

**Dry-Ambient Aerosol Size Spectrometer  
(Nano-SMPS, SMPS, APS)**

**Data Quality Statement  
Pittsburgh Air Quality Study July 1, 2001 – June 30, 2002**

**1. Introduction**

The purpose of this data quality statement is to provide information on the quality of size distributions measured by the Dry-Ambient Aerosol Size Spectrometer (DAASS) during the Pittsburgh Air Quality Study.

The Dry-Ambient Aerosol Size Spectrometer (DAASS) includes three particle sizing instruments with associated supporting equipment as shown in Figure 1. The particle sizing instruments include two Scanning Mobility Particle Sizers (SMPS) and one Aerosol Particle Sizer (APS). The SMPS instruments size particles from 3 – 80 nm (TSI 3936N25) and 13 – 680 nm (TSI 3936L10), while the APS (TSI 3320/3321) covered 0.5 – 10  $\mu\text{m}$ . These systems are referred to as the Nano-SMPS, SMPS, and APS systems. Two separate relative humidity controlled inlets served the aerosol sizing instruments. One inlet conditioned aerosols for the SMPS systems while a separate inlet conditioned aerosols for the APS. Supporting these components are a dry air supply system, and humidity conditioning systems for the sheath air flows of both SMPS systems and the APS.

The DAASS ran from June 1, 2001 – September 26, 2002. However, as of May 22, 2003 only the dried size distributions from the first 12 month period (2001/7/1 – 2002/6/30) have been submitted to NARSTO. Two papers summarize the first 12 months of results and the design and operation of the DAASS. These are:

- Charles O. Stanier, Andrey Y. Khlystov, Wanyu R. Chan, Mulia Mandiro, Spyros N. Pandis. (2003) A Method for the In-situ Measurement of Fine Aerosol Water Content of Ambient Aerosols: The Dry-Ambient Aerosol Size Spectrometer (DAASS). *Aerosol Science and Technology*, in press.
- Charles O. Stanier, Andrey Y. Khlystov, and Spyros N. Pandis. (2003) Ambient Aerosol Size Distributions and Number Concentrations Measured During the Pittsburgh Air Quality Study (PAQS). Submitted to *Atmospheric Environment*.

Also of interest to the data user may be the paper:

- Andrey Khlystov, Charles Stanier, Spyros Pandis. (2003) An Algorithm For Combining Electrical Mobility And Aerodynamic Size Distributions Data When Measuring Ambient Aerosol. *Aerosol Science and Technology*, in press.

For the design and operation of the DAASS, the reader is referred to the method paper listed above. The discussions of error and uncertainty in the cited papers are used in this data quality assessment with additional quantification.

## **2. Quality Control Information**

The data presented here are Level 2 validated, i.e. NARSTO flags were applied to all data points, data between the 3 aerosol size instruments were reviewed comparatively, and data was compared to other highly time-resolved measurements and checked for qualitative (meteorology, SO<sub>2</sub>, NO<sub>x</sub>, CO) and quantitative (TEOM PM2.5) agreement.

## **3. Methods for calculating MDL, Precision, Accuracy, and Data Completeness**

The following calculations are done to assess how faithfully the DAASS data represents the true aerosol size distribution. The DAASS size distributions are reported in the NARSTO data archive as 5 minute samples reported every 7.5 or 15 minutes. Ideally the reported size distribution would equal the true 5-minute average of the size distribution with perfect precision and zero bias.

### **3.1 MDL (Minimum Detection Limit)**

Each of the instruments operated on physical principles allowing detection of individual particles. Therefore, there is no inherent “minimum detection limit” in terms of aerosol number concentration. The smallest size particle detectable by the system was governed by the ability of the TSI 3025 ultrafine CPC to detect particles. The 50% detection cutoff of this particle counter was determined by laboratory tests at the University of Minnesota Particle Technology Laboratory to be 2.9 nm (Sakurai, 2002). The sampling of very small (<20 nm) particles and large (> 1 µm) particles was also affected by losses in the inlet. The effect of this is discussed in the accuracy and precision sections.

### **3.2 Precision (The coefficient of variation, CV(%))**

Sampling precision by an SMPS system is dependent on particle size and the ambient particle concentration. The equations for theoretical precision of the instruments are developed in Appendix 1 and then applied to the DAASS in Table 2. The coefficient of variation ( $\sigma_N/N$ ) for the individual size channels of the instruments when measuring a typical size distribution are below 15% for all instruments for aerosol sizes greater than 10 nm. The best precision (<2% coefficient of variation) is expected by the SMPS instrument between about 50 and 300 nm, and by the APS instrument between 0.63 and 1.0  $\mu\text{m}$ . The worst precision is expected by the N-SMPS below 10 nm, with decreasing precision at smaller sizes.

The coefficient of variation is calculated in Table 2 for some representative particle sizes and values of N. It should be noted that the precision is calculated in Table 2 is for the bin sizes reported for the DAASS in the NARSTO archive (64 channels per decade for SMPS & manufacturer size bins for APS). Precision can be improved by binning data less finely. The non size-dependent parameters are listed for the various instruments in the following Table.

	<u>N-SMPS</u>	<u>SMPS</u>	<u>APS</u>
$\Delta t$	2.34 sec	2.34 sec	90 sec
Q	1.5 LPM	1.0 LPM	1 LPM
$Q_{\text{mono}}/Q_{\text{sh}}$	1.5 / 7.0	1.0 / 3.2	NA
$DR_{\text{CPC}}$	50	1	1

