ON APPROXIMATION OF THE RELATIONSHIP OF THE SCATTERING COEFFICIENT AND THE MASS CONCENTRATION OF THE FINELY DISPERSED AEROSOL AND ON THE CONDITIONS OF ITS LINEARITY

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The relationship of the scattering coefficient and the aerosol fill factor is studied based on the calculated data for nonabsorptive aerosol with lognormal particle size distribution. The analytical approximation of this relationship is proposed which can be used for routine estimates with an error of 3–5% and for prediction of the examined characteristics for individual fraction or superposition of particle fractions. We find that condensation moistening and coagulation of particles result in the linear dependence of the scattering coefficient on aerosol mass concentration.

The problem of finding the relationship of the aerosol extinction coefficient and the aerosol mass concentration is important for the prediction of the transparency of the atmosphere and different aerosol formations under conditions of variability of their composition, determination of the aerosol substance content from the optical data, and foundation of the experimental techniques used for these purposes.

The results of numerous experimental investigations performed in a real atmosphere with aerosol pollutants of anthropogenic origin indicate a nearly linear correlation between the aerosol extinction (scattering) coefficient and the particle mass concentration in the visible range.[1–3] Variations of the correlation coefficient are large and can lay outside the range 1–10 $km^{-1}/(mg \cdot m^{-3})$. In general they are caused by the variability of the particle size distribution, complex refractive index, and shape and structure of aerosol particles.

It is interesting to study the effect of microphysical parameters of aerosol on the correlation coefficient and to determine the conditions of its stability, i.e., the linear or nearly linear relationship of the examined characteristics.

The analysis is carried out in this paper based on the calculated data given in Refs. 4 and 5 for a single–humped lognormal particle size distributions describing satisfactorily the microstructure and optical properties of fine and coarse fractions of atmospheric aerosol of different origin. In calculations made by the Mie theory, the value of the normalized scattering coefficient $\tilde{\delta}_s = \delta_s / N\lambda^2$ (where δ_s is the scattering coefficient at the wavelength λ and N is the number density of particles) was determined for the following values of the microphysical parameters of the lognormal distribution of nonabsorptive particles: the median diffraction parameter $\rho_0 = 2\pi a_0/\lambda = 0.2\ (0.2)\ 2, 3$ which corresponds to the increase of the median radius of particles a_0 from 0.017 to 0.26 μm at the wavelength $\lambda = 0.55$ μm; the variance of the natural logarithm of particle radius $s^2 = 0.2\ (0.1)\ 0.5$, and the refractive index of particles $n = 1.33$, $1.40\ (0.05)\ 1.55$. Taking into account that the fill factor of the aerosol (the volume occupied by aerosol in unit air volume) $V = 4/3\pi \bar{a}_3^3 N$, where $\bar{a}_3 = a_0 \exp(1.5\, s^2)$ is the root–mean–cube radius of the distribution function of the particle concentration over size, the relationship of the aerosol scattering coefficient and the fill factor, proportional to the aerosol mass concentration, can be represented in the form

$$\delta_s = [\gamma(\rho_0, s^2, n)/\lambda]\, V\ . \qquad (1)$$

Here the volume scattering coefficient (the scattering coefficient of unit aerosol volume) is a dimensionless value and is calculated from the formula

$$\gamma = 6\pi^2 \tilde{\delta}_s / \bar{\rho}_3^3\ , \qquad (2)$$

where $\bar{\rho}_3 = 2\pi \bar{a}_3/\lambda$.

The analysis of the calculated data shows that it is optimal to use the generalized (effective) parameter of the degree of coarseness of particles for describing the effect of the microstructural parameters ρ_0 and s^2 on the volume scattering coefficient. It can be characterized by $\rho_{0V} = \rho_0 \exp(3s^2)$ – the median size (radius) of the distribution function of particle volumes over size, which can be used to represent the dependences $\gamma(\rho_{0V}, s^2, n)$ in the form convenient for study (Fig. 1). In the representation in terms of ρ_{0V} the effect of aerosol polydispersity s^2 is localized essentially within the region of extrema in the dependences $\gamma(\rho_{0V})$, and the variation of s^2 results in no shift of the maxima along the ρ_{0V} axis. Exactly in this meaning we can assume the parameter ρ_{0V} to be optimal (effective) for describing $\gamma(\rho_{0V}, s^2, n)$.

