Radiative Properties of Carbonaceous Aerosols

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(Manuscript received 13 January 1971, in revised form 27 April 1971)

ABSTRACT

The complex index of refraction for various carbonaceous materials is presented for wavelengths from $0.3\mu \lesssim \lambda \lesssim 20\mu$. An ensemble of spherical carbon dust particles represented by two size distributions typical of urban aerosols is utilized in conjunction with Mie theory to determine the extinction coefficient, the albedo for single scattering, the asymmetry factor, $\langle \cos\theta \rangle$, the average phase function, and the polarization for wavelengths $0.3\mu \lesssim \lambda \lesssim 15\mu$.

1. Introduction

The present concern with the effects of pollution in the atmosphere on the climate creates an increased interest in the radiative properties of suspended particulate matter (SCEP, 1971). For example, Charlson and Pilat (1969) recently called attention to the fact that aerosols in polluted atmospheres may absorb solar radiation. Soot, tarry substances, "dirty" water, and industrial fly ash particles which may exist in polluted atmospheres all have this characteristic. The study of Cartwright *et al.* (1956) showed that soot particles were the main constituent of polluted air in the winter over Sheffield, England. Although other substances may be more important in some cities, we will confine our attention to the study of the radiative properties of carbonaceous particles, a significant constituent in at least some urban atmospheres.

In order to estimate the effect of carbonaceous pollutants on the transfer of radiation in an urban atmosphere, it is necessary to estimate the extinction coefficient, albedo for single scatter, asymmetry factor, and the phase functions which apply to an ensemble of carbonaceous aerosols. These quantities will be defined by Eqs. (4)–(9). Assuming two typical size distributions and an appropriate index of refraction, these quantities have been calculated from Mie theory for radiation characterized by various wavelengths. For the purpose of these computations, the particles are assumed to be spherical because the size distribution measurments of particles in the atmosphere are frequently given in terms of a "radius," and they do not include any measurements of the irregular shape of the particles.

2. Data

a. Index of refraction

A search of the literature revealed that a number of measurements of the refractive indices, $\hat{n}=n-ik$, have been made for various carbonaceous materials. These may be classified as graphite, coals and soots. The following is a review of these data.

1) GRAPHITE

Because of the crystalline structure of graphite, this material is birefringent. Of the five papers found in the literature in which the complex index of refraction was measured, only those of Greenaway *et al.* (1969) and Lenham and Treherne (1966) presented its anisotropic parameters.

Lenham and Treherne measured n and k for propagation of the electromagnetic waves along and perpendicular to the optic axis of graphite over the wavelength range 0.4–19 μ. Their results are shown as curves 1 and 1′ in Fig. 1. The most obvious feature of these data is that, for propagation with the electric vector perpendicular to the optic axis, the material behaves like a metal with n approximately equal to k and both indices increasing with λ.

Greenaway *et al.* (1969) determined n and k from 0.25–0.62μ by applying Fresnel's equations to reflectance measurements at two angles. These refractive indices were determined for propagation of electromagnetic waves with the electric vector in and perpendicular to the cleavage planes of the graphite. These data are shown as curves 2 and 2′ in Fig. 1. These data and those of Lenham and Treherne appear to be in disagreement. The two groups have apparently measured the parameters with respect to different crystal axes.

Carter *et al.* (1965) measured n and k for wavelengths from 0.11–0.30 μ. Their data are shown as curve 3 in Fig. 1.

Taft and Phillip (1965) measured the real and imaginary parts of the dielectric constant from about $\sim 0.6\ \mu$ into the far ultraviolet. The data were presented

