BNL-66602-99/12-Rev.

THE EFFECT OF REFRACTIVE INDEX ON SIZE DISTRIBUTIONS AND LIGHT SCATTERING COEFFICIENTS DERIVED FROM OPTICAL PARTICLE COUNTERS

Yangang Liu* and Peter H. Daum
Brookhaven National Laboratory
Department of Applied Science
Environmental Chemistry Division
Upton, NY 11973-5000

Original Manuscript Date: May 1999

Published in
Journal of Aerosol Science

*Corresponding Author

Research by BNL investigators was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

Pergamon

PII: S0021-8502(99)00573-X

J. Aerosol Sci. Vol. 31, No. 8, pp. 945–957, 2000
Published by Elsevier Science Ltd
Printed in Great Britain
0021-8502/00/$ - see front matter

www.elsevier.com/locate/jaerosci

THE EFFECT OF REFRACTIVE INDEX ON SIZE DISTRIBUTIONS AND LIGHT SCATTERING COEFFICIENTS DERIVED FROM OPTICAL PARTICLE COUNTERS*

Yangang Liu† and Peter H. Daum

Brookhaven National Laboratory, Environmental Chemistry Division, Bldg. 815E, P.O. Box 5000, Upton, NY 11973-5000, USA

(*First received* 7 *June* 1999; *and in final form* 18 *November* 1999)

Abstract—The effect of refractive index on particle size distributions measured by optical particle counters is examined. Similar to previous investigations, it is found that optical counters undersize ambient particles because the refractive index of these particles is generally lower than that of the latex particles commonly used for the calibration of optical counters. The maximum undersizing is found to occur when particle sizes are comparable to the wavelength of light used in the measurement. A new approach for modeling the effect of refractive index on the sizing of optical counters is presented. Previously derived optical response functions are compared and a generalized formulation is proposed which includes the existing response functions as special cases. Algorithms are presented for correcting size distributions measured by optical counters for the difference between the refractive index of ambient and calibration particles. Data collected by a Passive Cavity Aerosol Spectrometer (PCASP) and by an integrating nephelometer are compared. Light scattering coefficients calculated from the optical probe data uncorrected for the effect of refractive index differ from those measured by the integrating nephelometer by a factor of 2. An iterative procedure that adjusts the PCASP-measured size distribution for the effect of refractive index is used to derive the best agreement between calculated and observed light scattering coefficients. The refractive indices of aerosols at wavelength of 0.45 μm that best fit the data vary between 1.3 and 1.5, with an average of 1.41. The relative importance of the underestimation of light scattering coefficients calculated from the PCASP-measured size distributions due to the refractive index and the size truncation effect are evaluated. The former is found to be more important than the latter. Implications of this study for addressing aerosol shortwave radiative forcing and potential uncertainties relevant to this study are discussed. Published by Elsevier Science Ltd

1. INTRODUCTION

Light scattering coefficients can be measured directly with an integrating nephelometer (Heintzenberg and Charlson, 1996). They can also be calculated by applying Mie theory to known aerosol size distributions measured by an optical particle counter (OPC) such as the Passive Cavity Aerosol Spectrometer (PCASP) (Particle Measuring System, Inc., Boulder, CO). A number of studies have compared the two methods in the so-called closure experiments and good correlations have been reported (Ensor *et al.*, 1972; Hegg *et al.*, 1996; Anderson *et al.*, 1996; Quinn *et al.*, 1996). However, light scattering coefficients calculated from size distributions measured by OPCs have been found to be systematically lower than those measured with nephelometers. For this reason the credibility of OPCs for calculation of light scattering coefficients has been questioned (Wilson *et al.*, 1988; Eldering *et al.*, 1994; Hegg *et al.*, 1996).

OPCs are often calibrated with latex particles having a refractive index (m) of 1.588. Because refractive indices of real aerosols are often less, diameters measured by OPCs will be smaller than the real ones. This underestimation of particle size will in turn cause the calculated light scattering coefficients to be low. Recent studies using ambient particles shows that such undersizing is a function of particle size and reaches a maximum in the

* By acceptance of this article, the publisher and/or recipient acknowledges the U.S. government's right to retain a non-exclusive, royalty-free license in and to any copyright covering this paper. This research was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.
† Author to whom correspondence should be addressed.

region where particle sizes are comparable to the wavelength of the light (e.g., 0.628 μm) used for the measurement (Covert *et al.*, 1990; Hering and McMurry, 1991; Stolzenburg *et al.*, 1998). The occurrence of maximum undersizing in this region should be emphasized because particles of this diameter are also the most efficient at scattering shortwave solar radiation (Waggoner *et al.*, 1981; Schwartz, 1996). The first objective of this paper is to develop a theoretical approach for correcting particle size distributions measured by OPCs for the effect of the difference between the refractive index of particles used in the calibration of the counter and that of ambient aerosols, with focus on the PCASP.

Our second objective is to show that light scattering coefficients calculated by applying Mie theory to PCASP-measured size distributions can be reconciled with the nephelometer measurements by taking into account the difference between the refractive index of the calibration and ambient particles. Furthermore, we demonstrate that refractive indices of atmospheric aerosols can be estimated by matching the nephelometer measured-light scattering coefficients with those calculated from the PCASP-measured size distributions if particle sizes are corrected for refractive index by use of our new approach. The approach is applied to the analysis of data collected during a recent Intensive Observation Period (IOP) over the Southern Great Plains (SGP) Atmospheric Radiation Measurement (ARM) site in the spring of 1997 (1997-Spring IOP hereafter).

Our third objective is to compare the refractive index effect with the size truncation effect arising from the limited size range (nominally between 0.10 and 3.2 μm diameter) over which the PCASP measures particles. This effect has been cited as a reason for the underestimation of light scattering coefficients calculated from particle size distributions measured with an optical particle counter (Hegg *et al.*, 1996). To the best of our knowledge, however, no studies have quantitatively compared the relative importance of these two sources of error.

