The Effect of Particle Size Distribution on Light Transmittance Measurement

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Light transmittance by clouds of small particles has long been used as a method to measure particle properties such as size or concentration. However, this application of light scattering has resulted in empirical data dependent on the specific instrument. Deviations from light extinction theory result when scattered light enters the detector, increasing the apparent transmittance. Previous studies of light extinction measurements have mainly considered error as a function of particle size with only limited analysis of polydispersed particle size distributions. The ratio of the expected extinction coefficient to the theoretical extinction coefficient is reported as a function of the log-normal size distribution parameters, geometric mass mean radius, and geometric standard deviation, for various detector acceptance angles.

Introduction

Objective

THE OBJECTIVE of this paper is the calculation of the effects of the magnitude of the detector acceptance angle on the light transmittance measured for a polydispersed cloud of small particles. The acceptance angle, Θ_a, is defined as one-half of the vertex angle of the planer projection of the cone describing the view of the detector. Experimental deviations from theoretical light extinction predictions result if scattered light in addition to the transmitted light reaches the detector, increasing the indicated light transmittance. These results should be useful in circumstances where the light transmittance of a cloud of polydispersed particle is measured with an instrument containing an arbitrarily large acceptance angle.

Previous Work

Light extinction provides a convenient method of measuring the properties of a cloud of small particles without disruptive sampling. Excellent summaries of the application of light extinction measurements to the study of aerosols have been reported by Hodkinson[1] and for colloids by Kerker.[2]

The reduction in the measured light extinction by the inclusion of scattered light has been investigated as a function of particle size. Sinclair[3] reported that the apparent light extinction cross section of a particle 15 microns in radius could be doubled by reducing the detector acceptance angle. Sinclair's results were verified by Brillouin[4] with the use of Mie theory. Walton[5] correctly attributed variations in the acceptance angle of instruments used by various investigators to account for some of the variations in reported particle properties. Walton used light diffraction theory to calculate the expected differences in the light extinction measurements as a function of particle size and the instrumental acceptance angle. Lothian and Chappel[6] calculated the expected error in light extinction measurements with the use of Rayleigh light-scattering theory, diffraction theory, and tabulated Mie theory for a wide range of particle sizes. Rose[7] compared some particle properties measured with the use of instruments of different acceptance angles. Gumprecht and Sliepcevich[8] compared Mie theory and diffraction theory calculations and obtained good agreement for large particle sizes and small acceptance angles (less than 1.4°). Experimental verification of the theoretical calculations was reported by Gumprecht and Sliepcevich with the use of glass beads and a detector acceptance angle of 0.69°. Heller and Tabibian[9] reported variations in the specific turbidity of 0.163- and 0.824-micron-diameter latex particles in aqueous suspension for various concentrations and acceptance angles. Heirwegh[10] reported the error in the measurement of the properties of macromolecular solutions as a function of the detector acceptance angle.

The effect of the detector acceptance angle on the measurement of polydisperse clouds of particles has received limited analysis. Hodkinson and Greenleaves[11] indicated how acceptance angle effects can be estimated for polydisperse particles with correction factors calculated with the use of classical optics.

Calculation of Effects

Light-Scattering Theory

Light Extinction. The attenuation of a collimated beam of light through a cloud of small particles over a path length, L, is given by the Bouger law (Lambert-Beer law):

$$\frac{I}{I_o} = \exp(-bL) \tag{1}$$

where I/I_o is the fraction of transmitted light and b is the extinction coefficient.

The extinction coefficient for spherical particles is given by

$$b = \pi \int_{r_1}^{r_2} r^2 Q_E(\alpha, m)\, n(r)\, dr \tag{2}$$

where

- α = size parameter, $2r\pi/\lambda$.
- r = particle radius.
- λ = wavelength of light.
- m = particle refractive index relative to the medium.
- $n(r)$ = number size frequency distribution, number of particles of radius r per volume per Δr.
- Q_E = particle light extinction efficiency factor.