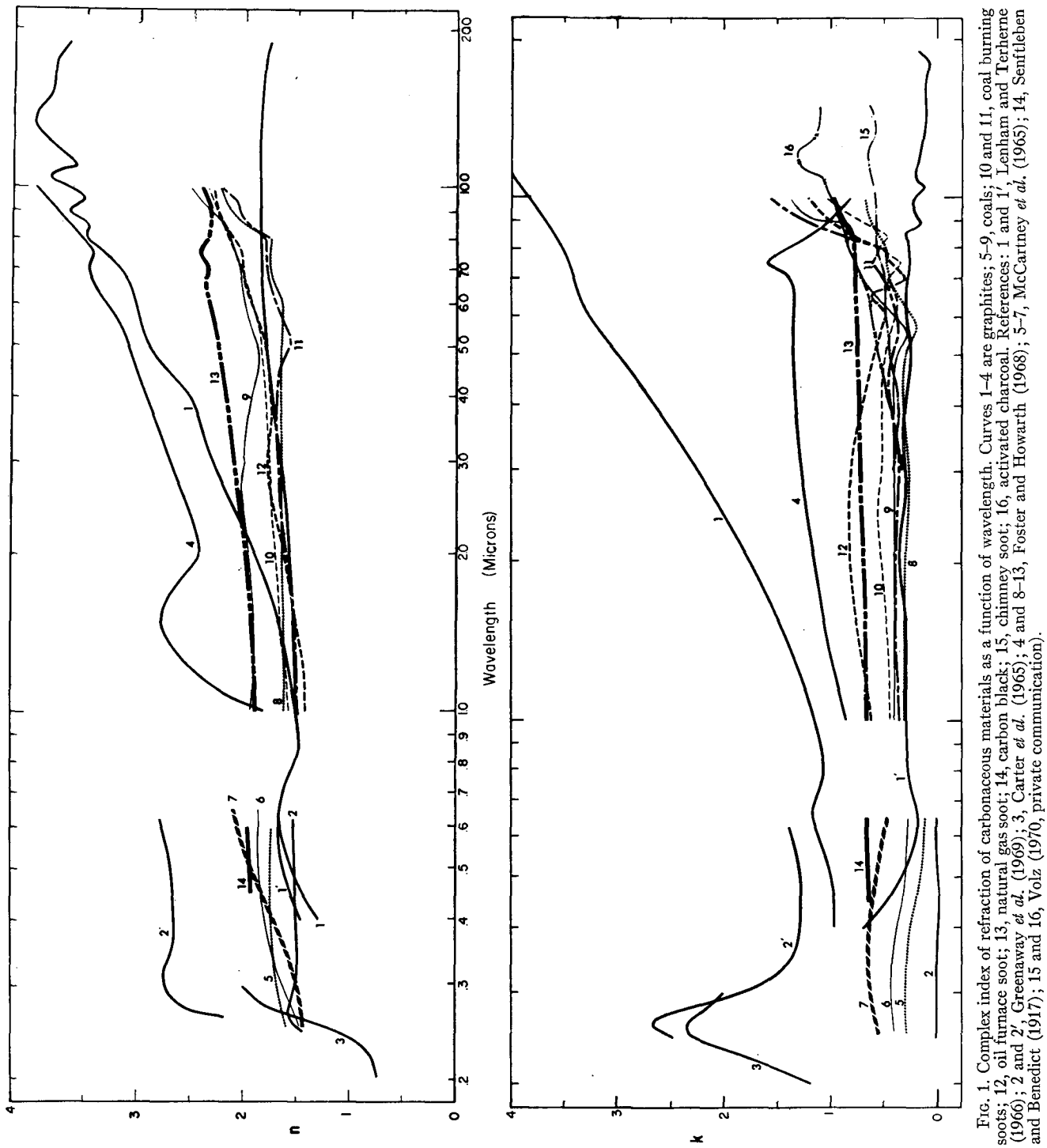

FIG. 1. Complex index of refraction of carbonaceous materials as a function of wavelength. Curves 1–4 are graphites; 5–9, coals; 10 and 11, coal burning soots; 12, oil furnace soot; 13, natural gas soot; 14, carbon black; 15, chimney soot; 16, activated charcoal. References: 1 and 1′, Lenham and Terherne (1966); 2 and 2′, Greenaway *et al.* (1969); 3, Carter *et al.* (1965); 4 and 8–13, Foster and Howarth (1968); 5–7, McCartney *et al.* (1965); 14, Senftleben and Benedict (1917); 15 and 16, Volz (1970, private communication).

in a graphic form which made it difficult to obtain n and k accurately; therefore, these data are not shown.

Foster and Howarth (1968) measured n and k for polycrystalline graphite. The way in which this sample was prepared caused the c axis to align itself parallel to the surface from which the reflectivity measurements were made. Their results are shown in Fig. 1 as curve 4.

2) COALS

McCartney *et al.* (1965) determined n and k for the visible portion of spectrum (from 0.3–0.65 μ) for a number of American coals with different carbon contents (78–94%, dry ash free basis). They used a reflectance technique at normal incidence with the sample

immersed in two media of differing indices of refraction. Some of their data are shown as curves 5, 6 and 7 in Fig. 1.

