On optical characteristics of some aerosols

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The paper describes the spectral and integral on solar spectrum volume extinction and absorption coefficients for two size distribution functions of sulfate particles. Approximate formulae for the dimensionless absorption coefficient of particles are proposed. The capabilities are demonstrated of the well-known Mathcad-2000 software package.

Introduction

Aerosol optical characteristics significantly affect the energy balance of the atmosphere and the Earth's surface. In theoretical calculations, the aerosol is presented by Mie particles. A vast scope of calculations of optical characteristics that can be done by use of the Mie theory for polydisperse ensembles of aerosol particles has been shown in the literature.[1,2] The calculated results are conventionally presented for a definite wavelength. In Ref. 3 the coefficients are integrated over 220 spectral bands of the Earth's surface emission spectrum. However, in this case, instead of the Mie algorithm, simpler approximate formulae are used for the dimensionless optical constants. Similar approach for the solar spectrum is realized in this paper. Spectrally integral single scattering characteristics are of practical significance. These characteristics are used in the calculations of the energy transfer equations. Below this is discussed in a more detail.

In Ref. 1 the formulae are presented for the dimensionless extinction coefficient K with the correction factors in the form of piecewise smooth functions $D_i + 1$ (i = 1, 2, 3, 4) in the entire range of particle size with the error below 5%. In the literature[2] the formulae were reproduced (with removing the misprint: $40.8 \to 4.08$) and the accuracy was confirmed. Below such formulae are presented for the particular cases of the absorption coefficients. This makes it possible to use the popular Mathcad software, which provide for the calculation and control, prompt tracking of the influence of separate parameters, and the illustrative form of the results. The package allows the integration of spectral optical constants over the solar spectrum to be done, although in a simplified algorithm the measures should be undertaken to decrease the scope of calculations. An effective method of investigating optical characteristics of the aerosol is given.

The aerosol is characterized by the aerodynamic diameter δ. In the complex index of refraction $m = n - \chi i$ the index of refraction χ exceeds 0.5 only for limonite, emitted from open pits, and soot. For all other aerosols $\chi \approx 0$. According to Ref. 4 the typical m value equals $m = 1.5 - i0.01$. However, in this paper this value is varied to $m = 1.3 - i0.01$ so that the tables of optical constants from Ref. 5 can be used when testing this method.

In making correct calculations the dimensionless absorption K_{abs}, scattering K_{sc}, and extinction $K = K_{abs} + K_{sc}$ coefficients are calculated by the Mie theory at a fixed particle size $x = \pi\delta\omega$, where ω is the wavenumber. The absorption coefficients α, m^{-1}, scattering coefficients β, and extinction coefficients $k = \alpha + \beta$, m^{-1}, are found with the account for particle size distribution, $n(\delta)$, m^{-3} μm^{-1}. For example, for the spectral absorption coefficient

$$\alpha_\omega = \frac{\pi}{4}{\cdot}10^{-12} \int\limits_0^\infty \delta^2\, K_{abs}\, n(\delta)\, d\delta. \qquad (1)$$

Hereinafter the diameter δ is in μm so that α_ω can be measured in m^{-1}.

In Ref. 6 the calculated values of the scattering coefficient were compared with the observation data for two particle size distributions similar to those selected in this paper. The discrepancies were significant, but with different sign and, on the average, they are compensated. Good agreement is obtained for monodisperse ensembles of particles, which are homogeneous in the composition and prepared artificially. In the error estimates the particle shape and nature turned out to be not so essential. Systematic error is obtained for hydrophilic particles at high humidity when the particles become heterogeneous. But the Mie theory can take into account this peculiarity. On the whole, we conclude that the Mie theory is a reliable instrument of the investigation.

Experimental data

In the atmosphere, where j kinds of particles are suspended, the volume single extinction coefficient is determined as

$$k = \sum_j C_j\, f_{kj}, \qquad (2)$$

where C_j is the concentration of the jth component in kg/m^3, f_{kj} is the extinction efficiency factor of the jth component, $f_{kj} = k_j/C_j$, m^2/kg.

According to Ref. 6 the values of f_{kj} are equal to 0.5−1.0, m²/g for dust, 2−4 for organic carbon, 3−10 for sulfates and nitrates, and 10 m²/g for elementary carbon.

In Ref. 7 the arithmetic mean values are given for 33 measurements in the daytime and for 11 measurements at night: 5.4 for nitrates, 5.1 for sulfates, 5.8 for carbon, 2.8 m²/g for the soil dust.