In general the values of γ vary within quite wide limits from 0 to 5, and every microphysical parameter of particles affects in its own way the volume scattering coefficient (Fig. 1).

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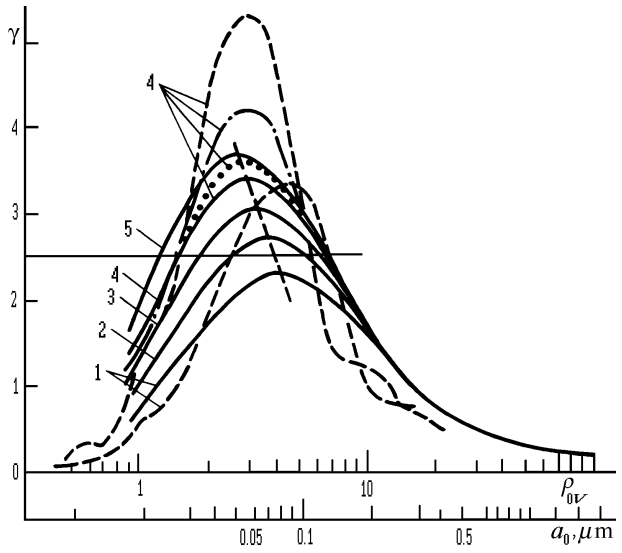

FIG. 1. The volume scattering coefficient γ of nonabsorptive aerosol with lognormal particle size distribution as a function of microstructure and refractive index of particles for different values of n: 1) 1.33, 2) 1.40, 3) 1.45, 4) 1.50, *and* 5) 1.55. *Solid lines are for* $s^2 = 0.5$, *dotted lines are for* $s^2 = 0.4$, *dot–dashed lines are for* $s^2 = 0.2$, *and dashed lines are for* $s^2 = 0.05$.

For small and large ρ_{0V} the value of γ is small, asymptotically approaching to zero for $\rho_{0V} \ll 1$ (due to the substantial decrease of the light scattering efficiency), and for $\rho_{0V} \gg 1$ (due to the prevailing increase of the particle volume). The dependences $\gamma(\rho_{0V})$ have a single–humped form with the maximum, i.e., the volume scattering efficiency of the aerosol has a clearly pronounced selective character, and there are particle distributions which attenuate most effectively the radiation in unit volume of particles. Such particle size distributions ρ_{0m} correspond to the maxima in the dependences $\gamma(\rho_{0V})$ and vary in the range of ρ_{0V} from 2.5 to 4.5 ($a_0 = 0.049 - 0.086$ μm for $s^2 = 0.5$ at $\lambda = 0.55$ μm). The position of maximum is independent of the degree of aerosol polydispersity and is determined by the particle refractive index n alone. When n decreases the particle size distributions with higher degree of coarseness attenuate the radiation more effectively. Fig. 2*a* illustrates the unambiguous nearly linear variability of $\log\rho_{0m}$ as a function of the refractive index.

The maximum value of the volume scattering coefficient γ_m varies unambiguously with n and s^2, indicating the linear dependence on these parameters (Fig. 2*a* and *b*). The decrease of the refractive index from 1.55 to 1.33 results in the corresponding decrease of γ_m from 3.7 to 2.2 ($s^2 = 0.5$), however the value of γ_m increases with the decrease of the degree of aerosol polydispersity s^2 and reaches its maximum for the monodispersed particles.