Foster and Howarth (1968) determined n and k at infrared wavelengths (1–10 μ). They measured reflectance at three angles from polished surfaces of English coals, which varied in carbon content. The main feature in the coal data, also observed in the soot data, is the increase in n and k with increased carbon content and the sharp rise in both above 7μ. These coal data are also shown in Fig. 1, labelled as curves 8 and 9.

3) Soots

Foster and Howarth (1968) measured n and k from 1–10 μ for several kinds of soots. These included natural gas, fuel oil and two different kinds of coal burning processes. All samples were compressed into a solid and were polished to a flat surface. These data are shown as curves 10, 11, 12 and 13 in Fig. 1.

Senftleben and Benedict (1917) measured complex indices for carbon black from 0.45–0.65 μ and reflectivity to 13 μ, using a reflectance technique. Their results are shown as curve 14 in Fig. 1.

Foster and Howarth (1968) are the only authors who give any estimate of the errors in their determination of n and k. Since they measured the reflectance at three angles and only two are required to determine n and k, they obtained three sets of values. They estimate errors of 6% in n and up to 20% in k.

Volz (1970)[1] has measured the imaginary parts of the index of refraction of chimney soot and Norit carbon, an activated charcoal, by means of a transmission technique from 3–15 μ. These measurements are less satisfactory than the previously considered measurements of n and k. Volz suggests that errors as large as 100% may exist in his measurements. However, these measurements are of considerable value in demonstrating that k remains fairly constant for wavelengths between 7 and 15 μ.

Fig. 1 shows that the general trend of all the curves, except those for graphite, is essentially constant from about 0.25 μ out to 15 μ. The composition and structure of carbonaceous aerosols in polluted atmospheres is not known. However, it is probably some mixture of the various soots. Since the individual measurements of n and k shown in Fig. 1 are probably not more accurate than 5–20%, we have therefore chosen the following representative constant values for $\hat{n}$ for subsequent analysis:

$$\hat{n}=n-ik=1.8-0.5i \quad (0.25\leqslant\lambda\leqslant 15\ \mu). \qquad (1)$$

b. Size distribution

The problem of selecting a representative size distribution for carbon particles in a polluted atmosphere is difficult.

[1] Private communication.

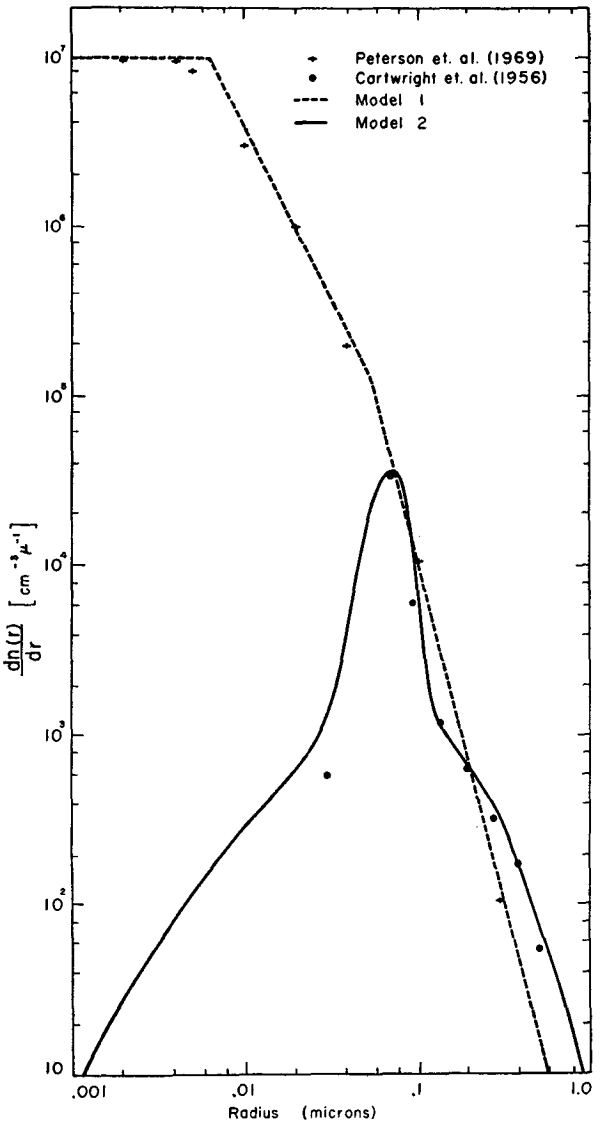

FIG. 2. Model size distributions used in this work. The points represent data of Cartwright *et al.* (1956) and Peterson *et al.* (1969) which the models are intended to represent.