Table 1. Important parameters for instrument precision

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
												perfect inlet		with inlet losses	
	<u>Concen.</u>														
<u>Size (nm)</u>	<u>dN/dln(Dp)</u>	<u>Inst</u>	<u>deltat</u>	<u>Q</u>	<u>Qmono</u>	<u>Qsh</u>	<u>Qmono/Qsh</u>	<u>DRCP</u>	<u>f+1</u>	<u>transinlet</u>	<u>effcount</u>	<u>c</u>	<u>CV</u>	<u>c</u>	<u>CV</u>
3	7000	N-SMPS	2.34	1.5	1.5	7	0.21	50	1.1%	1.0%	100%	19.3	22.8%	0.2	227.6%
6	7000	N-SMPS	2.34	1.5	1.5	7	0.21	50	2.3%	24%	100%	40.7	15.7%	9.8	32.0%
10	7000	N-SMPS	2.34	1.5	1.5	7	0.21	50	4.1%	55%	100%	72.1	11.8%	39.7	15.9%
15	7000	N-SMPS	2.34	1.5	1.5	7	0.21	50	6.4%	70%	100%	111.6	9.5%	78.1	11.3%
15	7000	SMPS	2.34	1	1	3.2	0.31	1	6.4%	70%	100%	5,427.0	1.4%	3,798.9	1.6%
50	7000	N-SMPS	2.34	1.5	1.5	7	0.21	50	17%	93%	100%	297.7	5.8%	275.4	6.0%
50	7000	SMPS	2.34	1	1	3.2	0.31	1	17%	93%	100%	14,471.9	0.8%	13,386.5	0.9%
100	7000	SMPS	2.34	1	1	3.2	0.31	1	21%	96%	100%	18,243.5	0.7%	17,513.7	0.8%
500	57	SMPS	2.34	1	1	3.2	0.31	1	14%	95%	100%	97.5	10.1%	92.6	10.4%
630	31	SMPS	2.34	1	1	3.2	0.31	1	13%	95%	100%	47.3	14.5%	44.9	14.9%
630	31	APS	90	1	na	na	na	na	na	100%	72%	33,486.7	0.5%	33,486.7	0.5%
1000	2.2	APS	90	1	na	na	na	na	na	100%	90%	2,970.6	1.8%	2,970.6	1.8%
2500	0.26	APS	90	1	na	na	na	na	na	83%	100%	390.1	5.1%	323.8	5.6%

Table 2. Results of precision calculation for size distribution measurements at PAQS. Notice that coefficient of variation (CV), columns 14 and 16 is very size (Column 1) dependent. Concentrations (column 2) are within 50% of the grand average for the study. Column 4 is the approximate time (sec) spent sampling at a given size channel during each 5 minute scan. Q is the inlet flow in LPM. Qmono and Qsheath are flows in the DMA (LPM). f+1 is the fraction of particles charged to +1. c (columns 13 and 15) are the expected number of particles seen at the detector during the sampling period and the CV (column 14) is the coefficient of variation expected from Poisson statistics.

### **3.3 Accuracy**

There are two types of accuracy required in the particle size distributions – sizing accuracy (i.e. reporting the correct mobility diameter of particle and correct position of modes in particle size distributions), and counting accuracy (e.g. reporting the correct concentration of particles for a given size).

#### **3.3.1 Sizing Accuracy, SMPS**

Sizing accuracy is mainly determined by performing the data inversion with correct values for sheath flow and column voltage. Sizing accuracy can be checked by sizing particles of known size (often monodisperse polystyrene latex (PSL) spheres). Sizing accuracy can also be assessed by comparing sizing results from one SMPS to another SMPS. Prior to the study, sizing accuracy of the SMPS instruments was measured at 3% or better using monodisperse aerosols in the laboratory. Sizing accuracy during the study was maintained to within about 10%, based on monthly checks of sheath flow values. After one year of operation, the SMPS was challenged with 155 nm PSL (6/11/02) and sized the PSL at 151-157 nm. Relative sizing between the SMPS and N-SMPS was checked extensively on 6/9/02 and 6/12/02 with agreement from 5-10% (on average N-SMPS was sizing 7% larger than SMPS).

#### **3.3.2 Counting Accuracy, SMPS**

Assessing counting accuracy is difficult as there is no primary standard for total or size resolved particle counts. However, estimates are made for the SMPS counting accuracy during PAQS. To summarize, the SMPS size-resolved counting accuracy is within 25% for sizes greater than 50 nm, accurate to a factor of 2 at 10 nm, accurate to a factor of 4 at 6 nm, and accurate to a factor of 10 at 4 nm.

Accurate counting by SMPS depends on accurate inversion of the raw data. The inversion requires knowledge of many parameters, including the charge distribution of particles, instrument flowrates, inlet transmission efficiency, and the DMA transfer function. The accuracy of the inversion at 5 nm is estimated by Birmili et al. (2003) as  $\sim \pm 30\%$  including errors

in CPC counting efficiency (~ 10%), DMA transfer function (~ 20%), and bipolar charge distribution (~ 20%). This accuracy improves to ~20% at larger sizes (50 nm – 500 nm). This can be thought of as a best case accuracy of SMPS in a long-term field deployment. Indeed, one spot check of counting efficiency was done during PAQS where aerosol in the 50-500 nm range was fed to the DAASS system and to a stand-alone 3010 CPC, with agreement in particle number to 20%.

This best case accuracy ( $\pm \sim 30\%$  at 5 nm and  $\pm \sim 20\%$  from 20-500 nm) is modified by circumstances specific to the DAASS and the Pittsburgh Air Quality Study. These are listed in the following table:

Feature or circumstance	Affect on SMPS accuracy	Reference																					
Inversion only considered +1 charges and impactor not used to reduce contribution of multiple charging	Bias count of large (>~300 nm) particles high by up to 10%	Khlystov et al. (2003)																					
Charging may be done at different relative humidity than particle sizing due to placement of charger relative to DMA. Charging was typically done at a RH higher than the final RH of the dried samples.	Bias count of particles <200 nm high by as much as 15%. Bias count of particles >200 nm low by as much as 15%.	Stanier et al. (2003a)																					
Larger inlet (for drying) than typically used for N-SMPS studies had high and uncertain losses	In data inversion, 50% transmission of inlet assumed at 9 nm, but could be anywhere from 3 nm- 10 nm. Therefore, particle counts become increasingly uncertain from 10 nm to 3 nm. The following estimates may be useful in interpreting data:  <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Size</th> <th>Transmission used In data reduction</th> <th>Possible range</th> </tr> </thead> <tbody> <tr> <td>10 nm</td> <td>54%</td> <td>50% - 75%</td> </tr> <tr> <td>8 nm</td> <td>40%</td> <td>38% - 69%</td> </tr> <tr> <td>6 nm</td> <td>26%</td> <td>21% - 58%</td> </tr> <tr> <td>5 nm</td> <td>14%</td> <td>13% - 50%</td> </tr> <tr> <td>4 nm</td> <td>5%</td> <td>5% - 40%</td> </tr> <tr> <td>3 nm</td> <td>1%</td> <td>0.6% - 25%</td> </tr> </tbody> </table>	Size	Transmission used In data reduction	Possible range	10 nm	54%	50% - 75%	8 nm	40%	38% - 69%	6 nm	26%	21% - 58%	5 nm	14%	13% - 50%	4 nm	5%	5% - 40%	3 nm	1%	0.6% - 25%	Experimental data on inlet loss down to 20 nm and modeling of losses using correlations in Willeke and Baron (1993)
Size	Transmission used In data reduction	Possible range																					
10 nm	54%	50% - 75%																					
8 nm	40%	38% - 69%																					
6 nm	26%	21% - 58%																					
5 nm	14%	13% - 50%																					
4 nm	5%	5% - 40%																					
3 nm	1%	0.6% - 25%																					