The paper is organized as follows. Theoretical models of the PCASP optical response are discussed in Section 2. The effect of refractive index is investigated, and a simple model is developed to correct the measured size distributions for the effect of the difference between the refractive index of ambient and calibration particles. A generalized response function is proposed to describe the optical response of the PCASP. Section 3 applies the model to a local closure experiment conducted during the 1997-Spring IOP. Refractive indices of ambient aerosols are estimated. In Section 4, the size truncation effect is compared with the refractive index effect. Major conclusions and implications of this study are outlined in Section 5.

2. A NEW THEORETICAL APPROACH FOR SIZE CORRECTION

2.1. *Theoretical models for response functions*

A key to accounting for the effect of refractive index on the sizing of the PCASP is modeling its optical response which, for this instrument, is complicated by the use of standing wave technology. Two theoretical formulations have been proposed. Pinnick and Auvermann (1979) expressed the response function as

$$R_1(D,m) = \frac{\pi}{k^2}\int_{\theta_1}^{\theta_2} [|S_1(D,m,\theta) + S_1(D,m,\pi-\theta)|^2 + |S_2(D,m,\theta) + S_2(D,m,\pi-\theta)|^2] \sin\theta \, d\theta, \quad (1)$$

where D represents the particle diameter; θ is the scattering angle, with $\theta_1 = 35^\circ$ and $\theta_2 = 120^\circ$ for the PCASP; $\kappa = 2\pi/\lambda$ is the wave number (λ is the wavelength), and $S_1(.)$ and $S_2(.)$ are the complex scattering amplitude functions corresponding to light polarized with electric field perpendicular and parallel to the scattering plane respectively. Garvey and Pinnick (1983) proposed a slightly different expression that adds the scattering intensities instead of the scattering amplitudes:

$$R_2(D,m) = \frac{\pi}{k^2}\int_{\theta_1}^{\theta_2} [|S_1(D,m,\theta)|^2 + |S_1(D,m,\pi-\theta)|^2 + |S_2(D,m,\theta)|^2 + |S_2(D,m,\pi-\theta)|^2]\sin\theta\,\mathrm{d}\theta, \quad (2)$$

They designated R_1 as the summed-amplitude response (hereafter SAR) and R_2 as the summed-field response (hereafter SFR).

The only comparison of these two response functions with experimental results was made by Garvey and Pinnick (1983), who concluded that "the experimental errors were sufficiently large that both SAR and SFR can be fit to the data equally well". In this paper, instead of comparing the response functions directly, we compare the performance of SAR and SFR by comparing the ratio of the apparent diameter measured by an OPC to the real diameter (diameter ratio hereafter) as a function of apparent diameter so that the effects of unknown uncertainties associated with the instrumentation is minimized.

It is well known that the response functions given above are multivalued. Usually a smoothing algorithm is used to overcome this problem (Kim and Boatman, 1990). Here we fit the response functions to polynomials over the range of refractive indices of atmospheric aerosols (m = 1.588, 1.5, 1.45, 1.4, and 1.3), and find that a polynomial of order 8 gives a good fit:

$$D = \sum_{i=0}^{8} c_i R^i, \quad (3)$$

where c_i is the fitting coefficient. The diameter is expressed as a function of the response so that the diameter correction can be conveniently made. With the polynomials for different refractive indices as described by equation (3), the diameter ratio is readily calculated given the optical responses. Note that in our calculations throughout this paper the prefactor (π/κ^2) is neglected because it does not affect the calculated diameter ratios.

2.2. *Effect of refractive index*

Tables 1 and 2 list the fitting coefficients and correlation coefficients at different refractive indices for the SAR and SFR formulations, respectively. The diameter ratio calculated by use of these polynomials is shown in Figs 1 and 2 for SAR and SFR, respectively, as a function of apparent diameter. The values (crosses) of the diameter ratio for ambient aerosols reported by Stolzenburg *et al.* (1998) are also shown for comparison. It can be seen that the measured values fall within our model results over the range of refractive indices expected for ambient aerosols, and that a minimum in the diameter ratio occurs near the resonance size range. Stolzenburg *et al.* (1998) found an effective refractive index of

Table 1. Coefficients of fitting polynomials for summed-amplitude response function

M	1.588	1.5	1.4	1.3
C_0	1.1128e − 1	1.2627e − 1	1.5660e − 1	1.4918e − 1
C_1	1.0249e − 3	9.0409e − 4	6.6678e − 4	1.6359e − 3
C_2	− 1.2132e − 6	− 7.8478e − 7	2.8696e − 7	− 1.4638e − 6
C_3	8.1732e − 10	4.7729e − 10	− 5.6142e − 10	9.3605e − 10
C_4	− 2.7645e − 13	− 1.5836e − 13	2.7784e − 13	− 3.8678e − 13
C_5	5.1425e − 17	3.0351e − 17	− 6.4849e − 17	9.9916e − 17
C_6	− 5.3699e − 21	− 3.3887e − 21	7.9082e − 21	− 1.5316e − 20
C_7	2.9503e − 25	2.0429e − 25	− 4.8727e − 25	1.2631e − 24
C_8	− 6.6316e − 30	− 5.1179e − 30	1.1987e − 29	− 4.3004e − 29
R*	0.939	0.948	0.981	0.995

* R represents the correlation coefficient of the fitting.

Table 2. Coefficients of fitting polynomials for summed-field response function

m	1.588	1.5	1.4	1.3
C_0	1.3813e − 1	1.4510e − 1	1.6042e − 1	1.7193e − 1
C_1	1.1847e − 3	1.3033e − 3	1.3802e − 3	1.9822e − 3
C_2	− 2.0440e − 6	− 2.0506e − 6	− 1.7220e − 6	− 2.9230e − 6
C_3	2.2126e − 9	2.0404e − 9	1.5101e − 9	3.2284e − 9
C_4	− 1.2806e − 12	− 1.0829e − 12	− 7.4151e − 13	− 2.0825e − 12
C_5	4.1431e − 16	3.1879e − 16	2.0463e − 16	7.6699e − 16
C_6	− 7.4677e − 20	− 5.2222e − 20	− 3.1533e − 20	− 1.5929e − 19
C_7	6.9909e − 24	4.4591e − 24	2.5332e − 24	1.7391e − 23
C_8	− 2.6467e − 28	− 1.5490e − 28	− 8.2689e − 29	− 7.7732e − 28
R*	0.987	0.995	0.998	0.999

* R represents the correlation coefficient of the fitting.