Among the most definitive measurement of *solid* particles in an urban atmosphere is that of Cartwright *et al.* (1956). Their use of a thermal precipitator assures that none of their particles are volatile and such an instrument has a collection efficiency which is independent of size. Furthermore, they use an electron microscope with resolution down to 0.02 μ to count their particles. This resolution was sufficient to yield information over the entire distribution of sizes. A micrograph of the particles that they collected showed the chain-like structure characteristic of carbon. In addition most of the particles burned up when the specimen was heated to ~500C. Thus, most of these particles were probably carbon. Their results show a peak in the size distribution near $r=0.07$ μ.

Recent measurements (Clarke and Whitby, 1967; Peterson *et al.*, 1969) of urban aerosols in Minneapolis indicate the presence of far more small particles ($r<0.1\ \mu$) than were previously believed to exist. These small particles are highly variable in number. They depend on meteorological conditions, local sources, etc. Whitby (private communication) believes that these small particles are photochemically produced liquid aerosols and are not likely to be carbon particles. However, for the sake of completeness, two models have been used for the optical calculations. In Fig. 2 these two analytical models are plotted along with the data points of Cartwright *et al.* and Peterson *et al.*

The analytical expression for Model 1 is

$$n(r)=\begin{cases}10^7, & r<0.006\ \mu\\ 400/r^2, & 0.006<r<0.05\ \mu\\ (1.6\times10^5)/r^4, & 0.05\ <r<2\ \mu\\ 0, & r>2\ \mu\end{cases}\qquad(2)$$

An upper limit of 2 μ was chosen because the Peterson data are highly variable for particles $>2\ \mu$. The small particle density was also highly variable. The value of $n(r)=10^7$ for $r<0.006\ \mu$ was chosen to provide the greatest contrast with Model 2.

Model 2 is a sum of two modified Gamma functions with different widths:

$$n(r)=5.34\times10^6(r/0.07)^{10}\exp[-5(r/0.07)^2]+6.55\times10^7(r/0.07)^2\exp[-4(r/0.07)^4].\qquad(3)$$

This represents a fit to the Cartwright *et al.* data for urban air in Sheffield, England, an industrial town.

Since these two distributions differ greatly in the number of small particles, it does not seem reasonable to normalize the distributions to the same total number of particles. Those particles which contribute most significantly to the scattering and absorbing properties at optical wavelengths are those particles with size parameter $x\gtrsim1.5$, where x is the ratio of the circumference of the particle to the wavelength, corresponding to radii of 0.07 μ. The cross sections for scattering and absorption decrease rapidly for $x<1.5$. We have therefore normalized both distributions to yield the same number of particles in this size region. Thus, we have

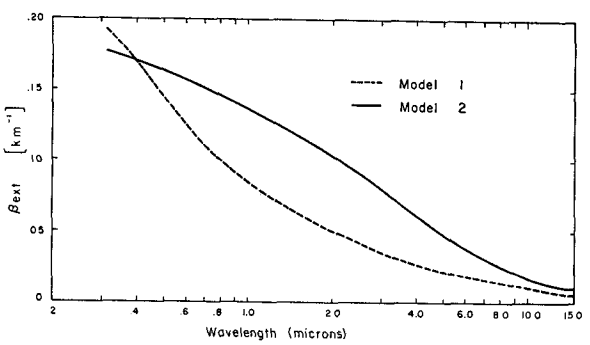

FIG. 3. Extinction coefficient, defined by Eq. (4), as a function of wavelength, for the two model polydispersions.

