

An Algorithm for Combining Electrical Mobility and Aerodynamic Size Distributions Data when Measuring Ambient Aerosol

A. Khlystov, C. Stanier, and S. N. Pandis

Carnegie Mellon University, Department of Chemical Engineering, Pittsburgh, Pennsylvania

Ambient aerosol particles vary in size from a few nanometers to several micrometers. No instrument is currently available to cover such a wide size range, and so a combination of several instruments is usually used. One such combination is that of electrical mobility classifiers and an aerodynamic sizer. Because of the differences in measurement principles between the instruments, difficulties arise in the combination of the measurements into a single size distribution. Here we report a simple algorithm that was developed to combine aerosol size distributions measured with commercially available scanning mobility particle sizers (SMPS; TSI Inc.) and an aerodynamic particle sizer (APS; TSI Inc.). This algorithm was tested during July 2001 in the Pittsburgh Air Quality Study. The aerosol during the study had both urban and regional origin and is characteristic of urban atmosphere in the Northeastern U.S. The integrated volume concentrations from the SMPS–APS showed a good correlation with $PM_{2.5}$ mass concentration measurements using a TEOM. The relation of the aerosol mass to its volume is an “effective” density, a ratio of the bulk aerosol density to the shape factor. As a result of the comparison with the TEOM the ambient aerosol in the Pittsburgh area was found to have an effective density of $1.5 \pm 0.3 \text{ g cm}^{-3}$. Given that the aerosol during the study was found to always contain water, the particles are expected to be spherical and thus the shape factor may be assumed to be 1. This assumption has been supported by a comparison with the MOUDI, using the aerosol density of 1.5 g/cm^3 . It should be noted that the estimated aerosol density and the shape factor are applicable to this study only and may be different in other locations.

INTRODUCTION

Ambient aerosol plays an important role in the atmosphere, influencing visibility, affecting global climate, and participating in atmospheric chemistry (Seinfeld and Pandis 1998). Recently, increased concentrations of ambient aerosol smaller than $2.5 \mu\text{m}$ ($PM_{2.5}$) have been associated with increased morbidity and mortality rates (Schwartz and Dockery 1992; Dockery et al. 1993). Size distribution of atmospheric particles spans a wide size range from a few nanometers to several micrometers. In order to study aerosol dynamics in such a broad size range a combination of several separate instruments is necessary. A typical combination has been a scanning mobility particle sizer (SMPS; TSI Inc., St. Paul, MN) with an aerodynamic particle sizer (APS; TSI Inc.). This combination was employed in several recent studies to measure ambient aerosol (Shen et al. 2002; Hand and Kreidenweis 2002; Shi et al. 2001). The integrated volume concentration measured with the SMPS–APS can be used to estimate the mass concentration using an assumed bulk aerosol density (Shen et al. 2002). If this approach proves accurate, the SMPS–APS can be used as high time resolution substitution for the filter-based mass measurements.

The SMPS and the APS have different measurement principles. The SMPS classifies particles according to their mobility in an electric field (Wang and Flagan 1989). The electrical mobility size depends on the particle cross section, and for a spherical particle this is the same as the physical size. Unlike the SMPS, the APS measures aerodynamic size; particles are accelerated in a nozzle and their time-of-flight is related to their aerodynamic size (Armendariz and Leith 2002). The aerodynamic size is proportional to the physical size and the square root of particle density (Hinds 1999). Thus, for a sphere the aerodynamic size is equal to the physical size only for unit density particles.

Because of the different measurement principles (i.e., electrical mobility versus aerodynamic sizing), difficulties arise in attempts to create a single size spectrum from the data measured with the SMPS and APS. Some researchers have approached this problem by selecting certain kinds of data from each instrument;

Received 23 October 2002; accepted 25 April 2003.

This research was conducted as part of the Pittsburgh Air Quality Study, which was supported by US Environmental Protection Agency under contract R82806101 and the US Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This article has not been subject to the EPA’s required peer and policy review, and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

Address correspondence to S. N. Pandis, Carnegie Mellon University, Department of Chemical Engineering, Pittsburgh, PA 15213. E-mail: spyros@andrew.cmu.edu

for example, the SMPS is used up to a certain size, and beyond that size the APS is used (Shen et al. 2002). Hand and Kreidenweis (2002) have developed an algorithm that combines electrical mobility, optical particle counter (OPC), and APS data into a single spectrum. The OPC data are first matched with the SMPS spectrum by finding an optimal refractive index. Then the APS data are matched to the modified OPC spectrum by finding an effective density that would provide the best fit with the OPC. The reason for matching the APS to the OPC and not directly to the SMPS was that the size overlap between the APS and the SMPS is rather small.

In this study we attempted to fit the APS size distribution to the SMPS distribution without using an optical particle counter as a middle ground. A simple algorithm was developed to combine the aerodynamic and electrical mobility spectra into a single distribution. The algorithm provides a ratio of the particle density to the shape factor of particles in the 540–800 nm size range, where the SMPS and the APS measurement ranges overlap. The ratio of aerosol density to its shape factor is usually called the “effective” density. However, the algorithm does not provide means of separating the density and the shape factor. It should also be noted that the particle shape factor and density may differ through the aerosol spectrum, as the composition and the physical properties of ambient particles usually vary with size. Instead of concentrating on the narrow overlap size range, we have determined the average (bulk) aerosol “effective” density during a month of ambient aerosol measurements within the Pittsburgh Air Quality Study (PAQS).

The measurements were carried out at the central site of the PAQS, in an urban park approximately 5 km from the downtown Pittsburgh. The aerosol originated from both urban and long-range sources. Ammonium salts of sulfate were the dominant aerosol components, comprising approximately 50% of the $PM_{2.5}$ aerosol mass. Carbonaceous material was the second largest component, contributing approximately 25% to the mass of fine particles (Wittig et al. 2003). The results obtained with the SMPS–APS system were compared to the simultaneous measurements of the aerosol $PM_{2.5}$ mass concentration using a tapered element oscillating microbalance (TEOM; R&P Co., Albany, NY, USA) and size-fractionated mass measurements using MOUDI (MSP Co., Minneapolis, MN, USA) cascade impactor. The comparison of the $PM_{2.5}$ particle volume concentration from the merged SMPS–APS distribution with the TEOM $PM_{2.5}$ mass concentration has provided us with an estimate of a bulk “effective” particle density.