In Ref. 8 the following values were determined: f_{kj} = 3 m²/g for sulfates and nitrates, 4.0 for organic particles and 1.0 m²/g for soil (all for the dry state). The values depend on a set of conditions, mainly on the humidity. In Ref. 8 the increase of the efficiency factor f_{kj} is shown with the increase of the relative humidity up to 90% for ammonium sulfate by a factor of five and higher. Calculations by the Mie theory with assumption of the lognormal particle size distribution agree well with the observational data.

Now we give an example of the observations at the wavelength of 0.55 µm near the ground surface in the city of Salonika with 1 million population and a developed industry.[9] The observations of the extinction coefficient were combined with the determination of the particle number density and the chemical composition (at least the content of five components was measured). Table 1 shows the physical characteristics of the components, and Table 2 shows the results of the experiment (OM − organic matter; WSM − water-soluble matter; C − carbon (soot); SS − sea salts; S − soil).

Table 1. Physical properties of 5 types of aerosol (OM − organic matter; WSM − water-soluble matter; C − carbon (soot); SS − sea salts; S − soil)

Matter	Density, kg/m³	Modal diam., µm	Index of refraction	C_j, µg/m³ 06.12.1997	C_j, µg/m³ 06.13.1997
OM	1500	0.09	1.55−i0.005	16	26.7
WSM	1700	0.06	1.53−i0.005	8.02	13.4
C	1500	0.06	1.95−i0.66	3.5	8.9
SS	2100	2.34	1.5−i2·10⁻⁸	−	−
S	2300	0.31	1.50−i0.001	20.9	38.6

Table 2. Results of observation for aerosol with characteristics in Table 1 for June 12, 1997 at 0.55 µm wavelength; N is the number density; f_{kj} is the extinction efficiency factor; k_j is the volume single extinction coefficient

Matter	N, cm⁻³	f_{kj}, m²/g	k_j, km⁻¹
June 12, 1997			
OM	2345	4.63	0.074
WSM	4800	3.1	0.025
C	39019	8.38	0.029
SS	0.75	0.49	0.01
S	0.1	0.04	0.0007
June 13, 1997			
OM	9851	3.85	0.143
WSM	8021	3.1	0.061
C	14777	9.7	0.086
SS	1.1	0.49	0.019
S	0.1	0.036	0.001

The first three components are the fine structures with the contribution of 95% to the radiation extinction. For these components the extinction coefficient, calculated by the formula (2), is 0.128 km⁻¹ (12 June). That day the weather was dry, and the humidity was less than 30%. Next day the humidity increased up to 45%, the mass concentrations of hydrophilic particles increased, and the extinction coefficient increased up to 0.290 km⁻¹. Soot carbon had the minimum mass fraction, but the maximum number density and the complex index of refraction. Therefore its contribution to the extinction coefficient is significant and equals 30%. To reproduce the result of Table 2 by the calculation, the particle size distributions are necessary. Because these are lacking, we can use the data for sulfates taken from other paper.

Models of particle fractions

In Ref. 4 the sulfates and organic carbon are presented by bimodal particle size distribution with the concentration maxima at 0.1 and 0.4 µm. In Ref. 10 the data of observations on the seashore are presented. At night, when the wind is blowing from the continent and the anthropogenic sulfates are brought by the wind, the coarse fraction at 5 µm is observed, and less coarse one at 1.4 µm is also observed. The distribution of coarse fraction remains during the daytime when the wind is blowing from the ocean, but with smaller concentration. In both papers[4,10] distribution of coarse fraction (No. 1) can be described by the formula

$$dC_1/d\log\delta = C_{m1} \exp[-(\delta - 5)^2/a], \qquad (3)$$

where δ is given in µm; C_{m1} = 15 and 22 µg/m³ are the maximum values of the derivative $(dC/d\log\delta)_m$ at δ_m = 5 µm during daytime and at night. The number a is selected by the total concentration of a fraction,

$$C_1 = (C_{m1}/2.3026) \int_{0.1}^{20} \exp[-(\delta - 5)^2/a] \, \delta^{-1} \, d\delta. \quad (4)$$

Further it was assumed that $a = 4$ µm² when $C_1/C_{m1} = 0.344$.

The distribution, in Eq. (1), is calculated in the form

$$n(\delta) = \frac{6·10^6}{2.3026\pi\rho\delta^4} (dC/d\log\delta), \qquad (5)$$

where ρ is the density of the particulate matter in t/m³ (2.32 t/m³), the value n is obtained in m⁻³ · µm⁻¹.