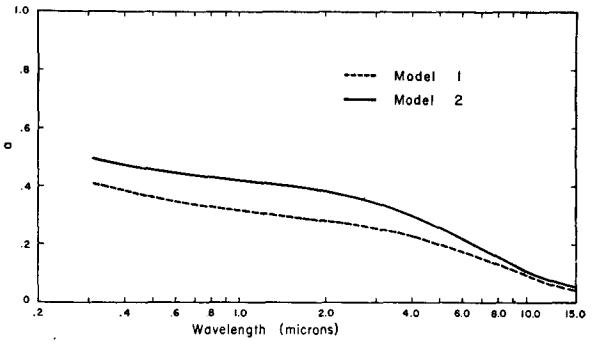

FIG. 4. Albedo for single scattering, defined in Eq. (6), as a function of wavelength, for the two model polydispersions.

set

$$\int_{0.07\mu}^{2\mu}n(r)dr=970\ \text{cm}^{-3}.$$

This is in agreement with a typical set of data as reported by Peterson *et al.*; it is also a characteristic density for a light haze.

3. Optical properties of aerosols

The Mie parameters were calculated using an adaptation for use on the UNIVAC 1108 of a program written by Dave (1968). This program yielded values of the efficiency factors, Q_{ext} and Q_{scat}, and the intensity parameters, $i_j(\theta)$, where $j=1$ and $j=2$ are scattered light intensities for linearly polarized light perpendicular to and in the scattered plane, respectively. These functions are defined in van de Hulst (1954, p. 29).

The actual parameters for a polydispersion of particles as found in the atmosphere can be obtained by numerically integrating these functions over the model size distributions. The integration method used Simpson's rule and a doubling procedure. After each iteration, the values of all integrals were checked against their previous values with half as many intervals. This was done until there was less than a 1% change in the value of any integral. This generally occurred for intervals in the size parameter of about 0.2–0.3. This is in agreement with the results developed by Dave.

The extinction coefficient was determined by

$$\beta_{ext}=\int_0^{5\mu}\pi r^2Q_{ext}(r)n(r)dr.\qquad(4)$$

Calculations for various wavelengths are plotted in Fig. 3. Similarly, the scattering coefficient was derived by

$$\beta_{scat}=\int_0^{5\mu}\pi r^2Q_{scat}(r)n(r)dr.\qquad(5)$$

It is possible to derive the albedo for single scatter

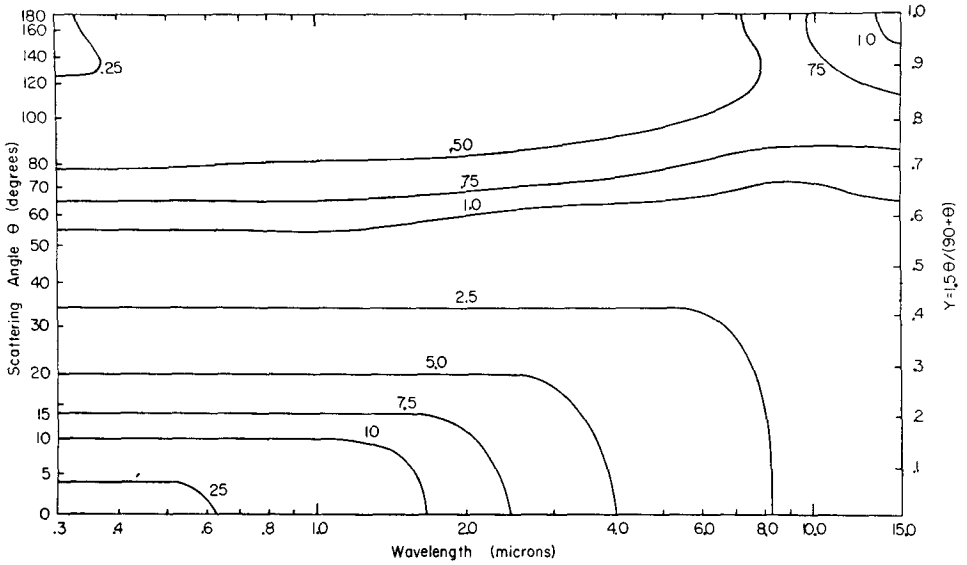

FIG. 5. Isopleths of the average phase function, $[P_1(\theta)+P_2(\theta)]/2$, as a function of scattering angle θ and wavelength for model 1. Note the nonlinear ordinate on θ which is linear in y (shown on right-hand side).

from (4) and (5), i.e.,

$$a \equiv \beta_{\text{scat}}/\beta_{\text{ext}}. \tag{6}$$

The wavelength dependence of the albedo for single scattering is shown in Fig. 4.