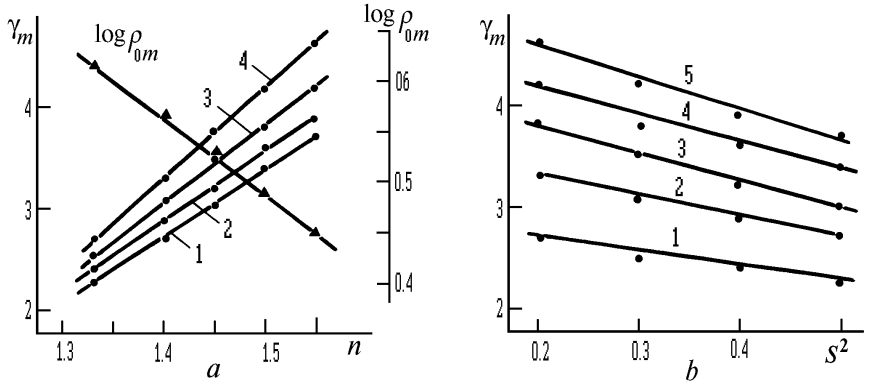

FIG. 2. The effect of microphysical parameters of particles on the position (a) and magnitude (a and b) of the maximum in the volume scattering coefficient (points and triangles show the calculated data and straight lines show their approximation for the values of s^2: *1)* 0.2, *2)* 0.3, *3)* 0.4, *and 4)* 0.5 (*a*) *and for the values of n: 1)* 1.33, *2)* 1.40; *3)* $n = 1.45$, *4)* 1.50, *and 5)* 1.55 (*b*).

The unambiguous dependences can be used to derive the linear approximation describing the position and magnitude of maximum in the volume scattering coefficient with an rms error of 2–3 %

$$\log \rho_{0m}(n) = 1.64 - 0.76n \; ; \qquad (3)$$

$$\gamma_m(s^2, n) = (n - 1)\,(9.4 - 5.3\,s^2) \; . \qquad (4)$$

Here and below, the numerical coefficients in the regression formulas were found by the least–squares technique.

The comprehensive analysis of the calculated data showed that the dependences $\gamma(\log \rho_{0V}, s^2, n)$ are symmetric about the maximum (Fig. 1) in the range $\rho_{0V} = 1$–10 ($a_0 = 0.02$–0.2 μm for $s^2 = 0.5$ at $\lambda = 0.55$ μm) corresponding to the range of variations of the microstructure of the fine fraction typical of atmospheric hazes,[3] and the lognormal distribution can be used for their description

$$\gamma(\rho_{0V}, s^2, n) = \gamma_m(s^2, n) \exp\,[-\log^2(\rho_{0V}/\rho_{0m})/2v^2] \qquad (5)$$

with $0.2 \le s^2 \le 0.5$ and $1.33 \le n \le 1.55$.

An estimate of the spread of the curves $\gamma(\rho_{0V})$ showed that the standard deviation of the common logarithm of particle size is determined primarily by the variance of the particle size distribution function s^2, weakly depending on the refractive index (Fig. 3a). These dependences are nearly linear and can be used to derive the following formula:

$$\nu = 0.28\, s^2 - 0.045\, n + 0.34 \qquad (6)$$

for describing $\nu = s_{\log \rho_{0V}}$ with an rms error of about 2 %.

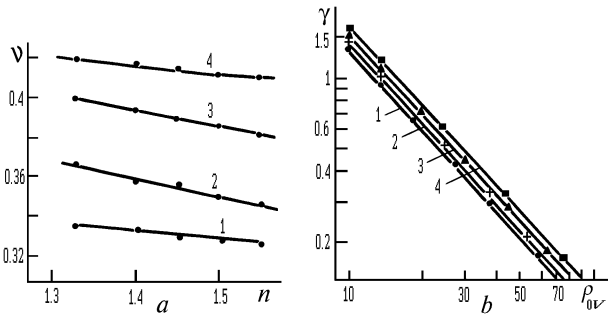

FIG. 3. The dependence of the spread of the curve $\gamma(\log\rho_{0V})$ *for finely dispersed particles (a) and of the volume scattering coefficient for coarsely dispersed particle size distributions on the microphysical aerosol characteristics for different values of* s^2: *1)* 0.2, *2)* 0.3, *3)* 0.4, *and 4)* 0.5.