The light extinction efficiency factor, Q_E, is the total light flux scattered and absorbed by a particle divided by the light flux incident on the particle. For pure scatterers with typical refractive indices of materials in air (1.3 to 1.6), Q_E can vary from near 0 for very small particles, to about 4 when the particle diameter is near the wavelength of light, and it approaches a theoretical limit of 2 for very large particles. Thus, large particles theoretically scatter double their projected area. This effect can be explained by considering the various mechanisms of light scattering. A spherical particle intercepts light with an area of πr^2. The particle also scátters light in a narrow forward angle by diffraction with an effective area of πr^2. Thus, the total extinction area is $2\pi r^2$.

Acceptance Angle Correction Factor. The effect of the detector acceptance angle when the instrument is applied to polydispersed clouds of particles may be described in a manner similar to that reported by Gumprecht and Sliepcevich.[8] They defined a correction factor, R, as the ratio of the actual Q_E to the theoretical Q_E for a specific size parameter. In our paper we define R for the acceptance angle correction factor for clouds of polydispersed particles as given by

$$R = \frac{b(\theta_a)}{b(O)} = 1 - \frac{\Delta b}{b} \tag{3}$$

where $b(\Theta_a)$ is the extinction coefficient for a given acceptance angle, $b(O)$ is the extinction coefficient for a zero acceptance angle (theoretical), and Δb is the difference between $b(\Theta_a)$ and $b(O)$. The correction factor, R, reduces to the same ratio as defined by Gumprecht and Sliepcevich for monodisperse particles. The Δb is given by

$$\Delta b = \pi \int_{r_1}^{r_2} \Delta Q\, r^2\, n(r)\, dr \tag{4}$$

where ΔQ is the reduction in the efficiency factor caused by the measurement of scattered light.

Reduction in Light Extinction Efficiency Factor. The reduction in the light extinction efficiency factor, ΔQ, from scattered light entering the detector is a function of the detector acceptance angle, the size parameter, and the particle refractive index. Calculation of ΔQ requires an integration of the angular intensity of scattered light over the acceptance angle. There are three general size parameter ranges of interest: Rayleigh scattering ($0 < \alpha < 0.1$), an intermediate region described by the general Mie scattering theory, and large particles ($\alpha > 5$) which can be approximated by means of classical optics.

The scattered light intensity per solid angle for a Rayleigh scatterer is proportional to $1 + \cos^2 \Theta$, where Θ is the angle with respect to the plane of the incident light beam. Lothian and Chappel[6] reported the correction factor for a monodisperse Rayleigh scatter as a function of the acceptance angle as given by

$$R = \frac{1}{8}(3\cos\theta_0 + \cos^3\theta_0 + 4) \quad (5)$$

Correction factors evaluated with equation 5 are presented in Table I.

Thus, for Rayleigh scattering particles the magnitude of the acceptance angle has very little effect on the observed extinction coefficient.

For intermediate-sized particles, the angular light-scattering intensity, described by Mie theory, is a complex function of the angle Θ, the size parameter α, and the particle refractive index. The number of oscillations of the angular light intensities is proportional to the size parameter. The reduction in the light extinction efficiency factor from the collection of scattered light from spherical particles in unpolarized light is given by

$$\Delta Q = \frac{1}{\alpha^2}\int_0^{\theta_0} \left[i_1(\theta,\alpha,m) + i_2(\theta,\alpha,m)\right] \sin\theta \, d\theta \quad (6)$$

where

$i_1(\Theta,\alpha,m)$ = scattered light intensity polarized perpendicular to the plane of scattering.

$i_2(\Theta,\alpha,m)$ = scattered light intensity polarized parallel to the plane of scattering.