Table 3. Known biases and uncertainties in SMPS particle counts

### 3.3.3 Combined Sizing and Counting Accuracy, APS

Because of the lack of a primary standard for particle number, a reasonable method for assessing sizing and counting accuracy for an APS is to first gage sizing accuracy by challenging with monodisperse aerosol, and then (with known sizing accuracy) compare the APS aerosol volume (in conjunction with other particle sizers) to continuous mass records such as TEOM2.5 or FRM filters. One can then compute an effective density required to reconcile the mass time

series (TEOM) and the volume (APS-SMPS) time series. If the counting and sizing of the APS is accurate, the effective density will be a reasonable value consistent with the aerosol chemistry.

Unfortunately, during PAQS, the APS was only challenged with monodisperse aerosol prior to deployment and once in the field. As a consequence, there is not a sufficient database to independently judge sizing and counting accuracy. Therefore, counting and sizing accuracy are assessed together, rather than independently. Details of the assessment follow, but results are summarized here:

- (1) July 1 – October 7, 2001. Assessment for this time period (1) is that sizing and counting are the least biased of the study. Calculated densities for overlap with SMPS are reasonable, if somewhat more variable than expected. Ghost particles distorting volume distribution at sizes above 5 microns. APS PV2.5 volume good to about a factor of 1.5.
- (2a) May 7, – May 31, 2002. APS response highly variable during this period. On average, either sizing is biased toward large sizes or counting is high. Accuracy of aerosol PV2.5 volume calculated from APS probably only good to a factor of 2. Ghost particle problem gone.
- (2b) June 1 – June 17, 2002. APS response less variable than previous period, but biased toward small sizes by about 20% and to low counts. APS calculated PV2.5 volume during this period good to about a factor of 3.
- (2c) June 18 – June 30, 2002. APS variability not too bad, although sizing and/or counting seem to be biased high. APS PV2.5 volumes during this period good to about a factor of 2.

An important note before the detailed QA considerations: The sizes reported in the NARSTO archive are the aerodynamic sizes recorded by the APS assuming a density of 1.0. The calibration curves are based on calibration with monodisperse PSL (correcting for density of 1.05) and monodisperse ammonium sulfate (correcting for density of 1.76) for sizes less than 2.5  $\mu\text{m}$  and manufacturer calibration curve at sizes  $> 2.5 \mu\text{m}$ . In other words, a spherical particle of diameter 1.0  $\mu\text{m}$  with density 1.0  $\text{gcm}^{-3}$  is reported as a 1.0  $\mu\text{m}$  particle. A 1.0  $\mu\text{m}$  with density 1.5  $\text{gcm}^{-3}$  is reported as a  $1.0/\sqrt{1.5} = 0.82 \mu\text{m}$  particle (neglecting slip correction). The relationship between density, size, and shape is discussed at length by Khlystov et al. (2003). Also reported in the NARSTO archive is an effective density, calculated for each hour of the study according to the procedures in Khlystov et al. (2003). Using the effective density, the reported aerodynamic number distribution can be converted to a “mobility” number distribution that should line up with the SMPS in the overlap region of 530-680 nm. The following section assesses the accuracy of the aerodynamic sizes measured by the APS, but not the accuracy of the effective density estimates or the “mobility” number distributions (for that, the data user is referred to Khlystov et al. 2003). The sizing of the APS depends on the calibration curve relating the time of flight of particles (measured by the APS) to their aerodynamic size. This

calibration table is provided by the manufacturer (TSI Inc.) based on individual instrument calibrations done with monodisperse PSL. For PAQS, the manufacturer calibration curve was discarded and new calibration curves were constructed, using the procedure described in Khystov et al. (2003).

For QA purposes, the APS deployment is divided into: (1) the APS 3320 deployment (July – October, 2001) where accuracy was relatively good; and (2) the APS 3321 deployment May 7 – June 30, 2002. Period (2) was characterized by poor stability of the sizing calibration, inlet flowrate, and sheath flowrate. Period (2) can be divided into three periods: (2a) May 7 – May 31; (2b) June 1 – 17; and (2c) June 18 – June 30, 2002.

#### Deployment period 1: July – October 2001

The APS was run for two distinct periods during PAQS, and was serviced and upgraded during the interval between. The APS ran from July 1, 2001 – October 7, 2001 in the “3320” model number configuration. The 3320 APS model suffers from an internal recirculation problem leading to the misclassification of small particles as large (Armendariz and Leith, 2002). This “ghost particle” problem has little effect on the number distribution, but badly distorts the volume distribution at sizes above 5  $\mu\text{m}$ , as can be seen from the impactor-APS comparison in Figure 2. The second problem experienced from July 1 – October 7 was an electronic problem specific to the instrument run at PAQS. During increasing frequent intervals, the APS reported unreasonably high particle counts, and reported particle counts even with a filter attached to the inlet. These periods typically lasted several hours and occurred during times of high (>80% RH) and low temperature (<18  $^{\circ}\text{C}$ ). This transient problem was determined to be an electronic problem in the photodetector sensitivity. During the problem periods, the threshold for particle detection was lowered such that particles were incorrectly counted. These periods have been identified through comparison with the LDMA and invalidated using NARSTO flag M2.