Basic approximation (5) simultaneously with formulas (3), (4), and (6) can be used to calculate analytically the volume scattering coefficient in the range $\rho_{0V} = 1$–10 for prescribed microphysical parameters of particles ρ_{0V}, s^2, and n with the error $\delta_c = 2$–3 % in the region $\rho_{0V} = 1.5$–4 and with the rms error $\delta_c \mid 3$–6 % for $\rho_{0V} < 1.5$ and $\rho_{0V} > 4$. Here the calculational error is understood as the relative error of the deviation of the results of calculations based on approximations (3)–(6) from the initially calculated data.[4]

The variability of the volume scattering coefficient for the coarsely dispersed particle size distributions with $\rho_{0V} = 10$–100 ($a_0 = 0.2$–2 μm for $s^2 = 0.5$ at $\lambda = 0.55$ μm) analyzed according to the calculated data given in Ref. 5 showed that its values depend weakly on the refractive index and for $\rho_{0V} > 20$ they are practically independent of the refractive index and are primarily determined by the microstructure parameters ρ_{0V} and s^2, varying unambiguously with their variations (Fig. 3*b*). The value of γ can be described by the power–law function of ρ_{0V} with an rms error of 3–5 %. The power of this dependence is linearly related to the variance of the distribution function

$$\gamma(\rho_{0V}, s^2) = 21.1\, \rho_{0V}^{0.2s^2 - 1.21} . \qquad (7)$$

Using the asymptotic analytical formulas for the scattering coefficients derived in Ref. 6 it is easy to show that for large ($\rho \gg 1$) particles with lognormal size distribution the formula

$$\gamma_l = 3\pi\rho_{0V}^{-1} \exp(0.5s^2) = \gamma_{lm}(r_0) \exp(0.5s^2) \qquad (8)$$

is valid while for the Rayleigh particle size distributions ($\rho \ll 1$) we have

$$\gamma_R = 3\pi\rho_{0V}^3 \left(\frac{n^2 - 1}{n^2 + 2}\right) \exp(4.5s^2) = \gamma_{Rm}(\rho_0) \exp(4.5s^2) . \qquad (9)$$

Here $\gamma_{lm}(\rho_0)$ and $\gamma_{Rm}(\rho_0)$ are the volume scattering coefficients of the monodispersed large and Rayleigh particles with the size ρ_0, respectively. The formulas for them follow from Eqs. (8) and (9) at $s^2 = 0$.

For $\rho_{0V} \simeq 100$ formula (8) is in agreement with the data calculated according to formula (7) with an error of about 5 % and hence can be used with the satisfactory accuracy in the region $\rho_{0V} > 100$ as an analytic continuation of formula (7). The range of applicability of the Rayleigh approximation given by formula (9) corresponds to ρ_{0V} 0.1 since for the minimum value $\rho_{0V} = 0.36$ employed in calculations,[4] the error in determining γ is 5–15 % increasing up to 100–250 % for $\rho \simeq 1$. Thus, for $\rho_{0V} = 0.1$–1 formula (5) on the side of maximum ρ and formula (9) on the side of maximum ρ yield large errors in determining γ. Hence, in the above–indicated range of ρ_{0V} the additional approximation must be employed on the basis of the corresponding calculated data.

The analytic approximation of the volume scattering coefficient (formulas (3)–(9)) derived for the wide range of variation of the particle size distributions and of the refractive indices can be used to determine with satisfactory accuracy the value of γ (or the scattering coefficient) for single fraction or the superposition of two or k fractions (modes) of aerosol particles without exact computations. Due to the additivity of the values σ_s and V, an account of the contribution of different fractions to γ is provided by the formula (mixture rule)

$$\gamma = \sum_{i=1}^{k} p_i\gamma_i \left(p_i = V_i/V\ ;\ V = \sum_{i=1}^{k} V_i\right) , \qquad (10)$$

where γ_i and V_i are the volume scattering coefficient and the fill factor of the ith particle fraction, respectively.