EXPERIMENTAL

General Description of the SMPS–APS System

The SMPS–APS system used in the PAQS was a part of the Dry-Ambient Aerosol Size Spectrometer (DAASS) described in Stanier et al. (2003). The system consists of an ultrafine SMPS system for 3–80 nm (TSI 3936N25), an SMPS for 13–680 nm (TSI 3936L10), and an APS (TSI APS 3320) covering 0.5–

10 μm . In this study we used data up to 2.5 μm in aerodynamic diameter. The DAASS system is equipped with a number of computer-controlled solenoid valves that direct the sample and sheath flows of the instruments either directly to the instruments or through nafion driers (Perma Pure Inc.). Single-channel nafion driers in stainless steel casing were used in the sample lines to minimize particle losses. The sheath lines were equipped with multichannel driers, because of the higher capacity needed to dry larger flows and because particle loss is not an issue in particle-free flows. To avoid losses of semivolatile aerosol components the whole system was maintained at a temperature that was within 2°C of the ambient temperature. When the aerosol is sampled through the driers, the DAASS provides measurements of dried ambient aerosol (at the relative humidity of 10–35%). When the sample bypasses the driers, the system measures the aerosol at ambient relative humidity. Four dried and four “ambient” (or “wet”) size distributions are measured each hour.

No impactor was used in front of the SMPS systems. It was found that the cutoff characteristics of the TSI impactor change as the sampling progresses because of accumulation of material on the impactor plate. Even with daily cleaning, it was observed that the impactor was cutting into progressively smaller-than-nominal sizes. The purpose of the impactor in SMPS systems is to facilitate the data inversion. The impactor removes particles larger than the measurement range of the SMPS, such that there is no contribution of multiple-charge particles to the last channels of the instrument. If no impactor is used, the concentration in the last channels will be overestimated due to the contribution of multiple-charge particles from particles larger than the upper instrument size limit.

The effect of multiple charging was minimal in the present study. During this study the ambient aerosol number concentration was rapidly declining with size for the particles larger than 100 nm, with the number size distribution at those sizes closely following the power law function of -3 to -6 power. In other words, when moving a factor of 2 in size the concentration drops by 2^{-3} to 2^{-6} (there are 8 to 32 times less particles). If an SMPS channel measures 700 nm single-charge particles, it will also measure approximately 2 times larger double-charge particles. Even though the charging for single charge at 700 nm is approximately equal to that for double-charge particles at 1400 nm, the maximum contribution of double charge particles to the last SMPS channel would be about 10%. A more rigorous analysis of the possible error due to the presence of multiple-charge particles in the last SMPS channels was done using the MICRON software package (Wolfenbarger and Seinfeld 1991). The results confirm that the error due to the presence of multiple-charge particles at sizes larger than the upper size limit of the SMPS is less than 10% in this study. It should also be noted that the SMPS is not designed to allow a 100% penetration of particles larger than 1 μm . Particle losses of the supermicrometer particles will further reduce the error due to particles carrying multiple charges outside the SMPS size range.

The APS can be operated in two modes: “summed,” in which the time-of-flight (TOF) and the optical signals are saved separately, and “correlated,” in which the TOF and optical signal are saved together on a per particle basis. Since less memory storage is required in the summed mode, more bits of the TOF information can be stored. Thus, the size resolution of the instrument in that mode is better. In this study the APS was operated in the summed mode, because the correlated mode has been reported to have problems at low aerosol concentrations (Armendariz and Leith 2002).

To facilitate the matching of electrical-mobility size distributions with the aerodynamic size data, the APS was “mobility” calibrated using ammonium sulfate aerosol. Ammonium sulfate was chosen because it is the dominant aerosol component in ambient aerosol in the Pittsburgh area (Rees et al. 2003). The almost monodisperse ammonium sulfate aerosol was produced by selecting a narrow mobility range with a differential mobility analyzer (DMA; 3081, TSI Inc.) from a wider spectrum of artificially generated ammonium sulfate particles. The artificial aerosol was produced by spraying aqueous ammonium sulfate solution with a constant output atomizer (Model 3076, TSI Inc.) and drying it with a silica-gel diffusion drier. After passing the drier the aerosol was fed to the DMA. The sheath and aerosol flows of the DMA were set to be 2 l min^{-1} and 0.2 l min^{-1} , respectively. This was done to extend the size range of the DMA to about a $1.2 \mu\text{m}$ mobility diameter. The monodisperse output of the DMA was diluted with 0.8 l min^{-1} of clean filtered air. The resulting flow of 1 l min^{-1} containing the monodisperse aerosol was fed directly to the inner inlet nozzle of the APS. The size of the monodisperse particles was adjusted by changing the voltage of the DMA. Monodisperse ammonium sulfate aerosol with sizes from 0.4 to $1 \mu\text{m}$ was used to calibrate the APS. The DMA output contained smaller amounts of double- and triple-charge particles, that have approximately 2 and 3 times larger sizes than the main peak of single-charge particles. Because the original polydisperse aerosol size distribution was rapidly decreasing with size and because the size resolution of the APS is substantially better than a factor of 2 in size, these double- and triple-charge particle peaks were not interfering with the analysis of calibration results. Since it was impossible to produce particles larger than $1.2 \mu\text{m}$ with the DMA, the calibration curve obtained at smaller sizes was extrapolated to the larger sizes.

Sizing precision of the SMPS was checked using monodisperse PSL aerosol as well as by sizing monodisperse ammonium sulfate in 14 different size ranges from 20 nm to 900 nm. The monodisperse ammonium sulfate particles were produced using a DMA. Similar to the APS, the double- and triple-charge particles did not interfere with the analysis of the calibration results. Differences in particle sizing were less than 3% across the entire size range.

Prior to the ambient study the APS was tested in the laboratory using artificial ammonium sulfate aerosol. As will be shown later, the merging algorithm requires the counting efficiency of the SMPS and the APS to be equal in the overlap range. The inte-

grated counting efficiency of the SMPS was compared to that of a standalone condensation particle counter (CPC Model 3025, TSI Inc) and was found to be within 10% of that of the CPC. The counting efficiency of the APS in the summed mode relative to that of the SMPS was assessed by comparing its counts with those of the SMPS in the overlap size range of $0.5\text{--}1 \mu\text{m}$ in mobility diameter. The APS was mobility calibrated with monodisperse ammonium sulfate aerosol, as described above, and the calibration information for this laboratory intercomparison was stored in the APS with the particle density and the shape factor set both to 1. In this way, no postprocessing was required for the APS data: the APS was reporting “mobility-equivalent” size of ammonium sulfate particles.

Merging of the SMPS and the APS Size Distributions

Data obtained with the SMPS/APS were combined into one single-size distribution in two ways. In the first approach, similar to Shen et al. (2002), the APS data were merged with the SMPS assuming the aerodynamic size is the same as the physical size. In the second, similar to Hand and Kreidenweis (2002), a size correction factor was searched for the APS data to be merged with the SMPS data. Unlike Hand and Kreidenweis (2002), who used optical counter measurements as an intermediate to match the distributions, we converted the APS data to the mobility spectrum by finding a size correction factor that gives the best least-squares fit directly with the SMPS in the overlap size range.