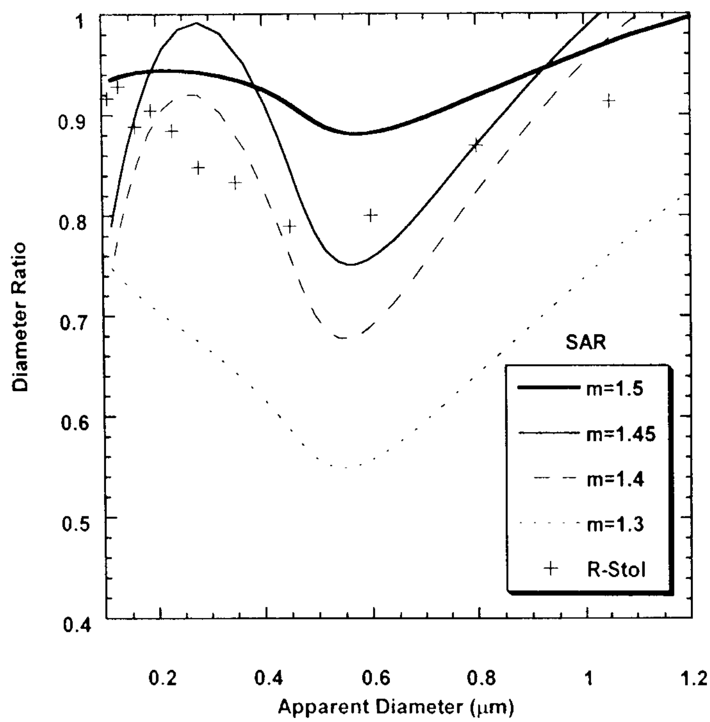

Fig. 1. Diameter ratio as a function of the apparent diameter measured with the PCASP when the SAF formulation for the optical response is used. The crosses are measurements from Stolzenburg *et al.* (1998).

1.45 ± 0.03 for the ambient aerosol particles by matching the response of an optical counter to size-selected ambient particles under the assumption that absorption may be neglected and that the particle size does not change as a result of heating. It is interesting to note that our model results are consistent with their measurements of diameter ratios when $m = 1.45$ is used. This suggests that refractive index may be estimated by matching diameter ratio measurements with our model results. A further examination of both figures reveals that the SFR formulation models the overall trend better than the SAR formulation (SAR gives peaks at small particle sizes that are contrary to observations), whereas SAR-modeled diameter ratios are closer to the measured minimum near the resonance diameter region.

That the SFR formulation represents the trend better than the SAR formulation is surprising because the latter is believed to be more physically based than the former for modeling the response of optical counters (Garvey and Pinnick, 1983). However, the

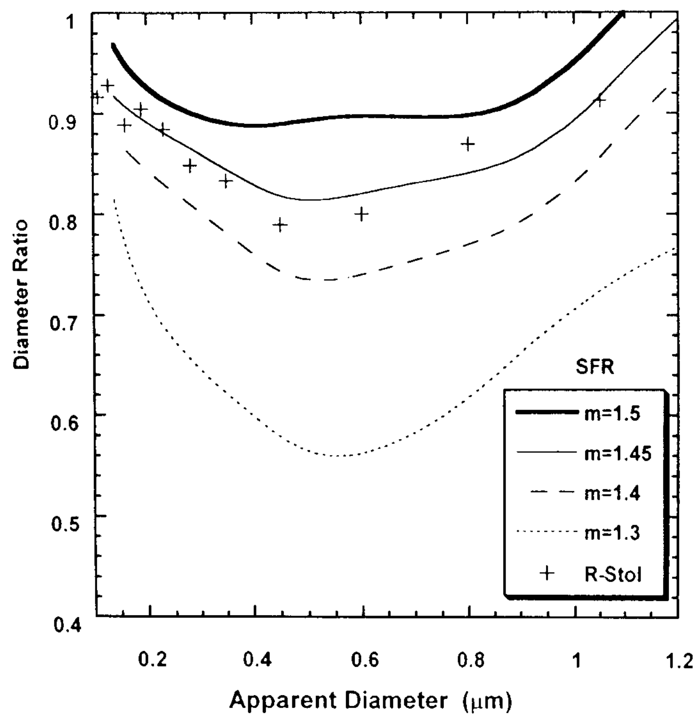

Fig. 2. Same as Fig. 1, except for the SFR formulation.

justification for use of the SAR formulation is based on Mie theory as applied to an ideal instrumental configuration which does not hold in practice. A real probe of this type cannot resolve the details of the resonance structure of the exact theoretical response, and smoothing is required to dampen the fluctuations of the response functions. Furthermore, large fluctuations in the SAR response function, make it more difficult to smooth the response. This is indicated by the correlation coefficients given in Tables 1 and 2: the correlation coefficients for SAR are always lower than those for the SFR formulation. This point is also illustrated in Fig. 3. where it can be noted that while the SFR and SAR formulations give responses that exhibit the same general trend, the SFR response is much smoother.

The better performance of SFR relative to SAR can also be argued from a physical perspective. Further examination of equations (1) and (2) reveals that SAR can be expressed as a sum of SFR and a term ΔR:

$$R_1 = R_2 + \Delta R, \tag{4a}$$

$$\Delta R = 2\int [a_1(\theta)a(\pi - \theta) + b_1(\theta)b_1(\pi - \theta) + a_2(\theta)a_2(\pi - \theta) + b_2(\theta)b_2(\pi - \theta)] \sin\theta \, d\theta, \tag{4b}$$

where a and b represent the real and imaginary part of the scattering amplitude function (Van de Hulst, 1980). The term ΔR actually describes the contribution to the response associated with light interference. As demonstrated in Fig. 4, this term is highly fluctuating and small in magnitude compared to SFR. The interference may exist for the ideal case; but it will be dampened (even eliminated) in practical instrumentation. Schuster and Knollenberg (1972) pointed out that the interferometric behavior of the laser cavity tends to suppress the normal Mie resonance. The other difficulty rests with the detection of phase differences in the scattering of standing-laser waves (Arnott, 1998, private communication).