The phase function may be calculated by using

$$P_j(\theta) = [\lambda^2/(\pi\beta_{\text{scat}})] \int_0^{5\mu} i_j(\hat{n},\theta,r,\lambda) n(r) dr. \tag{7}$$

The values of the phase function were computed at 5° intervals and various wavelengths. Figs. 5 and 6 are isopleths of the average phase function, i.e., $(P_1+P_2)/2$. The polarization, $P(\theta)$, is defined by

$$P(\theta) = [P_2(\theta)-P_1(\theta)]/[P_2(\theta)+P_1(\theta)]. \tag{8}$$

Figs. 7 and 8 are isopleths of polarization for the two models.

The asymmetry factor is defined by

$$\langle\cos\theta\rangle = \int_0^{\pi} [P_1(\theta)+P_2(\theta)] \cos\theta d(\cos\theta)/4 \tag{9}$$

and is presented in Fig. 9 for various wavelengths.

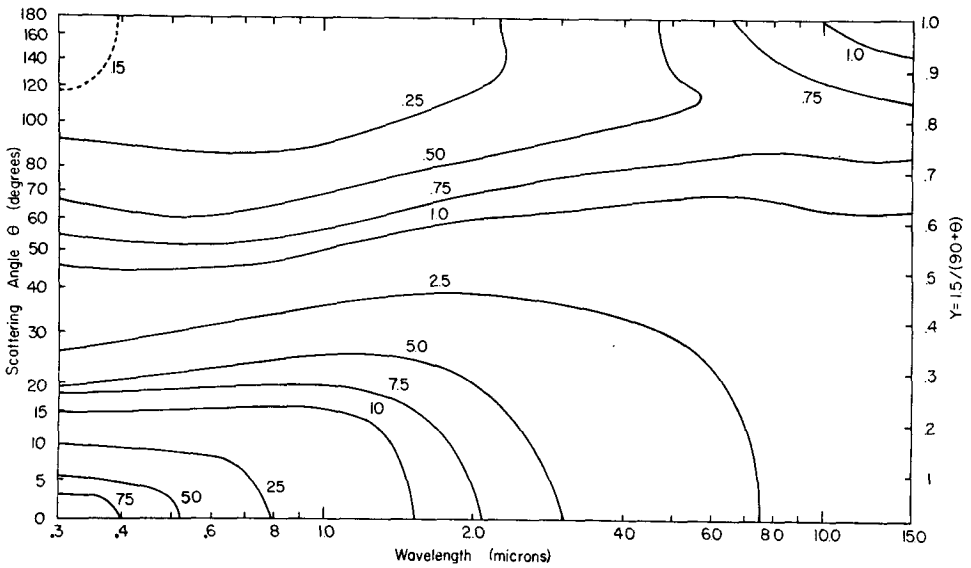

FIG. 6. Same as Fig. 5 except for model 2.

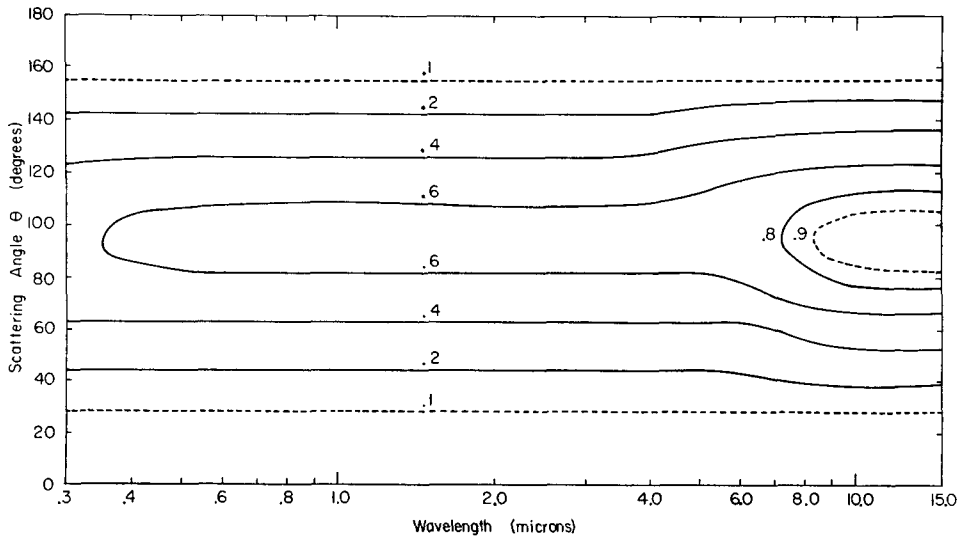

FIG. 7. Isopleths of the polarization P defined by Eq. (8), as a function of scattering angle θ and wavelength for model 1.