The fitting of the APS to the SMPS was done in the following way. The SMPS and APS systems overlapped from 542–680 nm for unit density particles. The SMPS data were fitted with a power-law (Junge size distribution) function (Willeke and Baron 1992) in this overlap size range. A size correction was then found for the APS size distribution, expressed as $dN/d\text{Log}(D)$, to have the least-squares fit with the power-law approximation of the SMPS data. Applying the correction factor preserves the shape of the APS distribution while shifting it along the $d\text{Log}(D)$ -axis to achieve a good fit with the SMPS size distribution. Given the narrow size range of the overlap region, the size-correction factor is assumed to be constant within the overlapping size range.

The size-correction factor is selected to minimize the difference between the SMPS and shifted APS size distributions, with the objective function S^2 shown in the following equation:

$$S^2(x) = \frac{1}{n_2 - n_1} \sum_{i=n_1}^{n_2} [\log(N_s(D_i)) - \log(N_a(D_i x))]^2, \quad [1]$$

where N_s is the power-law function representing the smoothed $dN/d\text{Log}(D)$ size distribution measured by the SMPS; N_a is the APS size distribution; x is the size-correction factor; and n_1 and n_2 are the numbers of the first and the last APS channel that fit, after applying the correction, into the 540–800 nm mobility size range. The first two channels of the APS were not used for the fitting procedure because of their unreliable counting. The logarithms of the size distribution values are used to give the same relative weight to all points in the overlap range.

It should be noted that a $dN/d\text{Log}(D)$ distribution should be used for the minimization procedure. If a dN/dD distribution is used, the APS distribution will need to be shifted not only along the abscissa but also vertically:

$$\left(\frac{dN}{dD_p}\right)_{\text{SMPS}} = \left(\frac{dN}{dD_a}\right)_{\text{APS}} \frac{dD_a}{dD_p} = \left(\frac{dN}{dD_a}\right)_{\text{APS}} x, \quad [2]$$

where D_a is the aerodynamic size, D_p is the physical size, and x is the size-correction factor ($D_a = xD_p$). In contrast, under the assumption that the shift factor does not vary within the overlap size range, the $dN/d\text{Log}(D)$ distribution does not need a vertical shift:

$$\begin{aligned} \left(\frac{dN}{d\log(D_p)}\right)_{\text{SMPS}} &= \left(\frac{dN}{d\log(D_a)}\right)_{\text{APS}} \frac{d\log(D_a)}{d\log(D_p)} \\ &= \left(\frac{dN}{d\log(D_a)}\right)_{\text{APS}} \frac{d\log(D_p x)}{d\log(D_p)} \\ &= \left(\frac{dN}{d\log(D_a)}\right)_{\text{APS}}. \end{aligned} \quad [3]$$

The size-correction factor relates the ratio of the aerosol density to its shape factor in the size range used for the fitting and is usually called an “effective” density (Hand and Kreidenweis 2002). This relationship can be seen from the formula relating the mobility size to the aerodynamic size (Hinds 1999):

$$D_p = D_a \sqrt{\chi \frac{C_s(D_a) \rho_0}{C_s(D_p) \rho_p}}, \quad [4]$$

where D_p and D_a are the mobility and the aerodynamic diameters, respectively; C_s is the Cunningham slip correction factor; ρ_0 is the reference density (1 g cm^{-3}); ρ_p is the density of the particle; and χ is the shape factor. At sizes of the APS–SMPS overlap size range the slip correction can be neglected; for the particle density of 2 g cm^{-3} , the shape factor of 1, and the physical diameter of 500 nm the error in calculating the aerodynamic diameter is 4%. At lower particle densities and larger shape factors the error will be even smaller. Neglecting the slip correction, Equation (4) becomes

$$D_p = D_a \sqrt{\chi \frac{\rho_0}{\rho_p}} = \frac{D_a}{x}. \quad [5]$$

Thus, the size-correction factor is

$$x = \sqrt{\frac{\rho_p}{\chi \rho_0}}. \quad [6]$$

The size-correction factor depends on both the particle density and the shape factor in the overlap size range. Consequently, it is not possible to determine each of these parameters from the size-correction factor without complementary measurements. However, the particle density in the overlap size range may differ

from the average bulk aerosol density, which will introduce errors in determination of the shape factor from the size-correction factor. This problem can be avoided by using mass measurements within the narrow overlap size range. For practical purposes, however, it is more useful to obtain integrated aerosol properties in the $\text{PM}_{2.5}$ size range such that, for example, the aerosol volume measured with the SMPS–APS can be converted to the aerosol mass, substituting filter-based measurements, and the volume size distribution can be converted to the aerodynamic size distribution to substitute cascade impactor measurements. For this reason we concentrated our efforts to find the bulk $\text{PM}_{2.5}$ aerosol effective density from comparisons of the SMPS–APS with a TEOM and a MOUDI cascade impactor.

It should be noted that errors may be introduced into the merged-size distribution if the SMPS and the APS have different counting efficiencies in the overlapping size range. To demonstrate the magnitude of the errors due to miscounting, a short analysis is performed here. As an example we will assume the SMPS to be correct and the APS is counting Z times lower than the SMPS. If the $dN/d\text{Log}(D)$ size distribution follows the power-law function proportional to D^{-B} , it can be shown that the merging procedure would shift the APS distribution by $Z^{1/B}$ times extra, relative to what the correction factor should be if the APS is correct. If the size distribution in physical sizes is $f_p(D) = A D^{-B}$, then the size distribution in aerodynamic sizes, $f_a(D)$, will be

$$f_a(D) = A D_p^{-B} = A (x D_a)^{-B} = x^{-B} f_p(D). \quad [7]$$

Consequently, the size correction factor is

$$x = \left(\frac{f_p(D)}{f_a(D)}\right)^{\frac{1}{B}}. \quad [8]$$

An error in concentration measurements of aerodynamic distribution of a factor of Z will translate to an error in the correction factor of a factor $Z^{1/B}$. In other words, a flatter distribution (lower B) will have a larger error in the shift factor. However, if the APS is miscounting with a constant factor throughout its size range and the distribution is power law, there will be no error in the volume concentration measurements after the merging procedure.

Comparison of the SMPS–APS with TEOM and MOUDI Measurements

The SMPS–APS was compared with the TEOM (Model 1400a, R&P Co.) and MOUDI cascade impactor (Model 110, MSP Co., Minneapolis, MN, USA) during measurements of ambient aerosol in Pittsburgh, PA during July 2001.