#### Deployment periods 2: May – June 2002

During the winter of 2001-2002, the APS was upgraded to the “3321” model configuration. The upgrade specifically includes a redesigned inlet to remove the particle recirculation causing the “ghost particle” phenomenon. The electronics are upgraded as well, improving performance in the correlated sampling mode (not used during PAQS). Through laboratory testing, it was verified that the ghost particle problem was eliminated by the upgrade. The APS 3321 was then deployed and sampled from May 7, 2002 – June 30, 2002, using an in-



house calibration curve. The APS 3321 was challenged with 2.06  $\mu\text{m}$  PSL on June 12, 2002 and sized it at 1.6-1.7  $\mu\text{m}$ . During this time, the APS sheath and aerosol flows were not as stable as normally seen (variations of  $\pm 30\%$  from setpoints). The APS inlet was cleaned on June 17, improving the flow stability issue, and recalibrated on 6/18/02. From June 18, 2002 – June 30, 2002, it performed well and compared reasonably to the SMPS results in the overlap range.

To quantify the performance of the APS, we rely on the fact that a “reasonable” density should reconcile the aerodynamic diameter measured by the APS with the mobility size measured by the SMPS. An effective density of 1.0 means that no adjustment to the APS distribution is required for agreement. Effective densities of greater than 1.0 mean that the APS distribution must be shifted to the smaller sizes to match SMPS data and that the raw APS particle counts at aerodynamic sizes 530-680 nm are greater than the particle counts at mobility sizes 530-680 nm by SMPS. Effective densities of less than 1.0 mean that the APS distribution must be shifted to larger sizes and that the raw APS particle counts at aerodynamic sizes 530-680 nm are less than the particle counts at mobility sizes 530-680 nm by SMPS. A time series of hourly effective densities is shown in Figure 3. Figure 3b shows that the counting (and possibly sizing) accuracy of the APS was poor after its redeployment on May 7, 2002. Figure 3b divides that data into three periods: May 7 – May 31, June 1-June 17, and June 18-June 30. As noted in section 3.3.1.2, flow control problems were noted during this period.

To make a quantitative estimate of bias, we assume a correct density, and calculate a combined sizing/error according to the following formula, adapted from Khlystov et al. 2003:

$$\frac{\rho_{eff,calc}}{\rho_{true}} = (Z)^{1/B} \sqrt{M} \quad (5)$$

Where  $Z$  is the factor by which the APS undercounts (e.g.  $Z=1$  is perfect counting;  $Z=1.1$  is undercounting by 10%),  $M$  is the factor by which sizing is off ( $M=1.1$  means measured aerodynamic size is 10% larger than actual),  $B$  is the slope of the power law that describes the decay of the number distribution (assumed to be -3 Khlystov et al. 2003), and  $\rho_{true}$  and  $\rho_{eff,calc}$  are the true particle density and density required for SMPS-APS reconciliation, respectively.  $\rho_{eff,calc}$  is graphed in Figure 3 for Periods 1 and 2 of the APS deployment.

By plugging in reasonable values\* of  $\rho_{\text{true}}$  into equation (5) we can calculate estimates of counting accuracy (assuming perfect sizing) and sizing accuracy (assuming perfect sizing).

These results of this analysis are shown in the following table.

Table 4. Assessment of sizing/counting accuracy of APS

Period	Range $\rho_{\text{true}}$	Range $\rho_{\text{calc}}$	Worst case sizing accuracy if perfect counting*	Worst case counting accuracy if perfect sizing*	Source
(1) July 1 – October 7, 2001	1.2 – 1.77	0.94 – 1.94	x 1.2, ÷ 1.4	x 1.25, ÷ 2	Figure 3a
	1.5	1.25 – 1.8	x 1.4, ÷ 1.4	x 1.7, ÷ 1.7	Figure 4
	<i>Assessment for this time period (1) is that sizing and counting are the least biased of the study. Calculated densities for overlap with SMPS are reasonable, if somewhat more variable than expected. Ghost particles distorting volume distribution at sizes above 5 microns. APS PV2.5 volume good to about a factor of 1.5.</i>				
(2a) May 7, – May 31, 2002	1.2 – 1.77	1.1 – 2.5	x 2.0, ÷ 1.15	x 2.8, ÷ 1.3	Figure 3b
	<i>APS response highly variable during this period. On average, either sizing is biased toward large sizes or counting is high (note factory calibration was used). Accuracy of aerosol PV2.5 volume calculated from APS probably only good to a factor of 2. Ghost particle problem gone.</i>				
(2b) June 1 – June 17, 2002	1.2 – 1.77	0.7 – 1.8	÷ 1.1 to 2.4	÷ 1.1 to 3.3	Figure 3b
				÷ 1.2	Challenge with PSL
	<i>APS response less variable than previous period, but biased toward small sizes by about 20% and to low counts. APS calculated PV2.5 volume during this period good to about a factor of 3.</i>				
(2c) June 18 – June 30, 2002	1.2 – 1.77	1.4 – 2.2	x 1.3 to 1.5	x 1.5 to 1.9	Figure 3b
	<i>APS variability not too bad, although sizing and/or counting seem to be biased high. APS PV2.5 volumes during this period good to about a factor of 2.</i>				

\*x 1.2 means APS is measuring 1.2 times true aerodynamic diameter or counting 1.2 times the true number of particles.

### 3.4 Data Completeness

Data completeness is calculated from Table 1 of Stanier et al. (2003b). A complete day of data is defined as having valid data for at least 75% of the hours of the day. (A complete hour has at least 75% of possible scans valid during the hour). Using this metric, data completeness was 83%, 90%, and 28% for the N-SMPS, SMPS, and APS respectively, versus a data completeness objective of 70%.

\* As both the SMPS and APS are measuring dried aerosol size distributions, we expect particle densities representative of ammonium sulfate and organic compounds, the main contributors to aerosol mass (Anderson et al. 2002). In other words, we expect densities between 1.2 and 1.77 gcm<sup>-3</sup> (Stanier et al. 2003a).

#### 4. List of key calibrations and maintenance activities

During the 12 months covered by this data quality statement, there were several major malfunctions, including the APS, the dry air supply system, a CPC 3010, and two N-SMPS sheath blowers. These are listed in Appendix 2 together with the routine checks performed for quality assurance.