4. Discussion

The visual range in an atmosphere containing carbon particles represented by these two models is ~20 km. This is a light haze, as previously stated. Number densities an order of magnitude higher were reported by Peterson *et al.* during inversions in Minneapolis and the particle density measured by Cartwright *et al.* in Sheffield was 30 times higher than the density in Model 2. Thus, in such "heavy" carbon hazes the visibility would be reduced to ~1 km and the optical depth of a 1-km deep layer could be about 0.5, at infrared wavelengths in the "atmospheric windows." This optical depth is significant compared to that produced by other atmospheric constituents at these infrared wavelengths. Thus, the radiative effects of carbonaceous aerosols may be important during prolonged periods of major pollution.

We have assumed that n and k are constant for wavelengths between 0.3 and 15 μ. The only data for soot and coal beyond 10 μ are the transmission measurements of Volz (*loc. cit.*). Because they are the least accurate measurements, there remains some question regarding the values of k for soots beyond 10 μ. It has been assumed that n is constant because k is constant. Unfortunately, there are no measurements to support this assumption beyond 10 μ.

We have only considered the effect of carbonaceous aerosols upon visible and infrared radiation. It should be stressed that aerosols in polluted atmospheres have been observed to contain others constituents. Although

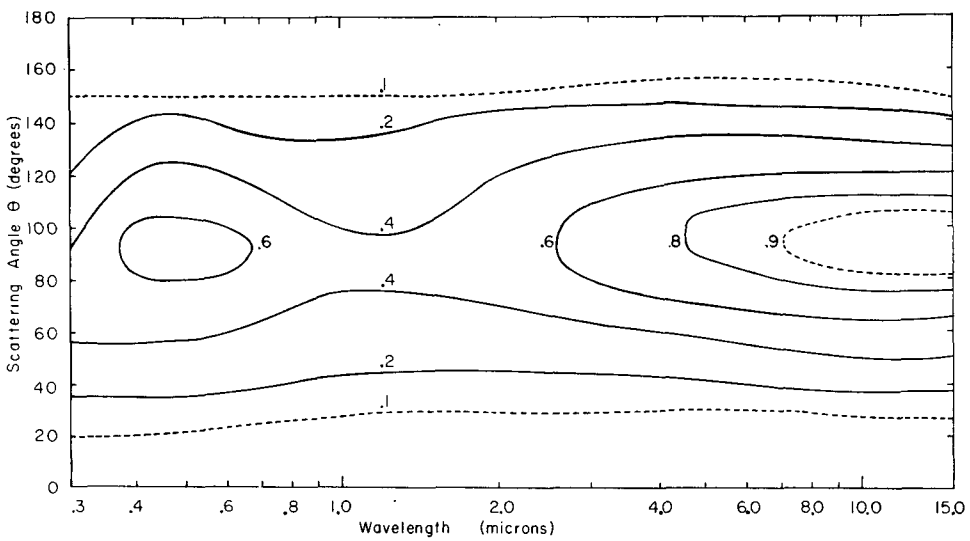

FIG. 8. Same as Fig. 7 except for model 2.

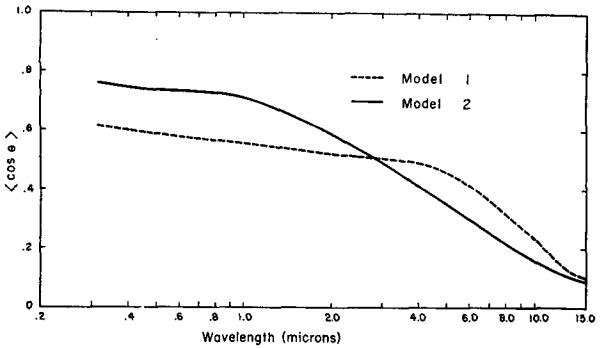

FIG. 9. Asymmetry parameter $\langle\cos\theta\rangle$ for the two model polydispersions, as defined in Eq. (9), as a function of wavelength.

carbon may be the most abundant solid constituents of pollution aerosols, hydrocarbons, iron oxides, sulfuric acid and other "dirty" water may also affect the transfer of radiation in urban atmospheres.

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