The angular intensities can be computed with Legendre polynomals and Riccati-Bessel functions as described by van de Hulst.[12]

With large particles a major portion of the light scattered by a particle is directed in the forward direction. Unfortunately, the Mie equations become time-consuming to evaluate (even with a computer) for large magnitudes of the size parameter. However, except for the glory (color rings and increased light intensity at the edge of a shadow projected on clouds or fog) and rainbows caused by internal light reflections with certain sized transparent particles, the intensity of scattered light can be approximated with classical optics. Hodkinson and Greenleaves[11] and Ellison and Peetz[13] reported the use of approximations for the lobe of forward-scattered light with diffraction, reflection through the particle, and external reflection on the particle. Agreement of these approximations to the angular scattered-light intensity calculated with Mie theory, averaged over a small range of particle sizes, was reported to be within at least $\pm 20\%$. The approximations are limited to forward-scattering angles (less than 40° for a refractive index of 1.50) and to refractive indices from 1.1 to about 2.0. The detector is assumed to measure the scattered light a relatively large distance from the particle compared to the particle size. The reduction in the efficiency factor is given by

$$\Delta Q = \Delta Q_{DIFFRACTION} + \Delta Q_{REFRACTION} + \Delta Q_{REFLECTION} \quad (7)$$

Each term in equation 7 is computed with an integration analogous to equation 6 with angular light intensities for various light-scattering mechanisms calculated with the equations reported by Hodkinson and Greenleaves. The changes in phase of the reflected and refracted light waves may be neglected if a small spread of particle sizes is assumed in equation 7. The reduction in the light extinction efficiency factor by reflection and refraction is a function of particle refractive index and the acceptance angle. Diffraction is a function of acceptance angle and particle size.

Most of the scattered light measured by the detector can be attributed to diffraction for large particles and small acceptance angles

TABLE I

Correction Factor, *R*, for a Rayleigh Scatterer

Acceptance angle, θ_a	0.1°	1.0°	10°	20°
Correction factor, *R*	1.000	0.999	0.989	0.96

($\Theta_a < 1.3°$ and $r > 3$ microns in visible light). Under these circumstances ΔQ diffraction approaches 1.0, resulting in an apparent efficiency factor, Q_E, of about 1 for interception effects. The magnitude of R for large particles will be about ½.

Particle Size Distribution

The log-normal particle size distribution model can be used to describe a wide variety of polydispersed particulate materials such as those resulting from comminution of solids and spraying of liquids. Herdan[14] reported a detailed description of the log-normal distribution and its application to characterizing small particles. The log-normal number size frequency distribution is given by

$$n(r) = \frac{N}{r\sqrt{2\pi}\,\ln\sigma_g}\exp-\left[\frac{\ln^2(r/r_{gn})}{2\ln^2\sigma_g}\right] \quad (8)$$

where $n(r)$ is the number frequency of particles of radius r per volume per Δr, N is the total number of particles of all sizes per unit volume, r_{gn} is the geometric number mean radius, and σ_g is the geometric standard deviation, a measure of the polydispersity or breadth of the particle size distribution. When $n(r)$ is multiplied by the radius increment, Δr, the number of particles of radius r between r and $r + dr$ is given. Log-normal distributions of particle number, area, and volume are mathematically related. The geometric standard deviation remains the same for these distributions. The relationship between geometric number, r_{gn}, and mass mean radii, r_{gw}, is

$$\ln r_{gn} = \ln r_{gw} - 3\ln^2\sigma_g \quad (9)$$

Size distribution data can be reduced graphically by plotting "smaller than" cumulative size frequency versus size on logarithmic probability paper; r_{gw}, for mass distribution data, is the radius at the 50% size, and σ_g is given by

$$\sigma_g = \frac{84.13\%\ \mathrm{SIZE}}{50\%\ \mathrm{SIZE}} = \frac{50\%\ \mathrm{SIZE}}{15.87\%\ \mathrm{SIZE}}$$

Computer Program

A computer program was developed using Fortran IV language for a CDC 6400 computer to calculate the correction factor, R, as a function of the log-normal distribution parameters and acceptance angle. Equations 2 and 4 were used to calculate b and Δb, respectively. Equation 6 was used to compute ΔQ for size parameters less than 25. Forward recursion equations reported by Abramowitz and Stegun[15] were used to calculate higher-order terms of the Riccati-Bessel functions and Legendre polynomials to calculate i_1, i_2, and Q_E. The angular intensity results were in agreement with those reported by Denman *et al.*,[16] and the Q_E results agreed with Penndorf.[17] For size parameters greater than 25 the classical optic approximations were used to calculate ΔQ with Q_E assigned the value of 2. The number size frequency, $n(r)$, was computed with equation 8, and equation 9 was used to convert from the geometric mass mean radius, r_{gw}, to the geometric number mean radius, r_{gn}.