#### 5. Overall Data Quality Findings

Relative to data quality objectives stated at the beginning of the project, the quality of the data collected during the period July 1, 2001 – June 30, 2002 met objectives except as noted below:

- APS data completeness 28% versus target of 70%
- APS accuracy goals of sizing ( $\pm 20\%$  goal) & counting ( $\pm 30\%$  goal) met during all operational periods except 5/7/02-5/31/02.
- SMPS sizing accuracy goal ( $\pm 4\%$  goal) not met for entire study. Sizing accuracy was maintained to  $\sim 10\%$  or better (and to 4% or better for Summer 2001 intensive)
- SMPS counting accuracy ( $\pm 30\%$  goal) met except at sizes below 10 nm, where uncertain aerosol charging and inlet losses increase uncertainty

#### 6. References

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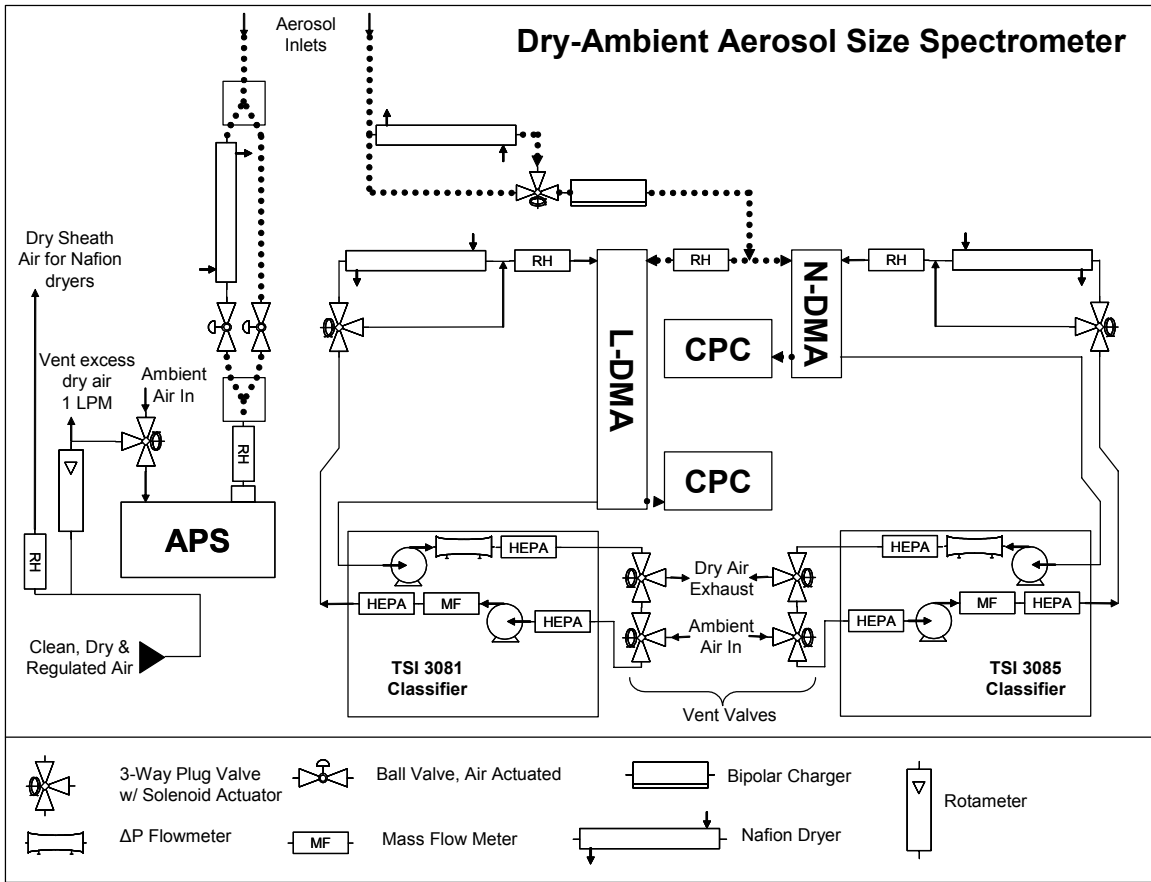


Figure 1. Flow diagram of Dry-Ambient Aerosol Size Spectrometer (DAASS). Aerosol streams are shown by dotted lines and other flows are indicated by solid lines.