It follows from Eq. (10) that when the aerosol particle size distribution becomes bimodal due to addition of the coarse fraction (γ_2, V_2) to the fine fraction (γ_1, V_1), this results in a decrease of γ for the mixture compared to γ_1, since $\gamma_2 < \gamma_1$ (Fig. 1) and the amount of decrease is the larger the higher is the mass ratio of the particles of the second fraction

$$\frac{\Delta\gamma}{\gamma_1} = \frac{V_2}{V_1 + V_2}\left(\frac{\gamma_2}{\gamma_1} - 1\right) . \qquad (11)$$

For example, for equal (moderate dust content in air) mass ratios of the fine fraction in the atmospheric aerosol composition described by the microphysical model presented in Ref. 3 ($\gamma_1 = 2.5$ from Eqs. (3)–(6)) and of the coarse dust fraction with the microstructure parameters $a_{0V} = 2.5$ μm and $s^2 = 0.6$ taken from Ref. 7 ($\gamma_2 = 0.55$ from Eq. (7)) the calculation according to Eq. (10) yields the value $\gamma = 1.52$, and, hence, for such a bimodal distribution the relative contribution of the coarse fraction to the total scattering coefficient at a wavelength of 0.55 μm is 18 %.

Approximations (3)–(7) describing analytically the variations of γ for a wide range of microphysical parameters of the particles, is suitable for study of the conditions of dynamic stability $\gamma(\rho_{0V}, s^2, n) \sim$ const, equivalent to the stably linear correlation between the scattering coefficient and the fill factor (mass concentration).

If we assume in Eq. (5) the condition of constancy of the discrete values of the coefficient $\gamma = \gamma_i$ to be satisfied and fix one of the microphysical parameters of particles, we will

succeed in studying the interrelationship of two other parameters at constant γ. The comparison of the obtained dependences with the well–known behavior of the variability of the atmospheric aerosol composition in the course of the processes typical of its transformation makes it possible to determine the degree to which these processes affect the linear relationship of the scattering coefficient and the mass concentration.

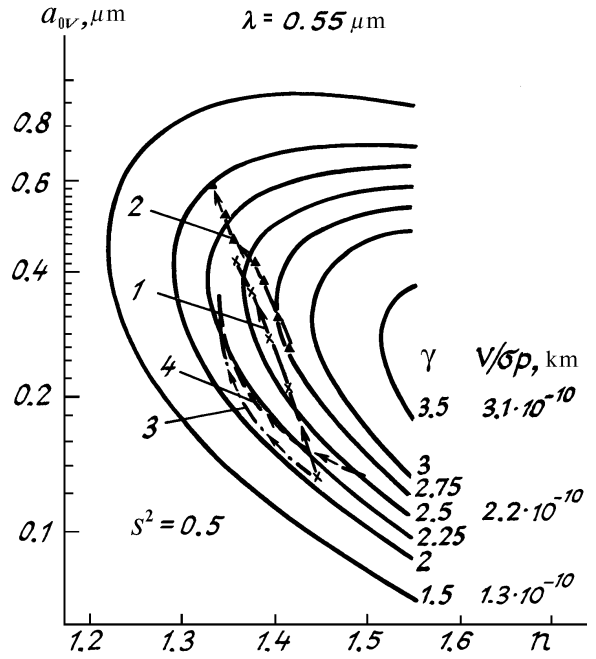

FIG. 4. The comparison of isolines of γ_i for $s^2 = 0.5$ (condensation) with experimental data and the results of calculations with the use of the equilibrium–solution model: 1) empirical model of the atmospheric haze proposed in Ref. 3 for the meteorological visibility range S_m = 2–50 km; 2) individual measurements in the atmospheric haze performed in Ref. 8 for relative humidity 75–98 %; the equilibrium–solution model for a_0 = 0.031 μm and s^2 = 0.5: 3) n_d = 1.45 and 4) n_d = 1.50.

The cases in which the degree of polydispersity $s^2 = 0.5$ (the value typical of the fine fraction of the atmospheric haze[3]) or the refractive index $n = 1.5$ (the value typical of aerosol of various origin at low air humidity) remain unchanged are shown in Figs. 4 and 5.