The integrated aerosol volume concentrations in the $\text{PM}_{2.5}$ size range were compared to the simultaneous measurements with the TEOM. Dried (low relative humidity) measurements of the DAASS were used for this comparison, because the relative humidity conditions were close to those of the TEOM (below

30%RH). The TEOM was operated at 30°C and was equipped with a Nafion diffusion dryer Sample Equilibration System (SES, R&P Co.) to minimize evaporative losses of volatile aerosol components. During the study, the TEOM has shown very good agreement with the federal reference method (FRM). The TEOM was on average 1.5% higher than the FRM, both instruments giving readings within 10% of each other during the whole study (Rees et al. 2004). Because of the relatively small fraction of ammonium nitrate in July in Pittsburgh, and because the TEOM was operated at 30°C, the volatilization artifact in the TEOM was relatively small during this study. The accuracy and the artifacts of the FRM observed during the study are discussed in detail in Rees et al. (2004).

Two combined spectra were calculated from the SMPS–APS measurements for comparison with the TEOM: (1) without converting the APS data to mobility diameter, similar to Shen et al. (2002) and (2) with the conversion of APS data to the mobility size using the procedure described in the Experimental section. These two spectra were used to calculate the volume concentrations in PM_{2.5} range. These volume concentrations were compared to the PM_{2.5} mass measured with the TEOM.

The MOUDI was operated with 47 mm ring-supported Teflon membrane filters (7592-104, Whatman) as the stage substrates to reduce bounce during the sampling. The mass size distribution of the aerosol collected with the MOUDI was determined gravimetrically by weighing the MOUDI stages before and after the sample using a precision microbalance (UMX2, Mettler-Toledo, Columbus, OH, USA). The MOUDI stages were weighed in a controlled relative humidity (35 ± 2%RH) and temperature (22 ± 1°C) glove box. Prior to the weighing the stages were equilibrated for 24 h at the conditions of the weighing box. The combined accuracy of determination of the mass was ±5 µg per impactor stage.

The PM_{2.5} mass collected with the MOUDI agreed well with the FRM measurements (Cabada et al. 2004). It was, however, found that volatile material was lost from the MOUDI stages. During the summer more than 70% of nitrate was lost from the MOUDI stages (Cabada et al. 2003). The nitrate contribution to the PM_{2.5} mass in summer is small in the Pittsburgh region, so the effect of nitrate loss on the fine mass is negligible. No evident losses of organic carbon from Teflon MOUDI substrates were observed.

The MOUDI was sampling at ambient conditions (temperature and relative humidity). Because of the hygroscopic growth at high relative humidities (especially at night), the aerosol mass size distribution is shifted to larger sizes relative to low relative humidity conditions. For the comparison with MOUDI size distributions, merged dried SMPS-APS distributions need to be converted to aerodynamic size and corrected for the hygroscopic growth. This was done in the following way.

The DAASS measures both dried and wet size distributions. Comparing the integrated volumes from the dried and ambient measurements provides us with the increase in volume due to water accretion. Assuming volume additivity, the aerosol density

at ambient conditions is

$$\rho_a = \rho_w + (\rho_d - \rho_w) \frac{V_d}{V_a}, \quad [9]$$

where ρ_d and ρ_a are the dried and ambient aerosol densities, respectively; ρ_w is the density of water; and V_d and V_a are the dried and ambient aerosol integrated volumes, respectively. The aerodynamic size at ambient relative humidity was then found using the following equation (slip correction is ignored here):

$$D_a = D_p \left(\frac{V_a}{V_d} \right)^{1/3} \sqrt{\rho_a}, \quad [10]$$

where D_p is the physical size and D_a is the corresponding size at ambient relative humidity.

The dry density of 1.5 g cm⁻³ was used (Tuch et al. 1997; Hand and Kreidenweis 2002). As will be shown in the Results section, this value of the aerosol density is also applicable to this study. Because during this study the ambient aerosol contained water even at low relative humidities (Stanier et al. 2003), the particles are expected to be spherical and thus the shape factor of 1 was used to convert physical to aerodynamic size.

The geometric mean diameters and geometric mean standard deviations of the distributions in the PM_{2.5} range measured with the MOUDI and the SMPS–APS were compared to assess the size-distribution comparability of the two instruments. To compare the SMPS–APS data with the size-fractionated mass measurements of the MOUDI, the SMPS–APS data have been summed up to match the MOUDI stage size ranges. Then, values from individual stages have been summed up such that the PM_{2.5} range is divided into 4 fractions: <0.1 µm, 0.1–0.3 µm, 0.3–1 µm, 1–2.5 µm. The grouping corresponds to summing 2 impactor stages. The values found with the MOUDI and the SMPS–APS within these size fractions are compared.

RESULTS AND DISCUSSION

Laboratory Tests of the APS

The counting efficiency of the APS in the submicrometer size range is assessed by comparing it to the SMPS in the overlap size range. The APS was mobility calibrated using ammonium sulfate aerosol. The calibration information was stored with the density and the shape factor both being one. In this way the APS was measuring the mobility equivalent size of ammonium sulfate particles and no further data reduction was needed. The APS was found to agree well with the SMPS in the overlap size range of 580–720 nm (mobility equivalent size), with the counting efficiency differences of no more than 10% (Figure 1). The first APS channel, however, had a lower efficiency of about 70%. Armendariz and Leith (2002) suggested that the counting efficiency was steadily going up from about 30% at 0.5 µm to about 90% at 1 µm. However, they did not test the efficiency between these sizes. Our results indicate, however, that the counting efficiency is constant and close to 100% except for the first APS channel.

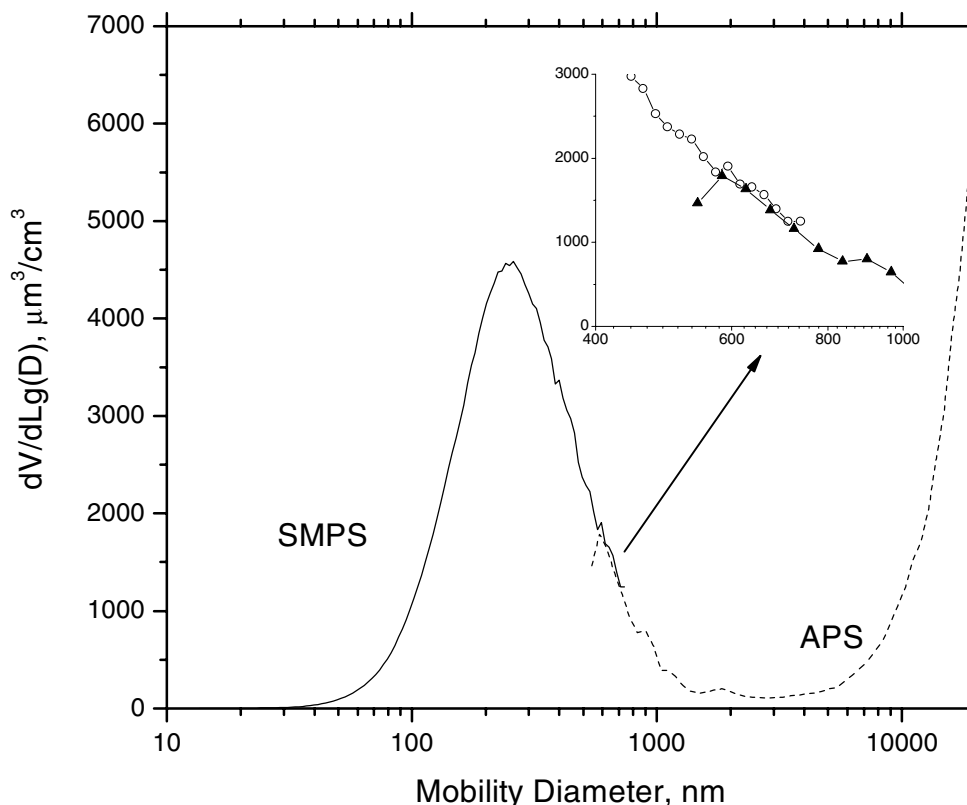


Figure 1. Comparison of the APS and the SMPS in the overlap size range using ammonium sulfate aerosol.