The Romberg integration method described by Wilf[18] was used to integrate equation 6 over the acceptance angle and equations 2 and 4 over the range of particle size. This algorithm is useful because it iterated to a desired tolerance (within 5% in our case), resulting in an increment size compatible with the function being integrated.

A wide range of radius integration limits was used (10^{-3} to 10^4 microns) to prevent truncation losses. However, only small increments of this size range were integrated at one time (usually less than a decade), and these sections were summed for the total integral. An additional check for numerical truncation losses was performed by evaluating

$$\int_{r_1}^{r_2} f(r)\,dr = F$$

where $f(r)$ is the normalized fractional particle radius distribution of radius r per volume per Δr. Agreement of the integration to the theoretical result of $F = 1.0$ was always within ±5%.

Discussion of Results

The correction factor, R, is presented as a function of the mass mean radius, r_{gw} (1 to

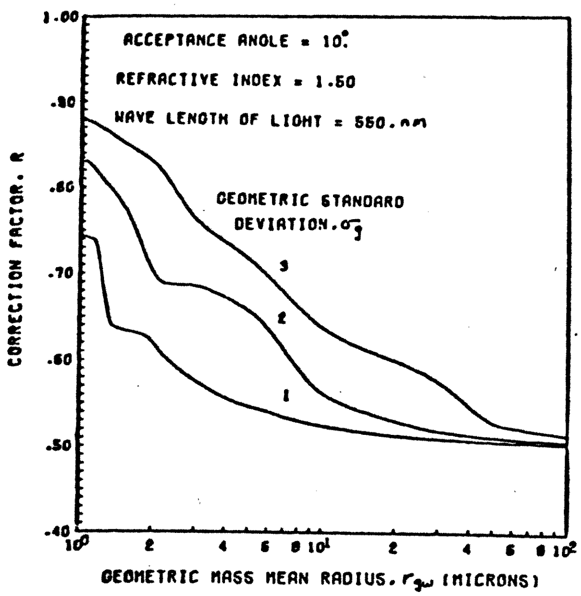

Figure 1. Correction factor, R, as a function of the log-normal size distribution parameters for an acceptance angle of 10°.

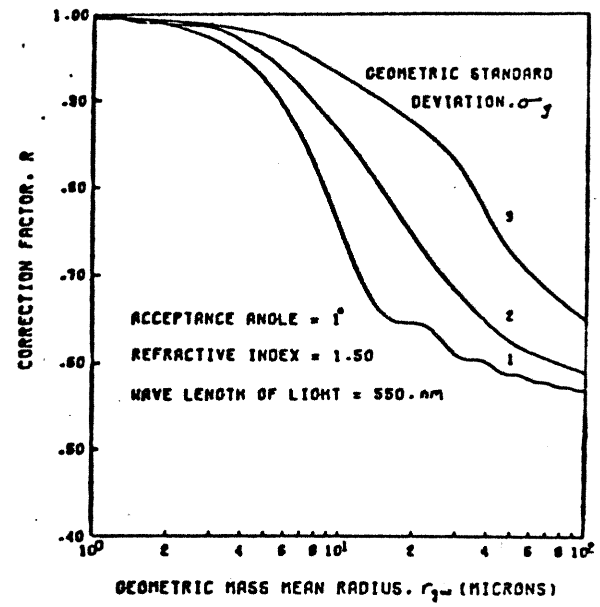

Figure 2. Correction factor, R, as a function of the log-normal size distribution parameters for an acceptance angle of 1°.