It can be seen from Fig. 4 (the isolines of the discrete values of γ_i lying in the range γ_i = 1.5–3.5 are shown by solid curves), that for the fixed value of s^2 the condition of γ stability is reduced to the requirement of the interrelated variability of the degree of coarseness a_{0V} and of the refractive index n. In the region a_{0V} 0.4 μm typical of the atmospheric hazes the isolines are described by the unambiguous nonlinear dependences, whose gradient increases with γ_i and are characterised by the growth of the aerosol particles with simultaneous decrease of their refractive index. As applied to the real aerosol, this is the characteristic feature of the condensation variability of particle moistening in the humidity field.[1,7] Thus, we can consider the isolines as off–beat curves of condensation growth of particles and *a priori* conclude that the condensation transformation of aerosol particles results in the nearly linear relationship of the scattering coefficient and the fill factor.

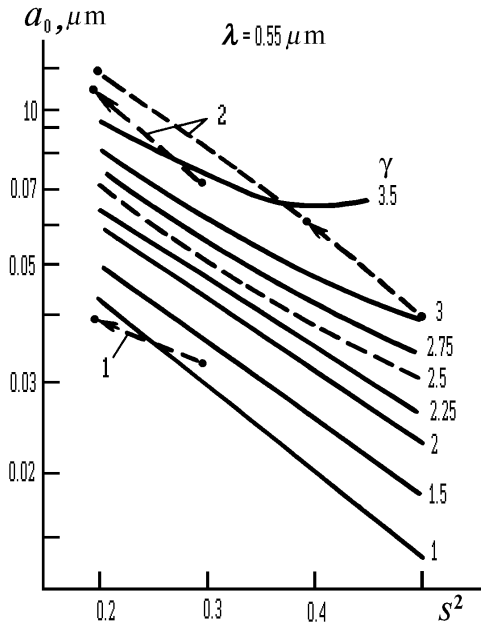

FIG. 5. The comparison of isolines of γ_i for $n = 1.50$ (coagulation) with the experimental data given in Ref. 10 for finely (curve 1) and coarsely (curve 2) dispersed wood smokes in the course of their aging at low air humidity.

Such a conclusion is corroborated by Fig. 4 which shows the results of comparison of the calculated dependences with the data obtained using the empirical statistical model proposed in Ref. 3 for atmospheric hazes for the meteorological visibility range S_m = 2–50 km (curve *1*), for which the aerosol variability is determined to a considerable degree by the condensation processes, as well as with the results of estimating the diurnal variations in the parameters of the haze particles presented in Ref. 8 for relative air humidity 75–98 % (curve *2*), and with the data calculated in the approximation of the model of the equilibrium–solution assimilation of moisture at condensation (curves *3* and *4*). Calculations of $a_{0V}(n)$ for the equilibrium–solution model were made based on the mixture–rule (formula (10)) with the following initial parameters of dry particles: a_0 = 0.031 μm, s^2 = 0.5, and n_d = 1.45 (curve *3*) and n_d = 1.50 (curve *4*). The arrows on the curves indicate the directions of increasing the relative humidity (curves *2–4*) and of decreasing the visibility (curve *1*). It can be seen from Fig. 4 that the data obtained with the use of the equilibrium–solution model (curves *3* and *4*) are in a good agreement with the isolines of γ_i. Experimental curves *1* and *2* illustrating the condensation transformation of the atmospheric hazes also have the behavior analogous to that of the isolines of γ_i.

Due to this fact, in spite of the significant variations in the microphysical parameters of particles at condensation, the value of γ varies insignificantly and does not exceed the 10 % deviation from its mean value for the statistical model (curve *1*) and the 20 % deviation for the individual measurement cycle (curve *2*). This fact allows us to use a fixed value of γ to approximate the linear relationship of the scattering coefficient and the aerosol fill factor. For example, the value γ = 2.5 corresponds to the empirical statistical model of the atmospheric haze (curve *1*). The analysis shows that the condensation results in the linear

relationship of the examined characteristics and, accordingly, such a correlation found in Refs. 1–3 under real conditions is probably explained by the processes of condensation moistening of aerosol particles.