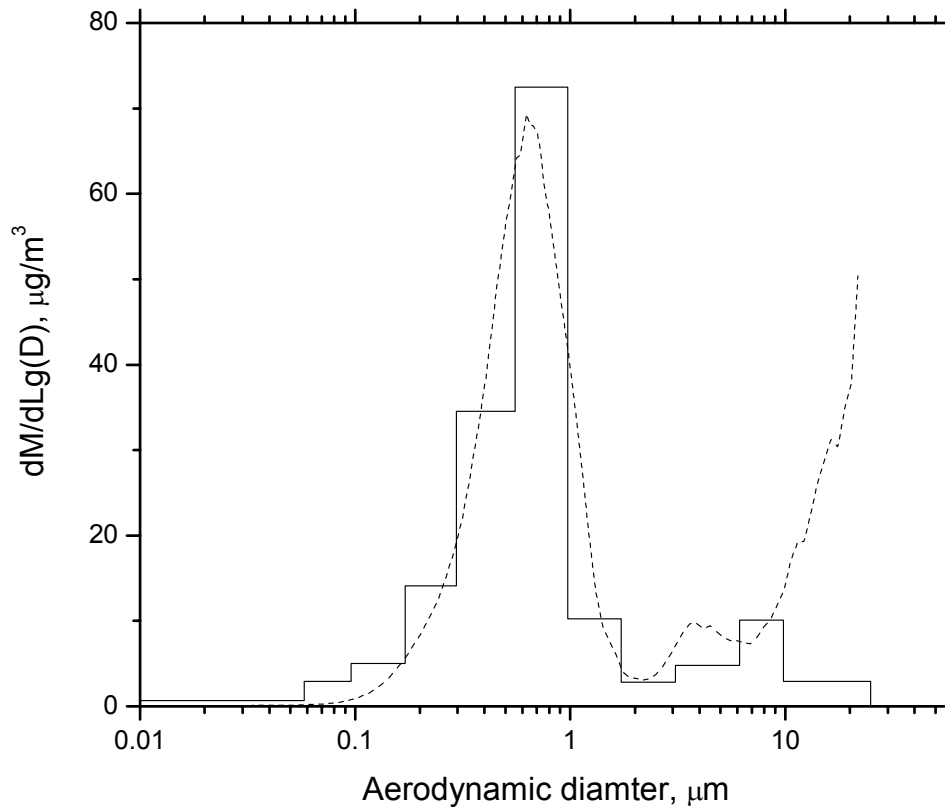


Figure 2. APS – MOUDI comparison

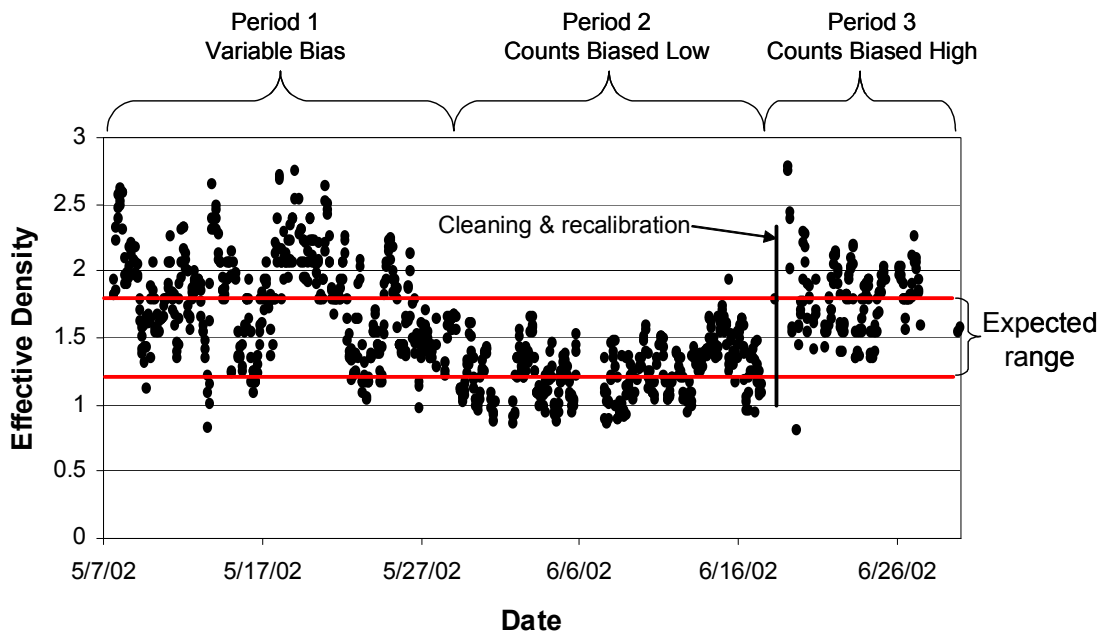
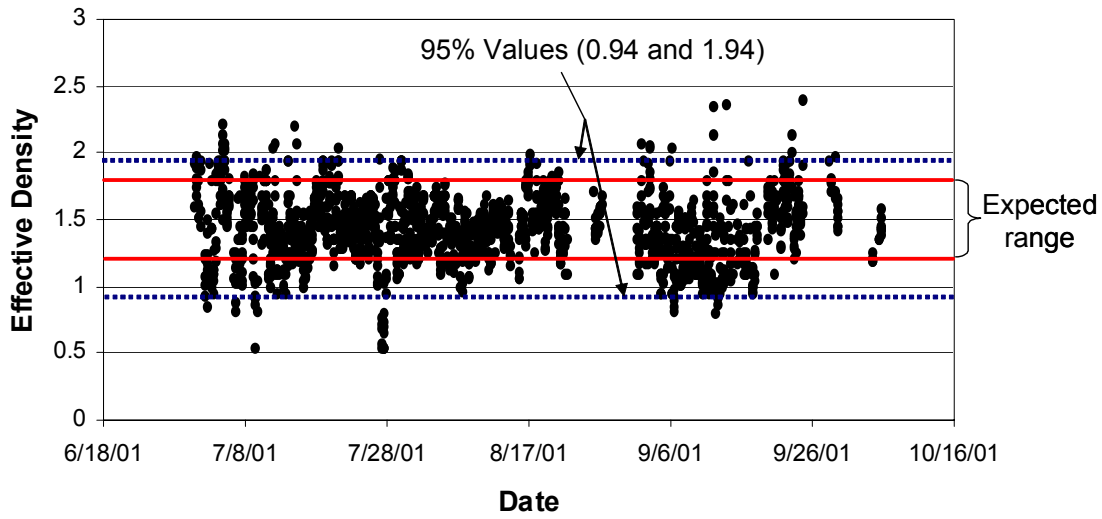


Figure 3. Time series of APS effective densities, (a) July – October 2001, and (b) May – June 2002.