Although the results somehow support the use of the SFR formulation, the SAR formulation cannot be completely ruled out. A specific response may as well fall between

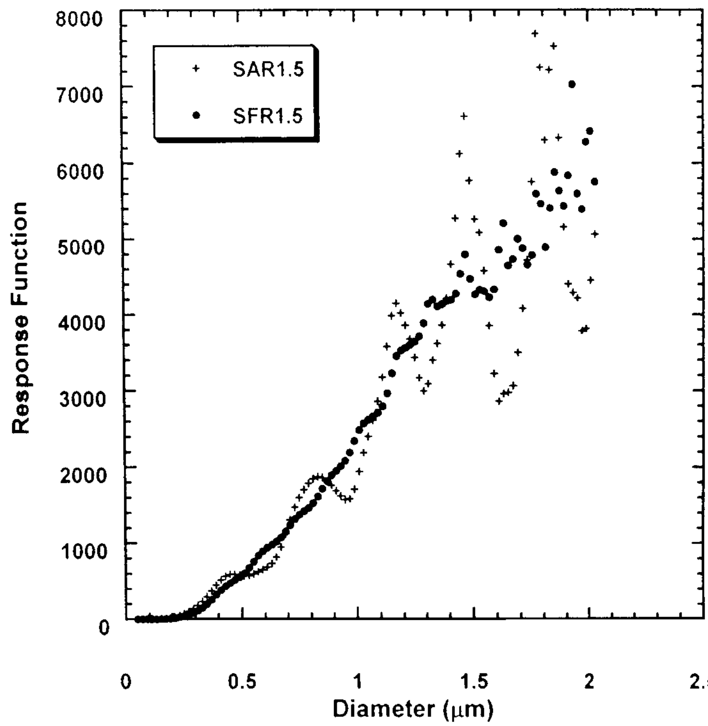

Fig. 3. Optical responses as a function of particle diameter for both SAR (crosses) and SFR (filled dots) formulation. Refractive index $m = 1.5$ is used in the calculations.

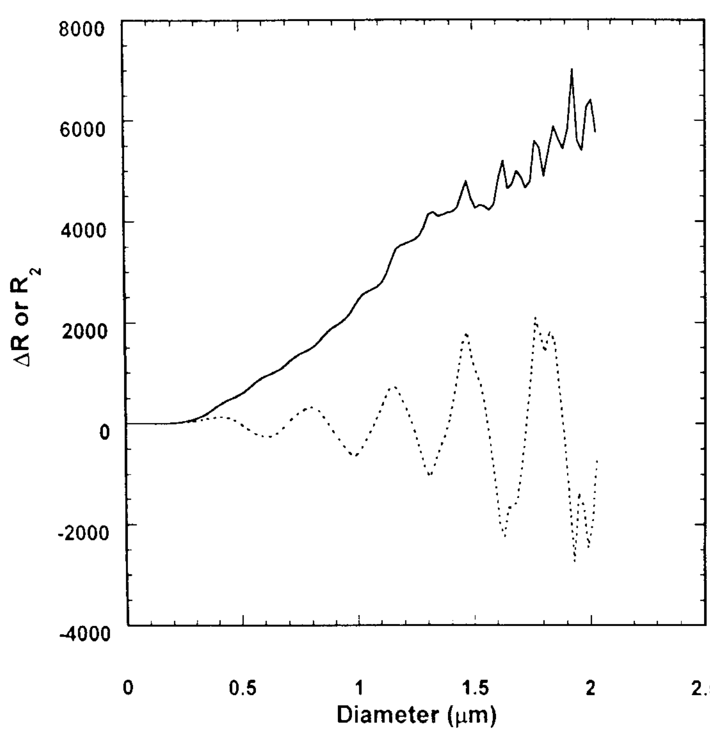

Fig. 4. Comparison of the term ΔR (dotted curve) against the SFR response (solid curve), showing that the ΔR term fluctuates around zero, with absolute values much smaller than the SFR response.

the two extremes. The complexity of non-ideal conditions even prevents the manufacture (PMS) from providing a robust theoretical response function for the probe of this type (PMS PCASP-100X Operating Manual). Based on the relationship between the SAR and SFR formulation as described by equation (4), the optical response of a specific probe be expressed as

$$R = R_2 + \alpha \Delta R, \tag{5}$$

where α is an empirical "constant" ranging from 1 to 0. Evidently, this new formulation includes the existing expressions as extreme cases. The SAR formulation corresponds to $\alpha = 1$ and SFR to $\alpha = 0$. This generalized formulation may provide an approach for characterizing response of a specific probe by empirically determining the value of α.

3. ESTIMATION OF THE REFRACTIVE INDEX AND LOCAL CLOSURE OF LIGHT SCATTERING COEFFICIENTS

A number of studies have been made to compare nephelometer-measured light scattering coefficients with those calculated from given size distributions. A common result of such studies is that calculated light scattering coefficients are systematically lower than nephelometer measurements if size distributions measured by OPCs are used (e.g. Ensor *et al.*, 1972; Hegg *et al.*, 1996) whereas there is no such underestimation if scattering coefficients are calculated from size distributions measured by non-optical counters (e.g. Quinn *et al.*, 1995; Anderson *et al.*, 1996). Efforts have been made to account for the effect of refractive index associated with OPCs. In a laboratory experiment, Wilson *et al.* (1988) compared light scattering coefficients of aerosols of known composition measured with a nephelometer to those calculated from size distributions measured by an OPC and an electrical aerosol analyzer. They showed that after correcting the OPC data for refractive index, calculated light scattering coefficients were closer to those measured by the nephelometer. Eldering *et al.* (1994) considered the refractive index effect according to the diameter ratio measurements made by Hering and McMurry (1991). Stolzenburg *et al.* (1998) measured the diameter ratio by combining an OPC with a differential mobility analyzer. They demonstrated that the agreement between light scattering coefficients measured by a nephelometer and those calculated from the OPC data was improved when the OPC data was corrected for the refractive index effect by use of the diameter ratio measurements. Although these studies have demonstrated the importance of the refractive index effect, their usefulness is limited because diameter ratio measurements are often not available, and the refractive index can vary greatly with time and location.