Comparison with TEOM

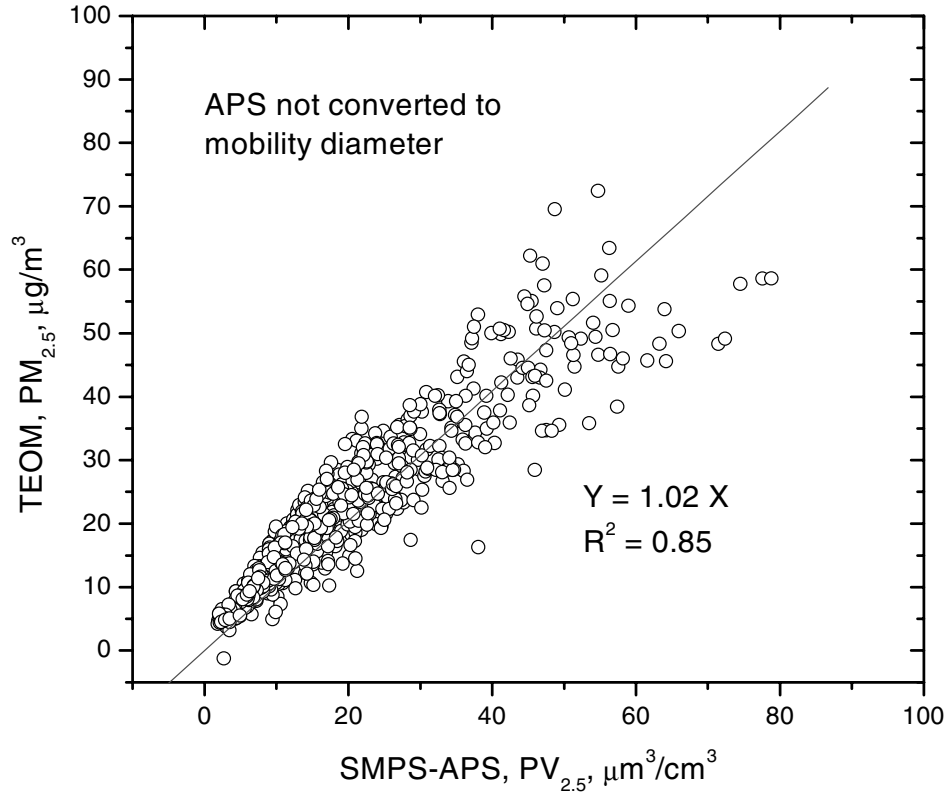
Figure 2 shows a comparison of the integrated ambient volume concentrations with the TEOM measurements. The agreement between the SMPS–APS and the TEOM is considerably improved when the APS is fitted to the SMPS distribution. The ratio of the aerosol mass to the aerosol volume is a measure of the aerosol effective density, which is equal to the bulk aerosol density if the shape factor is 1. If the APS data are used without any corrections, the density is unrealistically low (often below 1 g cm^{-3}). However, when the APS is fitted to the SMPS, the estimated density is 1.52 g cm^{-3} , which is very close to the values reported in the literature, around 1.5 g cm^{-3} (Tuch et al. 1997; Hand and Kreidenweis 2002). The density data appear to be normally distributed around the mean value with the standard deviation of 0.26 g cm^{-3} . It is thus concluded that the SMPS–APS size distribution data, in which the APS data are fitted to the SMPS, can be used to estimate the $\text{PM}_{2.5}$ mass concentration with an average standard error of about 20% by using an average aerosol density of 1.5 g cm^{-3} .

The estimated density is in good agreement with the density estimated from the average chemical composition of the aerosol during this study. The aerosol consisted of about 50% ammonium salts of sulfate, 25% organic carbon, 3% elemental carbon, 2% nitrate, and 2% crustal material (Wittig et al. 2003). It was also shown that the FRM and the TEOM retained water, which

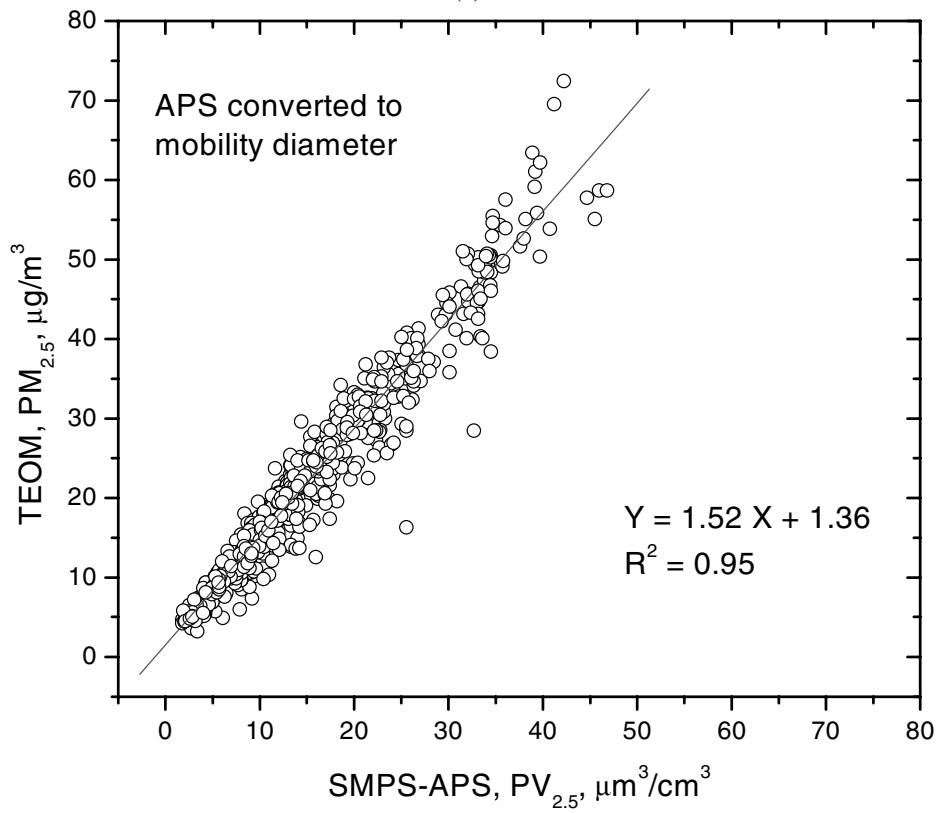
comprised on average about 20% of the aerosol mass measured with those instruments. Assuming the density of organics to be 1.4 g cm^{-3} and the density of crustal material and elemental carbon to be 2 g cm^{-3} , and taking the density of salts of ammonium to be 1.8 g cm^{-3} , the average density of the aerosol according to its chemical composition is estimated to be 1.56 g cm^{-3} , which is close to the density estimated from the SMPS–APS and TEOM comparison. This suggests that the aerosol during this study had a shape factor close to 1.

