Causes of Concentration Differences Between a Scanning Mobility Particle Sizer and a Condensation Particle Counter

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Accurate aerosol concentration measurement is important in many applications of aerosol science. Here we compare aerosol concentration measurements of classified NaCl aerosol in the size range of 20 to 80 nm (diameter) between a scanning mobility particle sizer (SMPS) and a condensation particle counter (CPC). The SMPS systematically measured higher concentrations than the CPC, with the difference increasing with decreasing particle size. Experiments suggest several causes for the discrepancy. First, the factory calibration of the SMPS impactor flow was incorrect for the study site at 780 mbar. Second, the neutralizer used in the SMPS was inefficient in bringing the classified aerosol to charge equilibrium, and third, there were significant losses of charged aerosol within the CPC. The comparisons were improved with proper impactor flow calibration and proper charge neutralization of the classified aerosol before measurement by the SMPS and CPC. The results of this study point to the importance of proper conditioning of aerosol below about 100 nm for measurement with the SMPS and condensation-based particle counters.

INTRODUCTION

Accurate in situ determination of aerosol size distributions requires instruments which have been calibrated for both their size and number concentration measurements. The size calibration issue has been studied in depth (e.g., Kinney et al. 1991; Mulholland et al. 1999), while the issue of calibration with respect to number concentration has not been as well addressed. For aerosol number concentration it is common practice to use a condensation particle counter (CPC) or, when size is also required, a scanning mobility particle sizer, (SMPS) (Wang and

Flagan 1990) as such a reference. Both of these instruments are used as reference instruments for particle number concentration in the submicrometer range; however, to our knowledge the two instruments have never been shown to agree well for particles below 100 nm. Here these instruments are compared and the results are somewhat troubling. For particles below 80 nm, the SMPS concentrations are systematically higher than the CPC concentrations, with the concentration difference increasing with decreasing particle size. The instruments used were a TSI Incorporated (TSI) SMPS (Model 3936L10) and CPC (Model 3010). The CPC in the SMPS was also a model 3010 and tuned to match the external CPC in stand-alone tests. The sources of the discrepancies between the SMPS and CPC concentrations were investigated in several experiments which compared, as a function of particle size, aerosol concentrations from the SMPS and CPC. The results indicated both obvious and subtle causes for the discrepancies.

Two TSI model 3010 CPCs, (CPC-A and CPC-B) were calibrated to give identical counting efficiency. CPC-A was used as part of the SMPS system, and CPC-B as the independent reference. Comparisons were made between the SMPS and CPC-B concentrations as a function of particle size in the 20 to 80 nm range for classified aerosol and for charge-equilibrated classified aerosol. Concentration comparisons were also made between CPC-A, with a neutralizer attached upstream of it, and CPC-B for similar aerosol sizes.