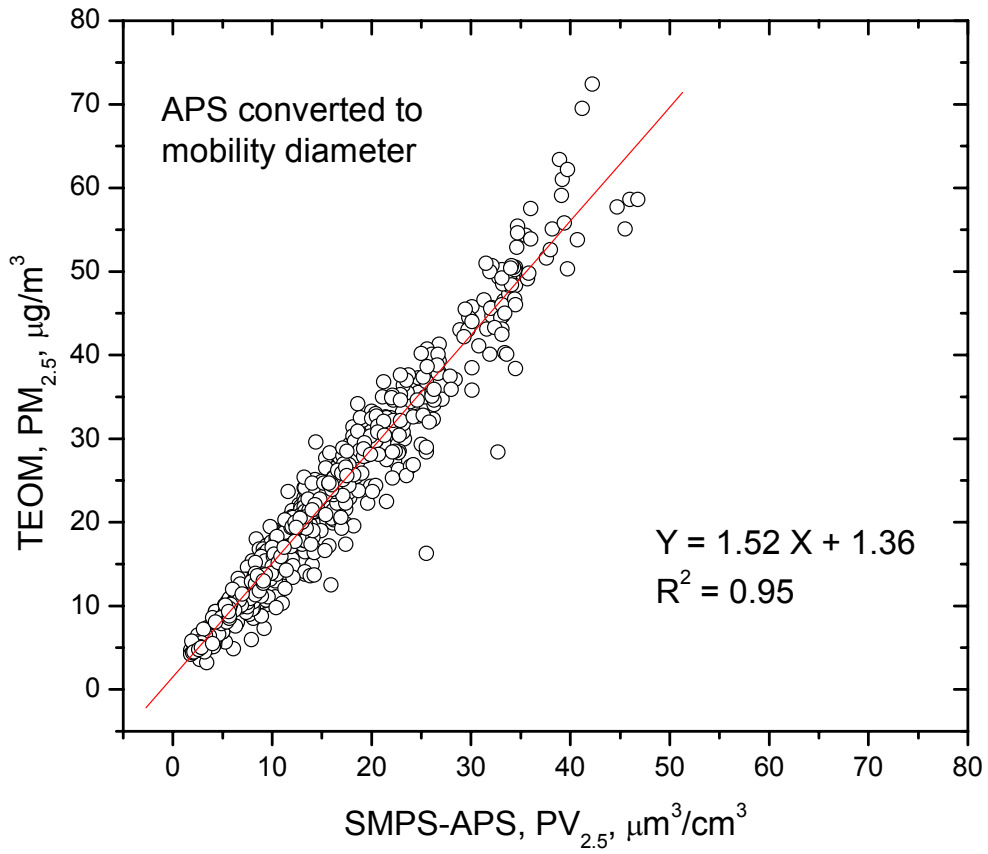


Figure 4. Comparison of SMPS-APS volume to TEOM PM2.5 for July 2001



## Appendix 1 – Theoretical Precision for Particle Sizing Instruments

In SMPS sampling, if the size distribution function ( $dN/d\ln D_p$ ) is  $n_N^e$  at the size in question, the concentration of +1 charged particles reaching the condensation particle counter, accounting for the DMA transfer function and particle charging (but not particle losses) is approximately.

$$N^{+1} = f^{+1}(D_p)n_N^e(D_p)\ln\left(1 + \frac{Q_{mono}}{Q_{sheath}}\right) \approx f^{+1}(D_p)n_N^e(D_p)\frac{Q_{mono}}{Q_{sheath}} \quad (1)$$

where  $f^{+1}$  is the fraction of +1 particles, and  $Q_{mono}/Q_{sheath}$  is the ratio of the aerosol to sheath flow in the DMA. Assuming that the SMPS system spends a time interval  $\Delta t$  sampling at this size channel, the number of +1 particles reaching the CPC (ignoring losses) is given by:

$$p = 16.67 N^{+1} \Delta t Q \quad (2)$$

where  $Q$  is the sample flowrate ( $L\text{min}^{-1}$ ), and  $\Delta t$  is the time (s) spent on that size channel.

Factoring in size dependent losses, CPC counting efficiency, and any internal dilution in the CPC, the number of particles counted by the CPC is given by:

$$c = \frac{p \text{trans}_{inlet} \text{eff}_{count}(D_p)}{DR_{CPC}} \quad (3)$$

where  $\text{trans}_{inlet}$  is the transmission efficiency through the inlet and transfer tubing,  $\text{eff}_{count}$  is the detector counting efficiency, and  $DR_{CPC}$  is dilution occurring within the CPC. This type of sampling follows a Poisson distribution such that the standard deviation on  $c$  is  $\sigma_c = \sqrt{c}$  (Weiss, 1995).

Precision will be calculated as the coefficient of variation (CV), the ratio of standard deviation of  $N$  to the value  $N$  ( $\sigma_N/N$ ). This coefficient can be calculated as:

$$CV = \frac{\sigma_N}{N} = \frac{\sigma_c}{c} = \frac{\sqrt{c}}{c} = \frac{1}{\sqrt{\frac{16.67 \Delta t Q \frac{Q_{mono}}{Q_{sheath}} f^{+1}(D_p) \text{trans}_{inlet}(D_p) \text{eff}_{count}(D_p) n_N^e(D_p)}{DR_{CPC}}}} \quad (4)$$

The formula for CV makes intuitive sense. The CV can be reduced by sampling for a longer time, increasing the inlet flow  $Q$ , and increasing the total concentration. The CV is increased as the DMA resolution is improved, CPC dilution is used, and as the charging fraction, counting fraction, and transmission efficiency are reduced. Equation (4) also applies to the APS, but ignoring (replacing by unity) the  $Q_{mono}/Q_{sheath}$ ,  $f^{+1}$ , and  $DR_{CPC}$  terms.