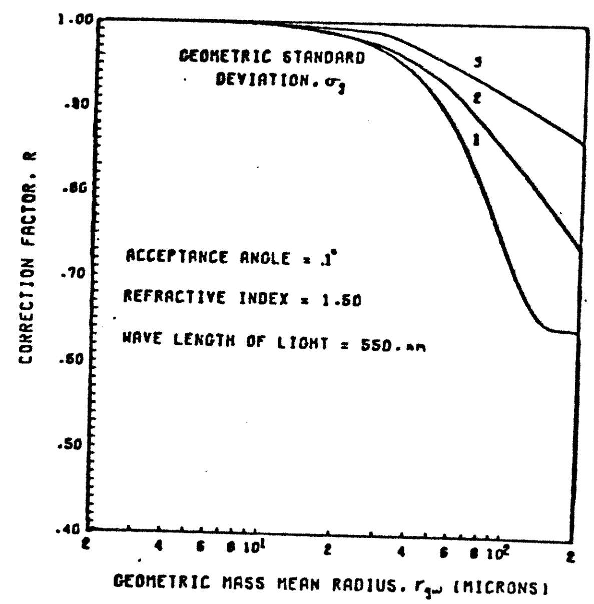

Figure 3. Correction factor, R, as a function of the log-normal size distribution parameters for an acceptance angle of 0.1°.

100 microns), with the geometric standard deviation, σ_g ($\sim$1 to 3) in Figures 1, 2, and 3 for acceptance angles of 10°, 1°, and 0.1°, respectively. The particle refraction index and the incident wavelength of light were kept constant at 1.50 and 550 nm, respectively.

The "monodispersed" ($\sigma_g = \sim 1$) results are for distributions close to being monodispersed but have enough particle size spread to allow smoothing of the Mie calculations and consistency with Hodkinson and Greenleaves's approximations. Wallace and Kratohvil[19] reported experimental evidence that even the small amounts of polydispersity existing in "monodispersed" polystyrene particle clouds produce important data smoothing.

The particle size and the detector acceptance angle are the most significant variables affecting R. This is probably due to the dominance of the light diffraction in the forward-scattering angles.

The correction factor, R, for very polydisperse particle size distributions is a weighted average (with $n(r)$) of the "monodispersed" results. Increased polydispersity increases the effect of the small particles which have correction factors near 1 for a given angle, as seen in Table I. Thus, the correction factor, R, approaches unity with increasing polydispersity for a given particle size and acceptance angle. Polydisperity has a second-order effect on the correction factor.

Conclusions

1. The particle radius and the magnitude of the detector acceptance angle have first-order effects on the correction factor, R.

2. The polydispersity of the particle cloud has a second-order effect on the correction factor, R.

Nomenclature

b	Extinction coefficient
$b(\Theta_a)$	Apparent extinction factor for a given acceptance angle
Δb	Difference between the theoretical extinction coefficient and the expected extinction coefficient for a given acceptance angle
$f(r)$	Fractional number radius distribution when multiplied by dr gives the fraction of particles of size r between r and $r + dr$
F	Value of the integral $\int_{r_1}^{r_2} f(r)$ determined by numerical methods
I	Flux of transmitted light
I/I_0	Transmittance
$i_1(\Theta,\alpha,m)$	Scattered light intensity polarized perpendicular to the plane of scattering
$i_2(\Theta,\alpha,m)$	Scattered light intensity polarized parallel to the plane of scattering
L	Illumination path length
m	Particle refractive index
N	Total number of particles per unit volume
$n(r)$	Number size frequency distribution
R	Acceptance angle correction factor
r	Particle radius
r_{gn}	Geometric number mean radius
r_{gw}	Geometric mass mean radius
$Q_E(\alpha,m)$	Light extinction efficiency factor
ΔQ	Reduction in the light extinction efficiency factor by the measurement of scattered light

Greek

α	Size parameter, $2\pi r/\lambda$
Θ	Angle of scattered light relative to the direction of the incident light
Θ_a	Acceptance angle of the detector, one-half of the vertex angle of the planer projection of the cone describing the view of the detector
λ	Wavelength of light
π	3.14159
σ_g	Geometric standard deviation

Acknowledgments

The research was supported in part by Air Pollution Training Grant AP 00029-05 and Air Pollution special Fellowship 1 F3 AP 45,523-01 from the United States Public Health Service National Air Pollution Control Administration. The discussions with Steinar Larssen and Leslie E. Sparks are gratefully acknowledged.

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Received July 16, 1970