Instrumentation and Aerosol Generation

The TSI Model 3936L10 SMPS system consists of an electrostatic classifier, (EC) (Model 3080), an aerosol impactor, an ^{85}Kr charge neutralizer (Model 3077) and CPC (Model 3010-S). The entire system is linked to a computer managed with TSI software. The operation of the SMPS is straightforward; however, appropriate hardware settings and physical parameters are required to scan particle sizes and to calculate particle size distributions. Among the physical parameters, gas viscosity and mean free path exhibit the most variation from sea level for the study site (Laramie, Wyoming) at 780 mbar. The sheath flow is set nominally to 6.0 $\ell\,min^{-1}$. The SMPS is operated in the
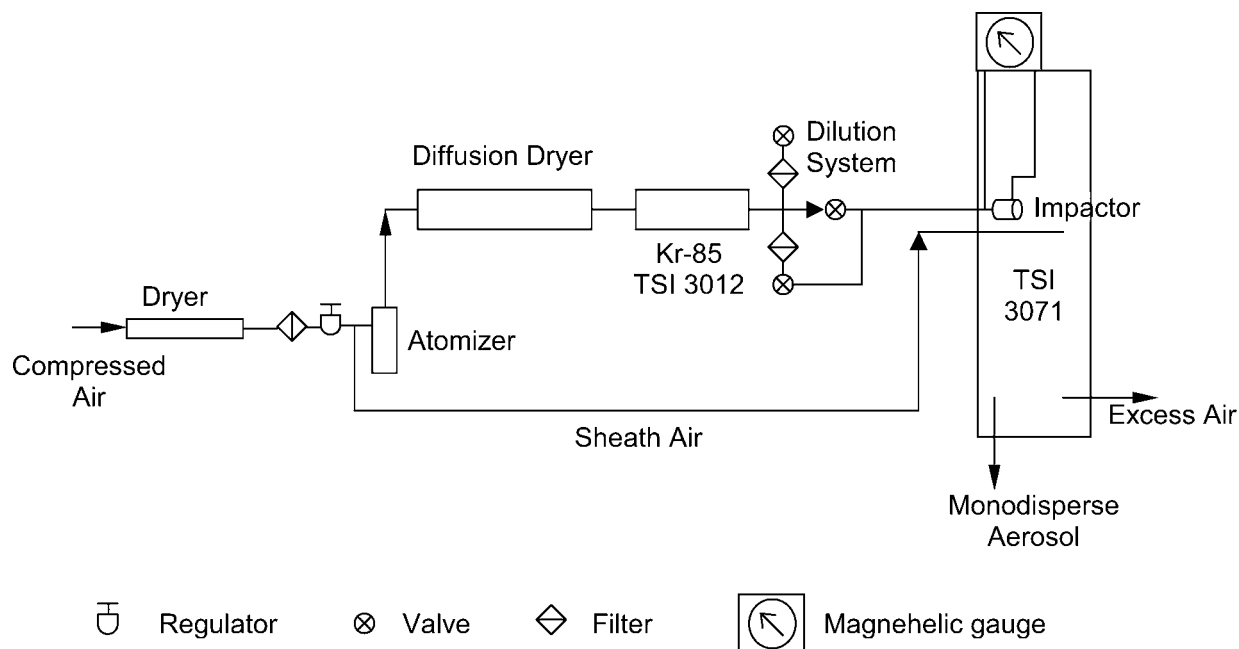
Figure 1. Monodisperse aerosol generation system TSI model 3940.

under-pressure mode in which aerosol is pulled through at the internal CPC flow rate of $1.0 \, \ell \, min^{-1}$. A flow equalizer attached upstream to the CPC flow allows for operation at lower aerosol flowrate by allowing filtered diluent air to mix with the classified aerosol. The sheath flow is recirculated and is volumetrically controlled with a microprocessor. The nominal ratio of sheath to aerosol flow is set to 10:1. A scan time of 300 s was chosen for all scans in this study to minimize broadening of the distribution (Collins et al. 2002).

Charge neutralizers are used to bring an aerosol to charge equilibrium through exposure to a bipolar ion source. Several bipolar ion sources are available, for instance [85]Kr, [210]Po, and [241]Am. It is generally assumed that the distribution of charge on aerosol leaving a neutralizer is close to charge equilibrium and can be described by the corrected Fuchs model (Fuchs 1963; Wiedensohler 1988). A neutralizer is used anytime this is desired, such as ahead of a classifier in the SMPS or in an aerosol generation system. Here, we used two different neutralizers in various configurations. The first was a TSI model 3077 which houses a 2 mCi [85]Kr source and is part of the SMPS system. At the time of the experiment the activity of the [85]Kr source is determined to be about 1.8 mCi based on the half life of [85]Kr. The second was from Aerosol Dynamics Inc., (ADI, Berkley, CA), and houses 2 mCi [210]Po source (model 2U500, NRD Inc., Grand Rapids, NY) when new. The activity of the [210]Po source at the time of the experiment is determined to be about 0.5 mCi.