Comparison with MOUDI

Comparisons of the geometric mean diameters (GMD) and the geometric mean standard deviations (GSTD) of the ambient aerosol size distributions measured with the MOUDI and the SMPS–APS converted to the aerodynamic size and corrected for the hygroscopic growth are shown in Figures 3 and 4, respectively. Both the GMD and GSTD show a good correlation between the instruments. The slope of the regression line for GMD is virtually 1. A shape factor of 1 was used to convert the SMPS–APS distributions to aerodynamic sizes. The equality of the GMDs suggests that the shape factor of 1 is justified for this study. During this study the aerosol was found to be always wet (i.e., contain water), even at relative humidities as low as 30%. Thus, particles are expected to be spherical droplets and have the shape factor of 1, which explains our observation.



(a)



(b)

Figure 2. Comparison of mass concentrations with volume concentration in the PM_{2.5} range. (a) APS size distributions were not converted to electrical mobility; (b) APS size distributions were converted to electrical mobility using the algorithm.

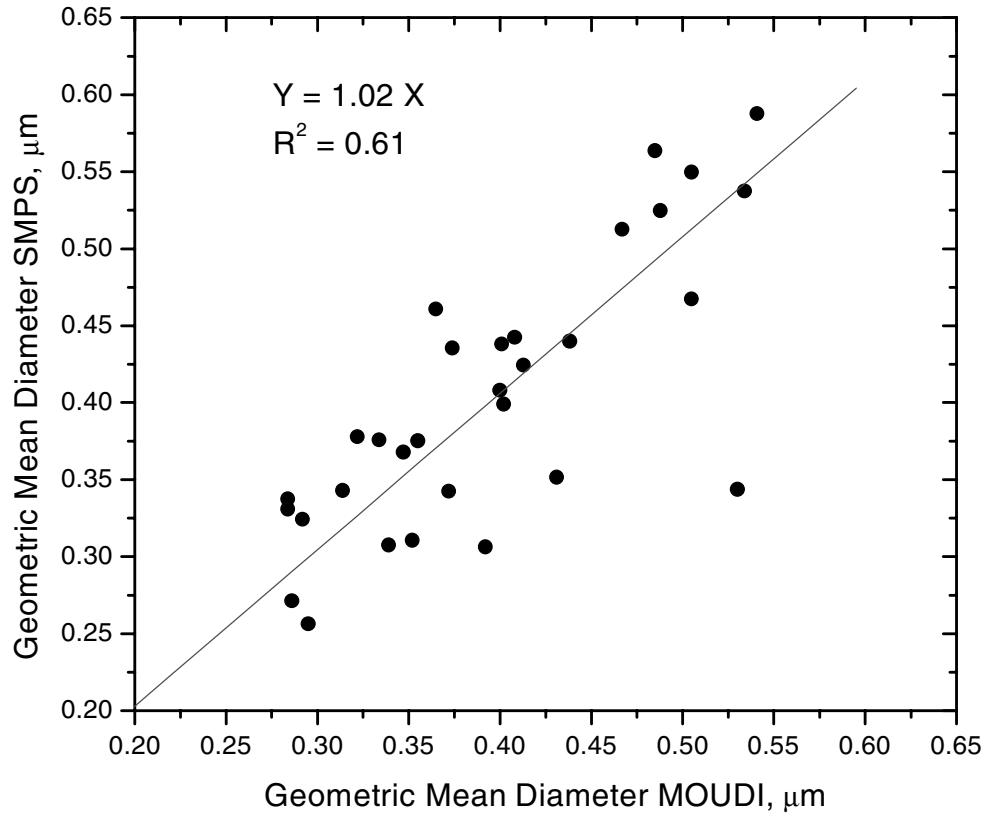


Figure 3. Comparison of geometric mean diameters.

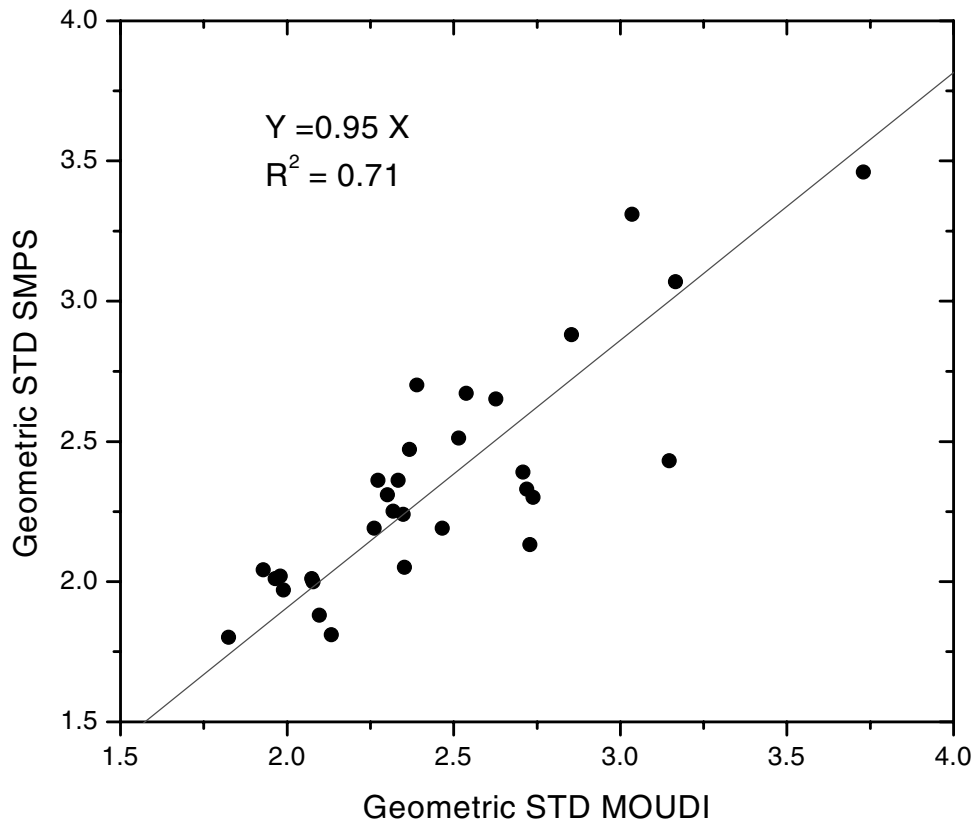


Figure 4. Comparison of geometric standard deviations.