Different dependence is observed under conditions of the dynamic stability of γ when the value of the refractive index remains unchanged (Fig. 5). In this case it follows from Eq. (5) that the condition of constancy of $\gamma = \gamma_i$ is reduced to the requirement of insignificant variability of the effective particle radius a_{0V} corresponding to the given isoline. In this connection each isoline of γ_i can be approximated by the linear dependence between the median radius a_0 and the variance of the distribution s^2 in the form: $\log a_0 \sim (-s^2)$. Such a relationship of microstructural parameters which is manifested in the growth of particle size a_0 with simultaneous narrowing of the particle size spectrum s^2 is typical of the coagulation variability of the aerosol under real conditions without continuous source of particles.[9]

In this connection we can tentatively consider the dependences shown in Fig. 5 as isolines of coagulation type. The experimental data (curves *1* and *2*) on the variability of the microstructural parameters of particles in the course of aging of the wood smoke aerosol at low relative humidity, obtained in Ref. 10 from the measurements of the polarization scattering phase functions in the visible range, are also shown in Fig. 5. The arrows on curves *1* and *2* corresponding to the finely and coarsely dispersed smokes, respectively, indicate the directions of the transformation of the particle microstructure with time. The comparison of the experimental data with isolines shows that the smoke aerosols are characterized by a wide range of γ variation depending on the degree of their coarseness. The transformation of the smoke particle microstructure with time has the behavior analogous to that of the isolines of γ_i. In this connection the value of the volume scattering coefficient varies insignificantly (by 10–20 %) in the course of the smoke aging. The estimates show that the aerosol coagulation after switching off the source of new particles, like the condensation variability, results in the stability of the volume scattering coefficient and, hence, in the manifestation of nearly linear relationship of the scattering coefficient and the aerosol mass concentration.

Thus, one should take into account the analytical formulas for the volume scattering coefficient derived in this paper and its variability depending on the particle parameters at condensation and coagulation when predicting and interpreting the optical–microphysical aerosol characteristics and developing the techniques for estimating the aerosol content from optical measurements.

REFERENCES

1. V.E. Zuev, B.V. Kaul, I.V. Samokhvalov, et al., *Laser Sounding of Industrial Aerosols* (Nauka, Novosibirsk, 1986).
2. D.V. Uvarov and G.P. Zhukov, Tr. Inst. Exp. Meteorol., Akad. Nauk SSSR, Obninsk, No. 15 (60), 101–117 (1976).
3. G.I. Gorchakov, A.S. Emilenko, and M.A. Sviridenkov, Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana **17**, No. 1, 39–49 (1981).
4. V.S. Kozlov and V.Ya. Fadeev, "*Tables of optical characteristics of light scattering by finely dispersed aerosol with lognormal particle size distribution*", Preprint No. 30, Institute of Atmospheric Optics of the Siberian Branch of the Academy of Sciences of the USSR, Tomsk (1981), 66 pp.
5. E.G. Yanovitskii and Z.O. Dumanskii, *Tables on Light Scattering by Polydispersed System of Spherical Particles* (Naukova Dumka, Kiev, 1972).
6. H.C. van de Hulst, *Light Scattering by Small Particles* (Willey, New York, 1957).
7. G.M. Krekov and R.F. Rakhimov, *Optical–Radar Model of Continental Aerosol* (Nauka, Novosibirsk, 1982).
8. G.I. Gorchakov and A.S. Emilenko, in: *Abstracts of Reports at the Second All–Union Conference on Atmospheric Optics*, Tomsk (1980), Vol. 1, pp. 125–127.
9. Ya.I. Tokar', in: *Abstracts of Reports at the Fifth All–Union Symposium on Laser Radiation Propagation in the Atmosphere*, Tomsk (1979), Vol. 1, pp. 248–252.
10. V.S. Kozlov, "*Experimental investigations of optical–microphysical properties of smoke aerosols,*" Author's Abstract Cand. Phys.–Math. Sci. Diss., Institute of Atmospheric Optics of the Siberian Branch of the Academy of Sciences of the USSR (1985), 19 pp.