In this section we examine the nephelometer and PCASP data collected during 1997-Spring IOP. The objective of this analysis is to demonstrate a new approach for accounting for the difference between the refractive index of the particles used to calibrate the PCASP probe, and ambient aerosols. The data were collected using the DOE Gulfstream-1 aircraft equipped with sensors for measuring temperature, pressure, humidity, solar radiation, and aerosol and cloud properties, including a PCASP and an integrating nephelometer. A Science Engineering Associates (SEA) Model 200 data acquisition system was used to collect data at a rate of 1 Hz. The aircraft flew a total of 15 missions that covered a variety of weather conditions. Typically, the aircraft conducted a step profile from about 100 m above the surface to an altitude of approximately 5 km. Only four flights in which the relative humidities were always less than 75% were analyzed to minimize the different "drying" effects of the integrating nephelometer and the PCASP. To alleviate the problem caused by differences in response times and sampling volumes between the nephelometer and the PCASP, we performed the calculations with 100 m-averaged data containing at least 50 data points. A total of 30 datasets from the four flights satisfied the criteria outlined above.

The procedure that we used to analyze the data is as follows. First we adjusted the PCASP-measured size distributions for refractive indices $m = 1.3$, 1.4, 1.45, 1.5, 1.588 (this represents the range of refractive indices expected for ambient aerosols). This is discussed in Section 2, and corrected diameters are summarized in Table 3. Then for each of these

Table 3. Corrected diameters (μm) at different refractive indices*

Apparent D	D ($m = 1.5$)	D ($m = 1.45$)	D ($m = 1.4$)	D ($m = 1.3$)
0.11	0.11	0.12	0.12	0.13
0.13	0.14	0.14	0.15	0.16
0.16	0.17	0.18	0.18	0.20
0.19	0.20	0.21	0.22	0.25
0.23	0.25	0.26	0.28	0.34
0.28	0.31	0.32	0.35	0.43
0.35	0.39	0.41	0.45	0.56
0.45	0.51	0.55	0.60	0.78
0.60	0.67	0.73	0.81	1.07
0.80	0.89	0.95	1.04	1.29
1.05	1.08	1.15	1.23	1.45
1.35	1.35	1.35	1.35	1.67

**Note*: Corrected diameter equals the apparent diameter when $D > 1.35\,\mu$m.

modified size distributions and their associated refractive index, we calculated the light scattering coefficients using

$$\sigma_p^i = \int \frac{\pi}{4} D^2 Q_s(D, m) n^i(D)\,dD, \tag{6}$$

where the superscript "i" denotes the ith measurement, the integration is taken over all the particles sampled by the PCASP, and the scattering efficiency factor Q_s is calculated by use of Mie theory (Van de Hulst, 1980).

The calculated light scattering coefficients are then compared to those measured with the nephelometer and the refractive index best fitting the data is chosen. The agreement between σ_p and that measured by the nephelometer (σ_n) is quantified by the least-squares difference defined by

$$e_1 = \sum_{i=1}^{N} (\sigma_n^i - \sigma_p^i)^2, \tag{7}$$

where N represents the total number of data used in the calculation. A similar idea has been used to estimate refractive indices of aerosol particles (Mathai and Harrison, 1980); however no size correction for refractive index was made in their study.

In Table 4 we list the refractive indices which allow the closest agreement between the scattering coefficient measured by the nephelometer and those calculated from the PCASP data, and the altitudes at which the data were collected. The refractive indices vary between 1.3 and 1.5, with an average of $\sim$ 1.41. There is no obvious height dependence of refractive indices. Note that instances where nephelometer-measured light scattering coefficients are smaller than $1\,\mathrm{M\,m^{-1}}$ are not considered here to minimize the effect of uncertainties associated with the nephelometer. This constrains our analysis mostly to boundary layer measurements.

It is noteworthy that because the maximum refractive index effect is in the vicinity of the resonance diameter a refractive index smaller than that (1.588) of the latex particles used in the calibration of the PCASP is needed to increase the calculated light scattering coefficients. This is demonstrated in Fig. 5, which shows the change with height of light scattering coefficients measured by the nephelometer and those calculated with different refractive indices for flight 970415a. However, if the apparent PCASP-measured size distributions are not adjusted for refractive index, an increase in the refractive index is required to match measured and calculated scattering coefficients, and the estimated refractive index will be larger than the refractive indices typically ascribed to ambient aerosol particles.

Figure 6 shows the relationship of the light scattering coefficients measured by the nephelometer with those calculated from the PCASP measured size distributions corrected by means of our procedure at the estimated refractive indices given in Table 4. Also shown are those calculated from the apparent PCASP-measured size distributions assuming

Table 4. Summary of estimated refractive indices

970413a*		970414b*		970415a*		970418a*	
Height (m)	*m*	Height (m)	*m*	Height (m)	*m*	Height (m)	*m*
439	1.45	444	1.45	749	1.40	482	1.30
732	1.45	732	1.45	1069	1.40	529	1.40
1044	1.45	1057	1.45	1380	1.45	787	1.30
		1353	1.40	1686	1.45	811	1.30
		1670	1.35	1983	1.45	1121	1.30
		1971	1.35	2014	1.50	1429	1.40
		2281	1.40	2290	1.45	1735	1.40
				2314	1.45	2045	1.40
				2590	1.40	2364	1.40
				2616	1.40	2659	1.45