## Appendix 2 – List of Major Maintenance and QA Activities

Date	Description	Value (if applicable)	Goal or Setpoint (if applicable)
7/17/01	HEPA on inlet	Acceptable	
7/28/01	HEPA on inlet	Acceptable	
8/4/01	SMPS Sheath Flow Calibration Check	3.21 / 6.94	3.20 / 7.00
8/17/01	SMPS Sheath Flow Calibration Check	3.25 / 7.05	3.20 / 7.00
	APS Sheath Flow Calibration Check	4.03	4.00
	LDMA Sheath Loop Integrity	Acceptable	
	Inlet Flow Rate	2.60 SMPS 1.02 APS dry	2.50 1.00
8/24/01	DMA Columns moved outside to reduce temperature difference between DMA's and ambient		
	HEPA on inlet	Acceptable	
8/26/01	Alternation between ambient RH and dried stopped due to compressor failure. Sampling in dried mode only, with limited drying capacity		
8/28/01	HEPA on inlet	Acceptable	
10/7/01	HEPA on inlet – APS failed due to electronic noise problem	FAILURE	
10/7/01	SMPS Sheath Flow Calibration Check	3.24 / 7.15	3.20 / 7.00
10/17/01	Inlet Flow Rate	2.51 SMPS 1.03 APS dry	2.50 1.00
10/23/01	HEPA on inlet – SMPS failed due to failure in CPC-3010 Laser	FAILURE	
10/26/01	“CPC3” is swapped in for malfunctioning “CPC2” S/N XXXX on SMPS system		
10/26/01	HEPA on inlet	Acceptable	
10/30/01	Inspection of APS inlet for buildup of aerosol	No buildup	
11/14/01	“CPC2” S/N is swapped in after repair by TSI Inc. on SMPS system		
11/14/01	HEPA on inlet	SMPS unusually high at 6 #/cm <sup>3</sup> (still OK)	
11/26/01	HEPA on inlet	SMPS unusually high at 0.6 #/cm <sup>3</sup>	
11/26/01	SMPS Sheath Calibration Check	3.25 / 7.07	3.20 / 7.00
11/26/01	Inlet flowrate check	2.51	2.50
12/05/01	HEPA on inlet; SMPS fails badly; CPC2 returned to TSI due to incomplete repair job		
12/06/01	“CPC3” S/N put in SMPS system		
12/06/01	HEPA on inlet	Acceptable	
12/07/01	SMPS CPC Zero Check (see if particles counted with zero flow)	Zero particles counted	
12/23/01	Desiccant dryer added to SMPS Sheath Loop to reduce RH		
12/31/01	Desiccant dryer added to N-SMPS Sheath Loop to reduce RH		
12/31/01	HEPA on inlet	Acceptable	
1/1/02	N-SMPS Desiccant moved to outside enclosure; comparison of size distributions shows that data reduction (for the period 12/31/01 – 2/2/02) requires a N-SMPS sheath flow rate of 6.0 LPM rather than setpoint of 7.0 LPM. Reason for this is (1) increased pressure drop due to dryer in loop; (2) gradual failure of N-SMPS bypass blower; (3) possible positive pressure leak.		
1/8/02	HEPA on inlet	Acceptable	
1/30/02	N-SMPS Sheath Calibration Check (check showed flowrate was not as steady as usual)	7.2±0.25	7.0
2/2/02	N-SMPS bypass blower replaced; still having trouble reaching and staying at 7.0 LPM setpoint		
2/2/02	HEPA on inlet	Acceptable	
2/2/02	Inlet flow check	2.56	2.50
2/11/02	HEPA on inlet	Acceptable	
2/11/02	SMPS Sheath Calibration Check – N-SMPS Flow out of	3.27 / 7.54	3.20 / 7.00

Date	Description	Value (if applicable)	Goal or Setpoint (if applicable)
	range		
2/13/02	N-SMPS desiccant dryer removed to reduce pressure drop		
2/15/02	Nafion dryer for N-SMPS sheath loop swapped for new unit (no change in drying performance)		
2/15/02	SMPS Sheath Calibration Check	7.01	7.00
2/15/02	Inline Sheath Flowrate Check	3.37 / 7.10	3.20 / 7.00
3/3/02	Failure of N-SMPS Sheath Blower; reconfiguration to run in “single blower mode” but with no drying of the sheath air loop. N-SMPS not dried as much as usual during the period 3/6/02 – 4/19/02		
3/6/02	HEPA on inlet	Acceptable	
3/6/02	N-SMPS Sheath Calibration Check	7.0±0.2	7.0
3/6/02	Inlet flowrate check	2.69	2.50
4/9/02	Inline sheath flowrate check	3.20±0.05	3.20
4/13/02	HEPA on inlet	Acceptable	
4/13/02	Inlet flowrate check	2.45	2.50
4/19/02	N-SMPS Sheath Calibration Check	7.0±0.1	7.0
4/19/02	N-SMPS Sheath blower replaced with new and system returned to “dual blower mode” with sheath air drying		
4/19/02	N-SMPS Sheath Calibration Check	6.96	7.00
4/19/02	N-SMPS and SMPS sizing of monodisperse ammonium sulfate compared	N-SMPS=42 nm SMPS = 41 nm	
5/6/02	APS returned to service after servicing, upgrade to 3321 model, and laboratory calibration		
5/6/02	APS inlet HEPA check	Acceptable	
5/12/02	SMPS inlet HEPA check	Acceptable	
5/27/02	U-CPC removed from service for calibration; replaced with 3010 CPC borrowed from Lynn Russell at Princeton University (N-SMPS)		
5/27/02	Inlet flowrate check (SMPS)	1.83	1.91
6/9/02	Inlet flowrate check (APS)	1.16	1.00
6/9/02	HEPA on inlet	Acceptable	
6/9/02	Inline sheath flowrate check	3.06 / 7.68	3.20 / 7.00
6/9/02	Challenge SMPS with 155 nm PSL	151-157 nm	155 nm
6/9/02	Compare sizing of monodisperse ammonium sulfate with N-SMPS and SMPS. Results listed as N-SMPS / SMPS size	60 / 56 40 / 36	
6/10/02	HEPA on inlet	Acceptable	
6/10/02	SMPS sheath calibration check	3.22	3.20
6/11/02	Inlet flow rate check (APS / SMPS)	1.10 / 2.45	1.00 / 2.50
6/11/02	Removed Princeton 3010 CPC from N-SMPS and returned the U-CPC to service.		
6/11/02	HEPA on SMPS inlet	Acceptable	
6/11/02	Challenge SMPS with 155 nm PSL	151-157 nm	155 nm
6/12/02	Challenge APS with 2.06 µm PSL	1.60-1.72 µm	2.06 µm
6/18/02	APS pulled from service for poor flow control and sizing; inlet cleaned; returned to service and recalibrated		
6/18/02	HEPA on SMPS and APS inlets	Acceptable	
6/18/02	APS Sheath Calibration Check	3.87	4.00
6/21/02	HEPA on SMPS and APS inlets	Acceptable	
6/25/02	U-CPC flooded with butanol; returned to service after replacing all internal filters and butanol fill valve		
6/25/02	HEPA on SMPS and APS inlets	Acceptable	
6/27/02	HEPA on SMPS and APS inlets	Acceptable	
6/27/02	SMPS sheath loop accidentally flooded with liquid water & took several days to dry out		
6/30/02	Inlet flow rate check	2.42	2.50

These results of the checks in Appendix 2, together with analysis of time series of aerosol size data, analyses of aerosol counts and mode positions in overlapping size ranges, and comparisons of TEOM PM2.5 data with SMPS and APS data, have been used to make minor adjustments to the size distributions entered into the NARSTO database.