABLE 1

$\bar{r}$, μ	0.2	0.4	0.6	1	2	5
$\beta_{\max}$ (deg)	130	55	35	20	10	5
$\beta_{\min}$ (deg)	30	15	10	6	3	1

The limiting angle of measurement of 180° corresponds to $\bar{r} = 0.175\ \mu$. For $\bar{r} < 0.175\ \mu$ it is impossible to satisfy the equation (15). We also see that the small scattering angles ($\beta \leq 20°$) practically contain all the information on the particle spectrum for $\bar{r} > 1\ \mu$. It is very important to estimate the minimum angle $\beta_{\min}$ of which the data on the scattering pattern are necessary. This minimum angle we shall determine by the minimum admissible values of x_1.

To make it more certain we shall take $\mu = 2$, $\tau = 2x_M$. Then having the error of 2 % we shall find $x_1 = 1.2$. We shall get for $\beta_{\min}$ values which are shown in the third line of the table. As for the number of the points in the sum of the formula (12), the analysis of the different variants shows that in the scattering pattern method the value of $n = 10 - 20$ gives an adequate accuracy.

6. Conclusion

The main drawback of the light scattering methods is the hypothesis on sphericity of the haze particles and their homogeneity. Often these conditions are not satisfied. In this case data obtained by the light scattering refer to some "effective" spheres. But the light scattering methods have the essential advantage they can be easily automatized and allow to obtain information on rapid processes and to follow the dynamics of the aerosol reconstruction.

REFERENCES

1. K. S. Shifrin, *a*) Light scattering in opaque medium, *GITTL* (1951); *b*) *Trudy WSLTI*, N. 2 (1956); *c*) Sbornic "Issledovanie oblakov, osadkov i grosovogo electrichestva", *GIMIS* (1957); *d*) *Trudy GGO*, N. 46 (1955); *e*) *Trudy GGO*, N. 109 (1961).
2. H. C. van de Hulst, *Light Scattering by Small Particles*. New York, London, 1957.
3. E. Titchmarsh, *Introduction to the Theory of Fourier Integrals*. New York, 1937.
4. K. S. Shifrin and A. Y. Perelman, *a*) *Opt. and Spectr.*, 15 (1963) N. 4; *b*) *Opt. and Spectr.*, 15 (1963) N. 5; *c*) *Opt. and Spectr.*, 15 (1963) N. 6; *d*) *Opt. and Spectr.*, 16 (1964) N. 1; *e*) Pageoph. 58, II (Basel, 1964); *f*) Proceedings II ICES (1965) N.Y.; *g*) *Isvestiya AN USSR*, Atmospheric and oceanic physics: 1, No. 9, N. 9 (1965); *h*) *DAN USSR*, 158 (1964), N. 3.
5. K. S. Shifrin and V. I. Golikov, *a*) *Sbornic* "Issledovanie oblakov osadkov i grosovogo electrichestva" *AN USSR* (1961); *b*) *Trudy Wsesoyusnogo nauchnogo meteorologicheskogo soveschniya*, 9 (1964); *c*) *Trudy GGO*, N. 152 (1964); *d*) *Trudy GGO*, N. 170 (1965).
6. V. I. Golikov, *a*) *Trudy GGO*, N. 109 (1961); *b*) *Trudy GGO*, N. 118 (1961); *c*) *Trudy GGO*, N. 152 (1964); *d*) *Trudy GGO*, N. 170 (1965).

ОПРЕДЕЛЕНИЕ СПЕКТРА ЧАСТИЦ АТМОСФЕРНОГО АЭРОЗОЛЯ С ПОМОЩЬЮ РАССЕЯНИЯ СВЕТА

Рассматриваются трудности при определении спектра частиц атмосферного аэрозоля. Описываются методы прозрачности и индикатрисы, которые позволяют определить функцию распределения частиц по размерам. Указаны требования, которые предъявляют эти методы к начальной оптической информации. Даны примеры обращения методов прозрачности и индикатрисы.