Total aerosol concentration for charged particles exiting an EC can be measured with an aerosol electrometer (Liu and Pui 1974). The number concentration is determined from aerosol

flow and the current generated as the charged particles are collected on a filter in a Faraday cage. Since the particles exiting the EC are not all singly charged, a correction factor K must be applied to correct for the multiply charged particles. Here we used a Faraday cage from an existing TSI electrical aerosol analyzer and a Keithley model 610C electrometer to test the counting efficiency for the two CPCs.

A TSI submicrometer monodisperse aerosol generation system (Model 3940) shown in Figure 1 was used to generate NaCl aerosols for this study. To generate these monodisperse aerosol, a solution of 150 mg NaCl dissolved in one liter of deionized distilled water was atomized, passed through a diffusion dryer, brought to charge equilibrium with an [85]Kr neutralizer (TSI Model 3012), passed through an aerosol impactor, and size classified with an appropriate center rod voltage setting on the EC (Liu and Pui 1974; Kinney et al. 1991). The sizes selected by the EC and reported here are the mobility diameters, which do not reflect the true physical diameters, as NaCl crystals are cubic.

Comparison of CPCs

To ensure comparable measurements for the two CPCs they were tested against an aerosol electrometer for a range of sizes. Monodisperse NaCl aerosol was generated, mixed with dry filtered air in a glass-mixing chamber, routed to a stainless steel buffer chamber, and then delivered by means of conductive rubber tubing to two branches. The first branch was to an aerosol electrometer, while the second was to an ADI neutralizer and then to both CPCs. It will be apparent later why the neutralizer was necessary for the second branch. Tube lengths from

the common delivery point were made as short as possible and adjusted depending on flow rates so diffusional loss was comparable (Gormley and Kennedy 1949). The aerosol electrometer sample flow was set at 6.0 ℓ min^{-1} using a critical orifice. The electrometer analog output and the CPCs' digital outputs were acquired simultaneously. Flow rates of both CPCs and of the aerosol electrometer were checked with a Gillian bubble flow meter.

The resulting counting efficiencies of the two CPCs, using the factory default temperature setting of $\Delta T = 17°C$, are shown in Figure 2a. Data points are 2–3 min averages of stable concentrations from the aerosol electrometer and CPCs. The error bars are the combined standard deviations of individual CPC-A or CPC-B and aerosol electrometer concentrations added in quadrature. The 50% counting efficiency for NaCl particles is estimated at about 20 nm. Below about 40 nm, the counting efficiency is slightly different between the two CPCs (Figure 2b). This slight difference may be caused by drift in the thermisters used to measure the temperatures in the CPCs. To improve the comparison between the two CPCs, the temperature difference between the saturator and the condenser on CPC-A was increased by 0.3°C. This adjustment resulted in better agreement between the two CPCs as shown in Figure 2b. All further experiments were performed with this temperature adjustment. Within the standard SMPS processing, the CPC counting efficiency, determined in a similar way as in Figure 2a, is included to provide number concentration. However, for these tests the SMPS data correction for the CPC counting efficiency was not employed to provide a straightforward comparison to the external CPC.

RESULTS

SMPS and CPC Concentration Comparisons

The experimental configurations for all comparisons of classified aerosol between SMPS and an external CPC are shown in Figure 3. The components encased within dotted rectangles were used in a fraction of the experiments and will be referenced as needed. The particle concentration ranged from about 1000 to 2900 cm^{-3}. The first SMPS to CPC comparison excluded the ADI neutralizer, but included the TSI 3077 neutralizer and is a configuration that is commonly used. For this comparison, using factory calibrated aerosol flow, the SMPS concentrations for 50–80 nm particles are about 20% higher than CPC concentrations, with this difference increasing for particles less than 50 nm. This discrepancy could arise from errors in the aerosol flow rate through the instruments, errors in one of the components of the SMPS system, or differences in the number of particles transiting the sample path.