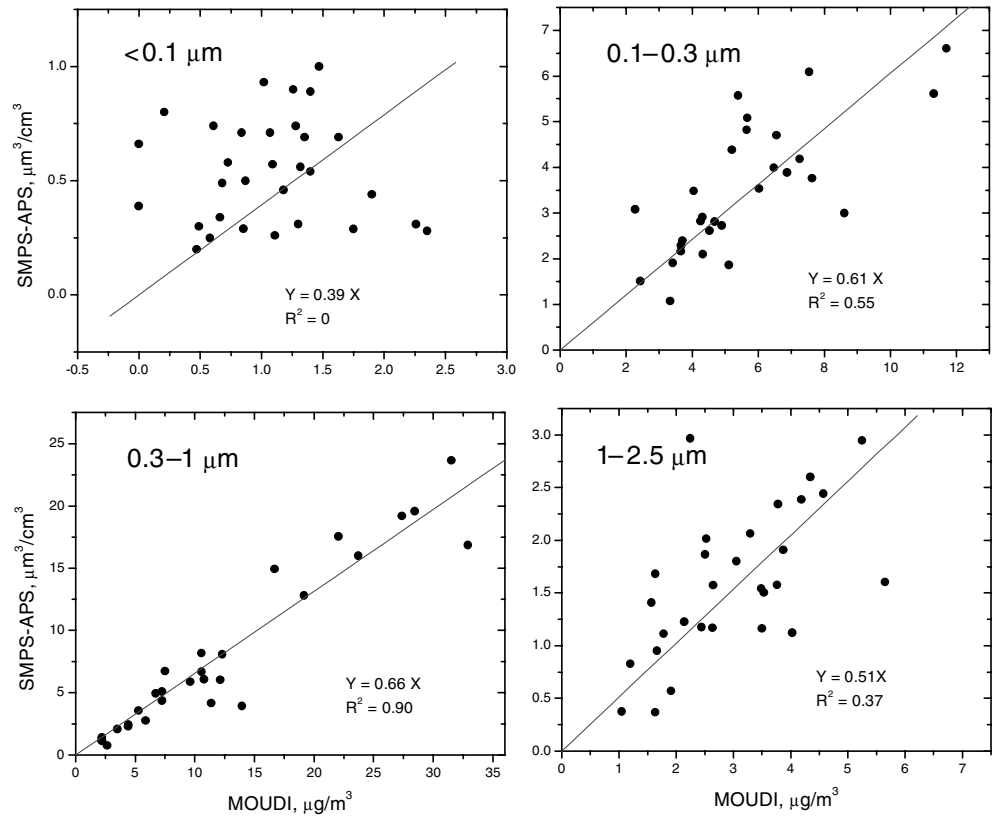


Figure 5. Comparison of size-fractionated mass concentrations from MOUDI and volume concentrations from SMPS-APS.

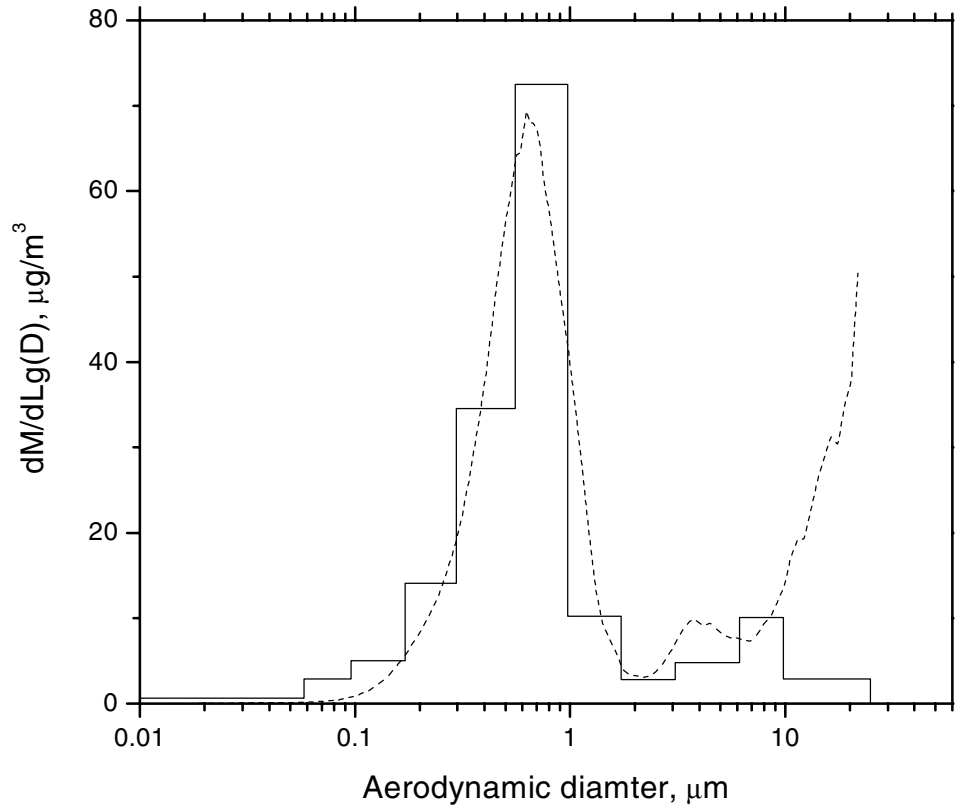


Figure 6. Comparison of size distributions measured with SMPS-APS (dashed line) and MOUDI (solid line).

Figure 5 shows a size-fractionated comparison of the MOUDI and the SMPS–APS. With the exception of the lowest stages (below $0.1\ \mu\text{m}$) the MOUDI and the SMPS–APS appear to be well correlated. The R^2 values are similar or higher than those found during a similar study by Shen et al. (2002). The slopes for the stages between 0.1 and $1\ \mu\text{m}$ are 0.61 – 0.66 . Such slopes correspond to aerosol densities between 1.52 and $1.64\ \text{g cm}^{-3}$, which again are close to ones reported in the literature and to the density found during the comparison with the TEOM. The slope for the 1 – $2.5\ \mu\text{m}$ range indicates a density of about $2\ \text{g cm}^{-3}$, which is probably due to a larger contribution of the crustal material to this size range.