For the second fraction (No. 2) with the maximum at 1.4 µm we can use the formula

$$dC_2/d\log\delta = C_{m2} \delta^2\exp[-\delta^2/2], \qquad (6)$$

where C_{m2} = 57 µg/(m³ µm²) is the constant chosen so that the derivative maximum $(dC_2/d\log\delta)_m$ = = 41.9 µg/m³ is located at 1.4 µm based on the observations. Further we can use the following relation:

$$\frac{C_2}{C_{m2}} = (1/2.3026) \int_{0.2}^{20} \delta \exp(-\delta^2/2) \, d\delta = 0.426 \, \mu m^2. \quad (7)$$

The small-diameter wing of Eq. (7) is cut at $\delta = 0.2$ due to the peculiarity mentioned below. The error is not introduced by the limitation of the upper boundary.

In calculating specific spectral single-component absorption $f_{\omega 2} = \alpha_{\omega 2}/C_2$, m^2/g, for the distribution No. 2 according to Eq. (1) we obtain

$$f_{\omega 2} = \frac{1.5}{2.3026 \cdot 0.426 \, \rho} \int_{0}^{\infty} K_{abs} \exp(-\delta^2/2) \, d\delta, \quad (8)$$

where the density ρ is given in t/m^3, and the diameter is given in μm.

For a group of particles No. 1

$$f_{\omega 1} = \frac{1.5}{2.3026 \cdot 0.344 \, \rho} \int_{0}^{\infty} \delta^{-2} K_{abs} \exp\left[-\frac{(\delta-5)^2}{4}\right] d\delta. \quad (9)$$

Absorption coefficient

As in the case of the extinction coefficient, the approximate formula for the absorption coefficient is obtained based on the Hulst asymptotic formula[1,11]:

$$K_{abs} = 1 + [\exp(-2z)]/z + \{[\exp(-2z)] - 1\}/2z^2, \quad (10)$$

where $z = pq \tan g$, $g = (\arctan \chi)/(n-1)$, $q = 2x(n-1)$; $x = \pi\delta\omega$ is the diffraction parameter; ω is the wave number; p is the correction factor chosen for the fraction No. 1 in the form

$$p_1 = 1.32 + 0.171 \, (\ln x)^{0.6}. \quad (11)$$

The correction (11) can be used only at $x > 1$, otherwise a peculiarity arises. At the subsequent integration over the spectrum it should be noted that, practically, solar energy is confined in the wavelength range from 0.29 to 2.4 μm with the maximum at 0.475 μm. The wavelength is used everywhere in μm as the diameter of particles. When integrating over the spectrum, a new variable v is introduced in the relation $\omega = 0.1 \, (v^{-1}-1)$, μm^{-1}; in this case from the interval $[0 \to \infty]$ we pass on to the limits $[0-1]$. The below mentioned limits of integration over the new variable v, $[0.02-0.2]$ mean, in relation to the wavelengths, $0.204-2.5 \, \mu m$, that overlaps with the range being of interest for us. In this case Eq. (9) does not show any peculiarity.

The values of K_{abs} approximated by (10) and corrected by Ref. 5 are given in Table 3. Table 3 also shows the precise albedo of single scattering λ. In this case we used the representative wavelength of solar spectrum 0.475 μm. In the concentration maximum of the coarse fraction $\delta_m = 5 \, \mu m$, $x = 30.4$. The accuracy of Eq. (11) is very high. The empirical factor p_2 in Eq. (10) for the fraction No. 2 with the maximum at 1.4 μm should vary since the aerosols with $x < 1$ are considered. For the distribution (6) (fraction No. 2) the factor is equal to

$$p_2 = 0.84 + 0.24 \, x^{(1.297-0.07x)}. \quad (12)$$

Table 3 shows that at $x \leq 10$ the approximate formula (10) with the correction by (12) is very accurate. At $x \geq 20$ the approximate values are underestimated, but they relate to the coarse fraction described separately. The high value of albedo is typical, $\lambda > 0.5$ at $x \geq 0.7$, although the absorption coefficient is very small (0.01).

Table 3. Comparison of the absorption coefficient K_{abs} by the approximate formula (10) and Table from Ref. 5. The single scattering albedo λ is also given

x	Eq. (10)	Ref. 5	λ
Correction factor p by Eq. (11)			
1	0.035	0.0284	0.7305
5	0.184	0.1900	0.9401
10	0.340	0.3682	0.8607
20	0.564	0.6006	0.7520
30	0.705	0.7047	0.6066
40	0.795	0.7912	0.6495
50	0.853	0.8534	0.6140
80	0.936		0.5577
100	0.959	0.9607	0.5416
∞	1	1	0.5
Correction factor p by Eq. (12)			
0.1	0.002247	0.002295	0.0040
1	0.28	0.284	0.7305
2	0.07	0.0705	0.8881
5	0.221	0.190	0.8607
10	0.367	0.3682	0.8007
20	0.404	0.6006	0.7520
100	0.847	0.9607	0.5416
∞	1	1	0.5