**Note*: 970413a, 970414b, 970415a, and 970418a denote flight numbers.

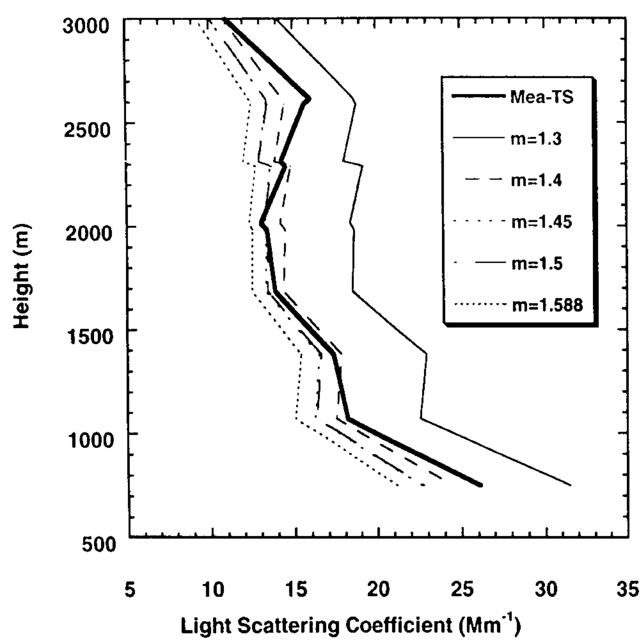

Fig. 5. An example of vertical profile of calculated and measured light scattering coefficients. Data are from the ascent of the flight 970415a. The thick line shows the profile of the measured light scattering coefficients; the remaining lines show those calculated from the PCASP measurements for various refractive indices. It is evident that the refractive index needs to be less than 1.588 for the calculated and measured light scattering coefficients to match.

a refractive index of $m = 1.45$. It is clear from this figure that the naïve use of the apparent PCASP measured-size distributions can cause as much as $\sim 50\%$ negative error in calculation of the light scattering coefficients. Our new approach for accounting for the effect of refractive index significantly improves the closure of light scattering coefficients.

4. QUANTIFICATION OF SOURCES OF UNDERESTIMATING LIGHT SCATTERING COEFFICIENTS CALCULATED FROM PCASP-MEASURED SIZE DISTRIBUTIONS

The PCASP sizes particles between 0.1 and 3.2 μm and yet the nephelometer measures light scattered from particles outside this range (Heintzenberg and Charlson, 1996). The effect of the size truncation has been suggested as a reason for the underestimation of light

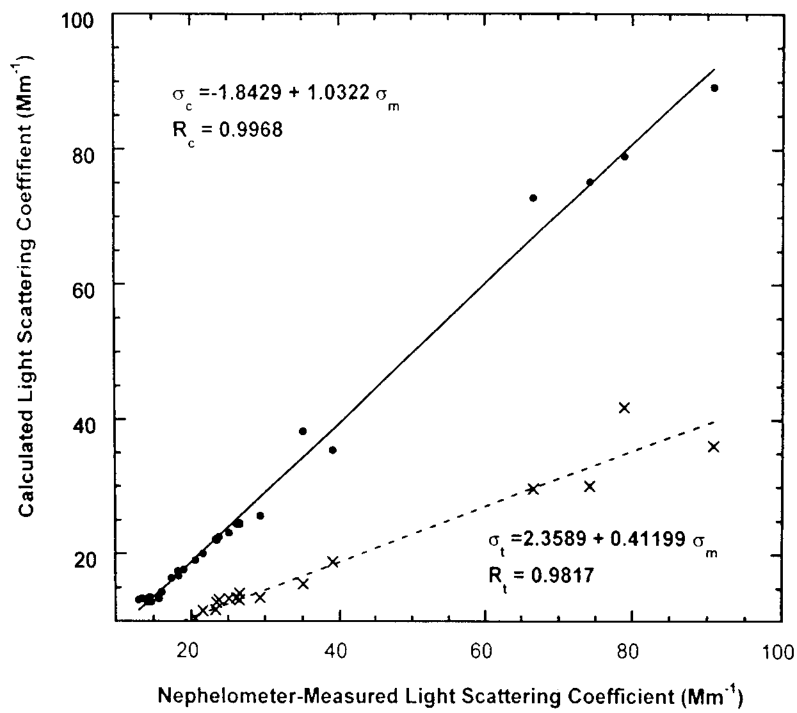

Fig. 6. Closure experiments between nephelometer-measured light scattering coefficients and those calculated from the PCASP-measured size distributions. The crosses (dots) represent the cases when the apparent (corrected) size distributions are used in the calculation of light scattering coefficients. Also shown are the fitting equations, where σ_m is the measured light scattering coefficient, and σ_c and σ_t are values calculated from corrected and uncorrected PCASP measured size distributions.

scattering coefficients calculated from PCASP-measured size distributions by Hegg *et al.* (1996). To the best of our knowledge, no studies have been made to quantitatively estimate the importance of this effect relative to the refractive index effect for typical ambient aerosol size distributions. This section serves to fill this gap.

An evaluation of the relative importance of the two effects requires robust knowledge of diameter ratio, refractive index and particle concentration between 0.05 and 0.1 μm. Since these pieces of information are not at our disposal, we examine these effects using an approximate method. We first obtain a size distribution by averaging all the size distributions of aerosols with estimated refractive index of $m = 1.45$ directly measured by the PCASP (without size correction), and then fit this distribution with a power-law function as shown by Fig. 7. The best fit power-law distribution (with a correlation coefficient of 0.96) is

$$n(D) = 0.8646D^{-4.2682}. \tag{8}$$

This power-law distribution is used in subsequent calculations. The apparent and the corrected light scattering coefficient are calculated from the apparent and corrected diameter of the PCASP respectively. The contribution due to the refractive index effect is the difference between the two. The contribution from small particles with diameters between 0.05 and 0.1 μm was calculated by extrapolating equation (8) to 0.05 μm and repeating the calculation. The contributions due to the refractive index effect and the size truncation effect relative to the apparent light scattering coefficient calculated by use of the PCASP apparent diameter are $\sim$ 60% and $\sim$ 2%, respectively. Therefore, the refractive index effect dominates the underestimation of calculated light scattering coefficients. It should be noted that these estimates accurately holds only for aerosols as described by equation (8); deviations are anticipated for real aerosols with different size distributions and refractive indices. Nevertheless, the basic conclusion is believed to hold.