The absence of correlation between the SMPS–APS and the MOUDI below $0.1\ \mu\text{m}$ is similar to the observations by Shen et al. (2002). Similarly, we found that the MOUDI measures on average more than the SMPS–APS in that size range. A possible explanation for this observation is the particle bounce from the upper stages of the MOUDI (Pak et al. 1992). The mass loading on the last stages of the MOUDI is usually small, and even a small contribution due to the bounce would introduce a large relative error on those stages, while losses from the larger stages will probably remain insignificant.

The comparison of representative size distributions measured with the SMPS–APS and the MOUDI is shown in Figure 6. The SMPS–APS distribution was converted to the mass size distribution in aerodynamic space using the density of $1.5\ \text{g cm}^{-3}$ and correcting for the hygroscopic growth as explained in the Experimental section. Qualitatively similar distributions are measured with the two instruments. The sharp increase in the volume concentration after $7\ \mu\text{m}$ measured with the SMPS–APS is most probably due to the well-documented artifact counts in the APS in the large size range (Stein et al. 2002). In this study, however, these artifact counts were not observed to contribute significantly to the $\text{PM}_{2.5}$ range.

CONCLUSIONS

A simple algorithm was developed to combine electrical mobility and aerodynamic size distribution data into a single size distribution. This algorithm was tested during a month of ambient aerosol measurements by comparing size distributions measured using an SMPS–APS combination with simultaneous measurements using a MOUDI cascade impactor and $\text{PM}_{2.5}$ mass concentration measurements using a TEOM.

Size distributions obtained by using the algorithm have better correlations with $\text{PM}_{2.5}$ measurements than do size distributions in which aerodynamic sizes were not converted to electrical mobility diameters.

A comparison of the TEOM $\text{PM}_{2.5}$ mass concentrations with the volume concentrations from the SMPS–APS data indicates that the ambient aerosol during the study had an effective density of $1.52 \pm 0.26\ \text{g cm}^{-3}$. This density is close to $1.56\ \text{g cm}^{-3}$, the density estimated from the average aerosol chemical composition during this study. This suggests that the aerosol shape factor during this study is close to 1.

The SMPS–APS size distributions obtained using the algorithm agree with the mass distributions measured with MOUDI cascade impactors within 0.1 – $2.5\ \mu\text{m}$ size range, if a density of $1.5\ \text{g cm}^{-3}$ and a shape factor of 1 are used, and the hygroscopic growth of aerosol is taken into account. However, there was no agreement below $0.1\ \mu\text{m}$, probably due to contamination of the low impactor stages because of the bounce of large particles, or a different shape factor based on the composition in this size range, which may affect the particle mobility of ultrafine particles.

REFERENCES

- Armendariz, A. J., and Leith, D. (2002). Concentration Measurement and Counting Efficiency for the Aerodynamic Particle Sizer 3320, *J. Aerosol Sci.* 33:133–148.
- Cabada, J. C., Rees, S., Takahama, S., Khlystov, A., Pandis, S. N., Davidson, C., and Robinson, A. L. (2004). Mass Size Distributions and Size Resolved Chemical Composition of Fine Particulate Matter at the Pittsburgh Supersite, *Atmos. Environ.* in print.
- Dockery, D. W., Pope, C. A., Xu, X., Splengler, J. D., Ware, J. H., Ferris, B. G., and Speizer, F. E. (1993). Mortality Risks of Air Pollution: A Prospective Cohort Study, *N. Engl. J. Med.* 329:1753–1759.
- Hinds, W. C. (1999). *Aerosol Technology: Properties, Behavior and Measurements of Airborne Particles*, 2nd ed. John Wiley & Sons, New York.
- Hand, J. L., and Kreidenweis, S. M. (2002). A New Method for Retrieving Particle Refractive Index and Effective Density from Aerosol Size Distribution Data, *Aerosol Sci. Technol.* 36:1012–1026.
- Pak, S. S., Liu, B. Y. H., and Rubuw, K. L. (1992). Effect of Coating Thickness on Particle Bounce in Inertial Impactor, *Aerosol Sci. Technol.* 16:141–150.
- Rees, S. L., Robinson, A. L., Khlystov, A., Stanier, C. O., and Pandis, S. N. (2004). Performance of the U.S. Federal Reference Method for $\text{PM}_{2.5}$ in Pittsburgh, PA, *Atmos. Environ.* in print.
- Seinfeld, J. H., and Pandis, S. N. (1998). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, Inc., New York.
- Schwartz, J., and Dockery, D. W. (1992). Increased Mortality in Philadelphia Associated with Daily Air Pollution Concentration, *Am. J. Epidemiol.* 135:12–19.
- Shen, S., Jaques, P. A., Zhu, Y., Geller, M. D., and Siuotas, C. (2002). Evaluation of the SMPS-APS System as a Continuous Monitor for Measuring $\text{PM}_{2.5}$, PM_{10} and Coarse $\text{PM}_{2.5-10}$, *Atmos. Environ.* 36:3939–3950.
- Shi, J. P., Harrison, R. M., and Evans, D. (2001). Comparison of Ambient Particle Surface Area Measurement by Epiphaniometer and SMPS/APS, *Atmos. Environ.* 35:6193–6200.
- Stanier, C. O., Khlystov, A., Chan, W. R., Mandiro, M., and Pandis, S. N. (2004). A Method for the in-situ Measurement of Aerosol Water Content of Ambient Aerosols: The Dry-Ambient Aerosol Size Spectrometer (DAASS), *Aerosol Sci. Technol.* 38:215–228.
- Stein, S. W., Gabrio, B. J., Oberreit, D., Hairston, P., Myrdal, P. B., and Beck, T. J. (2002). An Evaluation of Mass-Weighted Size Distribution Measured with the Model 3320 Aerodynamic Particle Sizer, *Aerosol Sci. Technol.* 36:845–854.
- Tuch, Th., Brand, P., Wichmann, H. E., and Heyder, J. (1997). Variation of Particle Number and Mass Concentration in Various Size Ranges of Ambient Aerosols in Eastern Germany, *Atmos. Environ.* 31:4193–4197.
- Wang, S. C., and Flagan, R. C. (1989). Scanning Electrical Mobility Spectrometer, *J. Aerosol Sci.* 20:1485–1489.
- Willeke, K., and Baron, P. A. (1992). *Aerosol Measurement: Principles, Techniques, and Applications*. John Wiley & Sons, New York.
- Wittig, B., Anderson, N., Khlystov, A. Y., Pandis, S. N., Davidson, C., and Robinson, A. L. (2004). Pittsburgh Air Quality Study Overview and Preliminary Scientific Findings, *Atmos. Environ.* in print.
- Wolfenbarger, J. K., and Seinfeld, J. H. (1991). Regularized Solutions to the Aerosol Data Inversion Problem, *SIAM J. Sci. Stat. Comput.* 12:342–361.