Below we present the volume spectral scattering (extinction) coefficients, Ref. 1, for the haze M at the wavelength of 0.45 μm with the index $m = 1.34$ ($\lambda = 1$) and maximum of distribution at $\delta = 0.1 \, \mu m$, the number of particles $N = 100 \, cm^{-3}$, the water content $4.948 \cdot 10^{-11}$. Now we have $\beta = 0.101$ instead of $0.106 \, km^{-1}$. At $m = 1.33$ and at the wavelength of 0.7 μm instead of the table value $0.105 \, km^{-1}$ the value $0.100 \, km^{-1}$ is found. With the decrease in the wavelength to 0.4 μm the coefficient β increased up to $0.104 \, km^{-1}$. We emphasize that there is a small change in the coefficient β at significant (in solar spectrum) variation of the wavelength from 0.7 to 0.4 μm.

Integration over the spectrum modified the result in the first example from 0.101 to $0.110 \, km^{-1}$. This insignificant spectral effect can be explained as follows. In the haze M the extinction coefficient K in the entire particle size range $[0, \infty]$ is shown by three piecewise-smooth parts, with the internal boundaries at $x = 2.5$ and 6. The particle fractions from $x = 0$ are: 78, 13, and 9%. But the contribution of these fractions to the spectral scattering coefficient is, roughly, the opposite: 1, 24, and 75% since the extinction coefficient K increases from 0 to 2 with the particle size growth. On the ascending branch of the particle size distribution the value K is small and it is of no importance. On the descending branch, the particle fraction related to the

particle size range decreases but the extinction coefficient increases so that the contributions to the coefficient β become equal. The dependence of the spectral coefficient β on the size x is rather weak. This, with higher error, can be related to the absorption coefficient.

Integration over the spectrum

Using the volume absorption coefficient as an example, the integration is performed by the formula

$$\alpha = (0.66/\theta^4) \times$$

$$\times \int_{0.02}^{0.2} \alpha_\omega(v)(v^{-1}-1)^3 dv / \{v^2 \exp[1.4388(v^{-1}-1)/\theta] - 1\},$$

$$(13)$$

where $\theta = T/1000$; the variable v and its limits are determined above; for the fraction No. 2 with the correction factor by Eq. (12) this peculiarity is not manifested and the lower limit is taken to be natural, $0.02 \to 0$. The upper limit is decreased from 1 to 0.2 to reduce the computation time. Instead of the absorption coefficient in Eq. (13) we can substitute any other optical characteristics. At $\alpha_\omega = 1$ the integral (13) within [0–1] gives 1, as it should be at any temperature. In this case the temperature 6000 K is taken.

First, the calculations were performed for the integral extinction coefficient $F = k/C = (\alpha + \beta)/C$. In Eqs. (8) and (9) the dimensionless extinction coefficient K is substituted based on the formulae from Refs. 1 and 2. The particle material is gypsum. Its density is 2.32 t/m^3. For the coarse fraction No. 1 with the maximum at 5 μm we obtain $F_1 = 0.45$ m^2/g. For the fraction No. 2 $F_2 = 1.15$ m^2/g. For the submicron fraction (No. 3) the data are unavailable. But the above haze M with the modal diameter of 0.1 μm and close value of the complex index of refraction can imitate it. The water content multiplied by the gypsum density gives the mass concentration of the fraction, $C_3 = 1.15$ g/m^3; $F_3 = k_3/C_3 = 0.92$ m^2/g. As a result of the sum of three fractions $F = 2.14$ m^2/g. The calculated results are smaller then the observational ones presented above.

In the calculations the index of refraction $(1.5 \to 1.3)$ is underestimated, and in the particle size distributions, taken for the size distribution fractions, taken for the fractions Nos. 1 and 2, the wings are cut.

In recent years, we have given much importance to the accumulation of sulfate aerosols in the stratosphere (see Refs. 12, 13, and many other papers). Unfortunately, the data for sulfate aerosols are insufficient.

The specific absorption coefficient for the fraction No. 1 (coarse) equals: $f_{\omega 1} = 0.15$ m^2/g for a given wavelength of 0.475 μm, and in the complete spectrum $f = 0.13$ m^2/g. Integration over the spectrum varied the result slightly as in the case of the radiation extinction. For the fraction No. 2 we obtain 0.38 and 0.30 m^2/g, respectively, with a higher divergence.

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