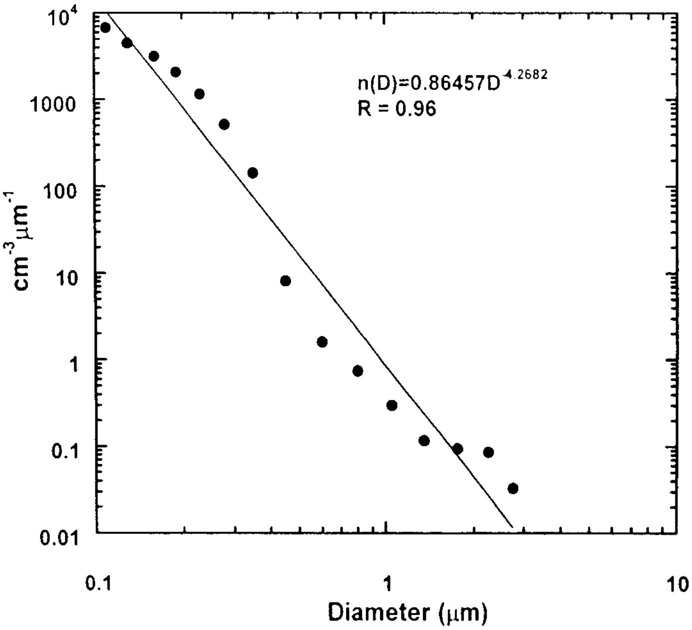

Fig. 7. The size distribution obtained by averaging all the cases with $m = 1.45$. The fitting power law is also given.

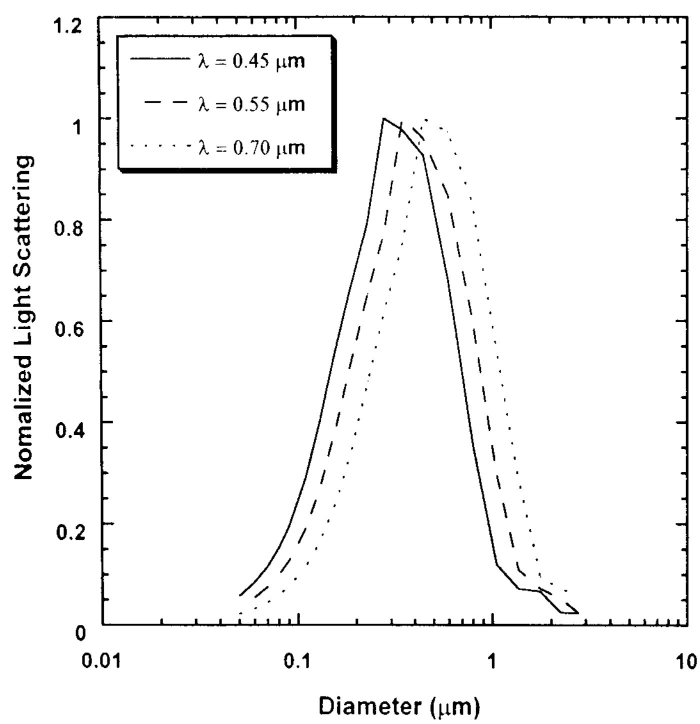

Fig. 8. Light scattering coefficient normalized to the maximum value as a function of particle diameter at the three wavelengths of the nephelometer. The size distribution described by equation (8) and $m = 1.45$ are used in the calculation. A combination of this figure with Fig. 2 demonstrates that the maximum undersizing of the PCASP corresponds to the size region where maximum light scattering occurs.

The above results can be further understood by examining Fig. 8 together with Fig. 2. Figure 8 displays the distribution (at the three wavelengths of the nephelometer) of light scattering coefficient normalized to the corresponding maximum values with respect to particle diameter, showing that the contribution from particles less than 0.1 μm is very small. Furthermore, a combination of Figs 8 and 2 shows that the diameter range of the maximum refractive index effect corresponds to that over which particles scatter visible light most efficiently.

5. CONCLUDING REMARKS

Two theoretical functions (SAR and SFR) for representing the optical response of the PCASP are compared in terms of diameter ratio as a function of apparent diameter. The SFR formulation is found to be somewhat better than the more frequently used SAR formulation. It is argued that the SFR formulation is better, plausibly because it does not attempt to represent the resonance structure that exists for ideal Mie scattering. There is good evidence to believe that this resonance structure is dampened by scattering of standing waves in an optical particle counter, and that these phase differences are not present in practical instrumentation. A generalized response function is proposed which includes the existing functions as special cases. A new approach for deriving the refractive index of ambient aerosols and correcting the PCASP-measured size distributions is developed. The results from this approach are in agreement with the limited ambient measurements of diameter ratios that have been made, and clearly demonstrate the existence of a minimum in the diameter ratio near the resonance diameter region.

The new approach is used to improve the closure experiment between light scattering coefficients calculated by applying Mie theory to aerosol size distributions measured with the PCASP and those directly measured with an integrating nephelometer. It is found that the use of uncorrected PCASP-measured size distributions causes calculated light scattering coefficients to be significantly underestimated. Correcting PCASP-measured size distributions for the difference between the refractive index of calibration and ambient aerosols yields light scattering coefficients that agree quite well with those measured by the integrating nephelometer. Refractive indices of ambient particles are estimated using this procedure and are found to vary between 1.3 and 1.5, with an average of 1.41. Such values are within the range of refractive indices measured, or estimated for ambient aerosols by other means. The relative magnitude of the refractive index, and size truncation effects on the PCASP-derived light scattering coefficients are compared. It is found that the refractive index effect predominates.

This study shows that undersizing of particles by optical counters can lead to significant negative errors in calculation of ambient light scattering because optical counters undersize aerosol particles mostly in the size range where particles are most efficient at scattering solar radiation. These findings could be important for the assessment of the effects of aerosols on climate change, because data from the PCASP and/or its equivalent are widely used to estimate the effect of aerosols on the amount of solar radiation reaching the Earth's surface.

It should be noted that neither aerosol absorption nor particle non-sphericity has been considered in this analyis. Although modeling the effect of absorption on the diameter ratio is straightforward, estimating imaginary parts of refractive indices requires additional data that are not available. We speculate that the effect of absorption is somewhat equivalent to lowering the real part of refractive index. Therefore, the estimated refractive indices reported in this paper may be somewhat lower than the actual values, depending on the degree of absorption of the aerosols. The effect of non-sphericity of aerosol particles on light scattering and subsequent results introduces further complication. Although the non-sphericity effect on total light scattering may be small, the phase function is rather sensitive to particle shapes (Mishchenko *et al.*, 1997). Therefore, particle nonsphericity may affect angular truncation effect of integrating nephelometers. Particle nonsphericity may also affect the performance of the PCASP, among others, by reducing the resonance structure of light scattering (Liu *et al.*, 1998,1999). Unfortunately, the issue of particle non-sphericity is almost intractable at present due to the lack of information on particle shapes and the difficulty involved in calculating light scattering by non-spherical particles. The counting efficiency of an OPC, and the mixing nature of ambient aerosols may also cause errors in size distribution measurements and calculated light scattering coefficients.