Aerosol flow measurement in the SMPS is obtained from the pressure drop across the impactor which is factory calibrated. The SMPS operating manual (TSI 2000) tabulates the pressure drop across the impactor orifice and the corresponding
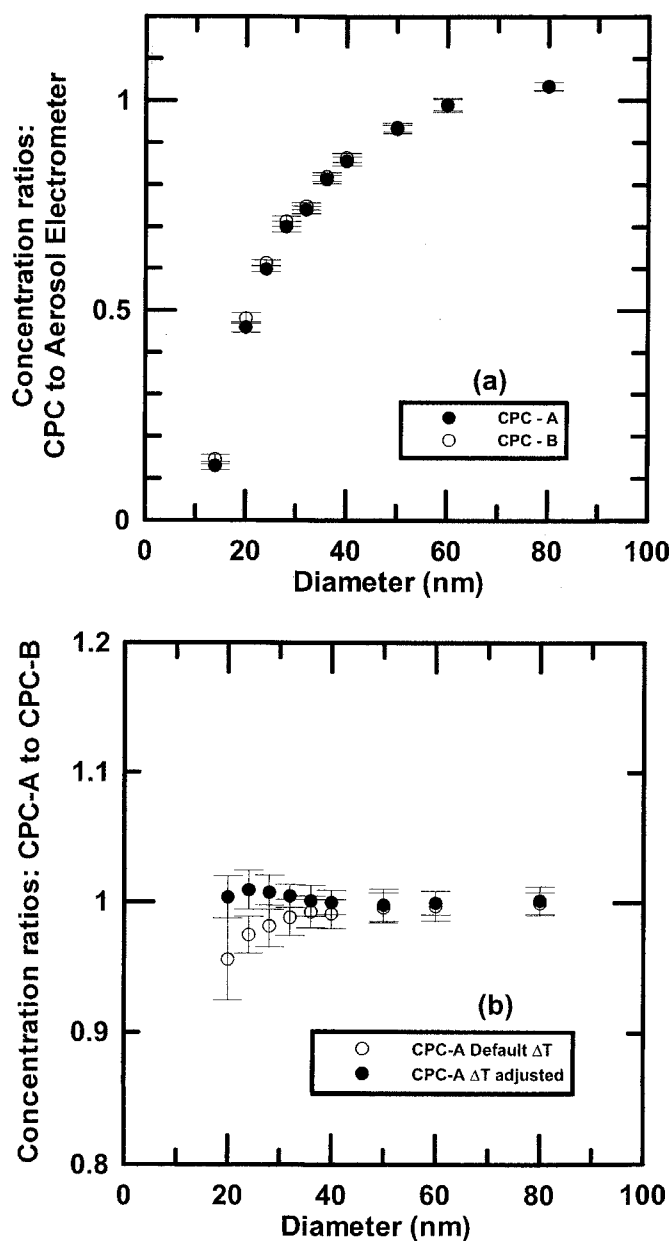

Figure 2. (a) CPC-A and CPC-B efficiency curves for NaCl aerosol using an aerosol electrometer as the standard. (b) Concentration ratios, CPC-A to CPC-B, for factory temperature settings (hollow circles) and after temperature adjustment on CPC-A (filled circles).