Acknowledgements—We are indebted to Dr. L. Newman at Brookhaven National Laboratory, who have carefully read the manuscript and provided valuable suggestions. We would like to acknowledge constructive discussions with Drs. S. E. Schwartz, R. McGraw, R. N. Halthore, Y.-N. Lee, D. Imre, F. Brechtel, and S. R. Springston at the Brookhaven National Laboratory. Comments by the anonymous referees were very constructive and insightful. This research was supported by the Environmental Sciences Division of the U.S. Department of Energy, as part of the Atmospheric Radiation Measurements Program and was performed under contract DE-AC03-98CH10886.

REFERENCES

Anderson, T. L., Covert, D. S. and Marshall, S. F. *et al.* (1996) Performance characteristics of a high-sensitivity, three-wavelength, total scatter/back-scatter nephelometer. *J. Atmos. Ocean. Technol.* **13,** 967–986.

Arnott, W. P. (1998) Private communication.

Covert, D. S., Heintzenberg, J. and Hansson, H. (1990) Electro-optical detection of external mixtures in aerosols. *Aerosol Sci. Technol.* **12,** 446–456.

Eldering, A., Cass, G. R. and Moon, K. C. (1994) An air monitoring network using continuous particle size distribution monitors: connecting pollutant properties to visibility via Mie scattering calculations. *Atmos. Environ.* **28,** 2733–2749.

Ensor, D. S., Charlson, R. J., Ahlquist, N. C., Whitby, K. T., Husar, R. B. and Liu, B. Y. H. (1972) Multiwavelength nephelometer measurements in Los Angeles smog aerosols: I. Comparison of calculated and measured light-scattering. *J. Colloid Interface Sci.* **39,** 242–251.

Garvey, D. M. and Pinnick, R. G. (1983) Response of characteristics of the Particle Measuring Systems Active Scattering Aerosol Spectrometeor Probe (ASASP-X). *Aerosol Sci. Technol.* **2,** 477–488.

Hegg, D. A., Hobbs, P. V., Gasso, S., Nance, J. D. and Rango, A. L. (1996) Aerosol measurements of some in the Arctic relevant to direct and indirect radiative forcing. *J. Geophys. Res.* **D101,** 23,349–23,363.

Heintzenberg, J. and Charlson, R. J. (1996) Design and applications of the integrating nephelometer: a review. *J. Atmos. Ocean. Technol.* **13,** 987–1000.

Hering, S. V. and McMurry, P. H. (1991) Response of a PMS LAS-X laser optical particle counter to monodisperse atmospheric aerosols. *Atmos. Environ.* **25A,** 463–468.

Kim, Y. J. and Boatman, J. F. (1990) Size calibration corrections for the Active Scattering Aerosol Spectrometer Probe (ASASP-100X). *Aerosol Sci. Technol.* **12,** 665–672.

Liu, Y., Arnott, W. P. and Hallett, J. (1998) Anomalous diffraction theory for arbitrarily oriented finite circular cylinders and comparison with exact T-matrix results. *Appl. Opt.* **37,** 5019–5030.

Liu, Y., Arnott, W. P. and Hallett, J. (1999) Particle size distribution retrieval from multispectral optical depth: Influences of particle nonsphericity and refractive index. *J. Geophys. Res.* **D104,** 31753–31762.

Mathai, C. V. and Harrison, A. W. (1980) Estimation of atmospheric aerosol refractive index. *Atmos. Environ.* **14,** 1131–1135.

Mishchenko, M. I., Travis, L. D., Kahn, R. A. and West, R. A. (1997) Modeling phase functions for dustlike tropospheric aerosols using a shape mixture of randomly oriented polydisperse spheroids. *J. Geophys. Res.* **D102,** 16,831–16,847.

Pinnick, R. G. and Auvermann, H. J. (1979) Response characteristics of Knollenberg light-scattering aerosol counters. *J. Aerosol Sci.* **10,** 55–74.

Quinn, P. K., Marshall, S. F., Bates, T. S., Covert, D. S. and Kapusin, V. N. (1995) Comparison of measured and calculated aerosol properties relevant to the direct radiative forcing of tropospheric sulfate aerosol on climate. *J. Gephys. Res.* **D100,** 8977–8991.

Quinn, P. K. *et al.* (1996) Closure in tropospheric aerosol-climate research: a review and future needs for addressing aerosol direct shortwave radiative forcing. *Beitr. Phys. Atmos.* **69,** 547–577.

Schwartz, S. E. (1996) The whitehouse effect—shortwave radiative forcing of climate by anthropogenic aerosols: an overview. *J. Aerosol Sci.* **27,** 359–382.

Schuster, B. G. and Knollenberg, R. (1972) Detection and sizing of small particles in an open cavity gas laser. *App. Opt.* **11,** 1515–1520.

Stolzenburg, M., Kreisberg, N. and Hering, S. (1998) Atmospheric size distributions measured by differential mobility optical particle size spectrometry. *Aerosol Sci. Technol.* **29,** 402–418.

Van de Hulst, H. C. (1980) Light Scattering by Small Particles, 470pp. Dover Publications, New York.

Waggoner, A. P., Weiss, R. E., Ahlquist, N. C., Covert, D. S., Will, S. and Charlson, R. J. (1981) Optical characteristics of atmospheric aerosols. *Atmos. Environ.* **15,** 1891–1909.

Wilson, J. C., Gupta, A., Whitby, K. T. and Wilson, W. E. (1988) Measured aerosol light scattering coefficients compared with values calculated from EAA and optical particle counter measurements: improving the utility of the comparison. *Atmos. Environ.* **22,** 789–793.