estimated flow rates, emphasizing the fact that the pressure drop is approximate and should not be substituted for the calibration data provided with each SMPS system. These calibration data, however, are valid only for the factory calibration conditions near sea level. The aerosol flows displayed on the front panel of the SMPS are not valid for operations at pressures significantly different from the factory calibration conditions, as,
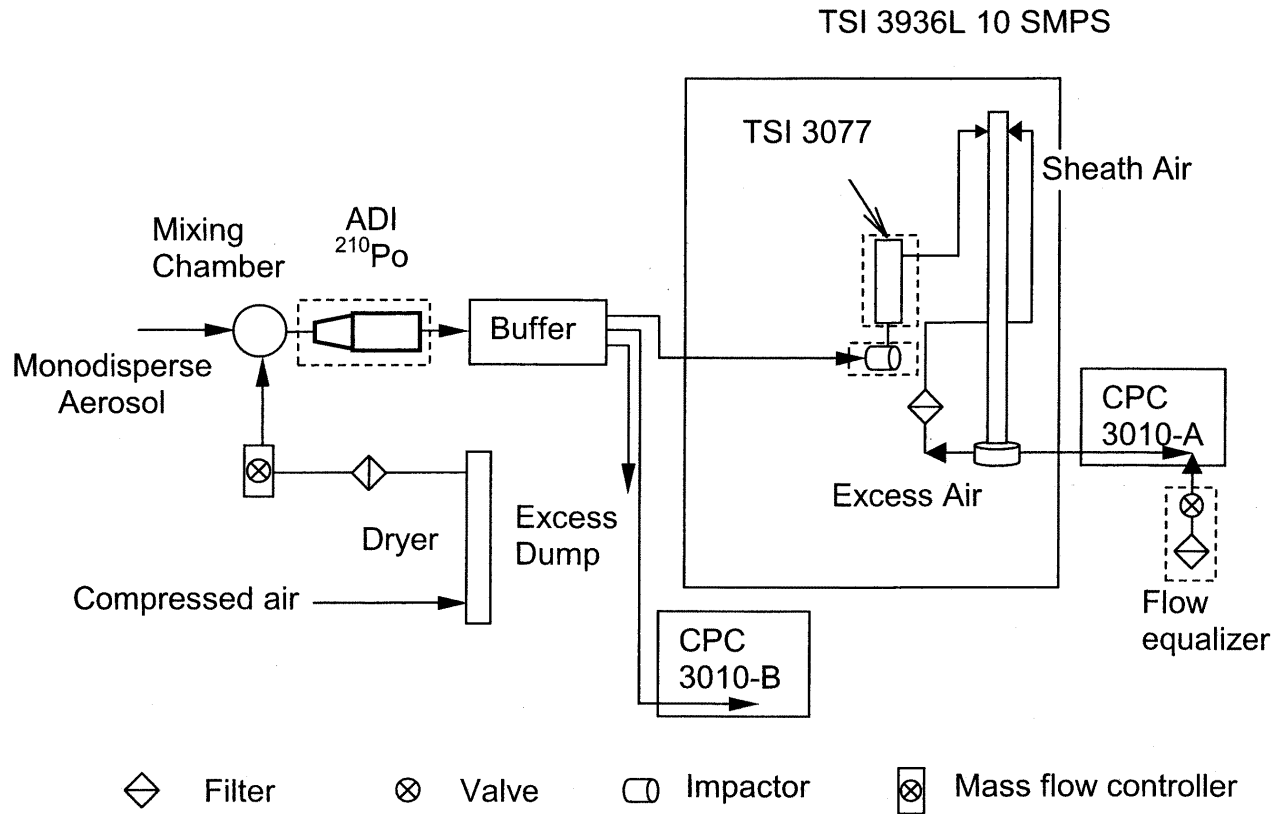
Figure 3. Experimental setup for comparison of concentrations of diluted classified aerosol measured by SMPS and CPC. Components enclosed in dotted rectangles were included only in some experiments. The ADI neutralizer was inserted later for charge equilibration of the classified aerosol. The TSI 3077 neutralizer, the impactor, and the flow equalizer were removed for later experiments. (see text for explanation).

for example, this study site at 780 mbar. In this case the impactor needs to be calibrated for ambient air pressure where the measurements are being made, otherwise errors in aerosol concentration measurement will occur. The impactor was calibrated with a Gilian bubble flow meter and included in the SMPS calibration software following the calibration procedure outlined in the operating manual. Figure 4 illustrates the difference between the factory calibration near sea level and one at 780 mbar. At the SMPS operating flow of 0.6 ℓ min^{-1}, the factory calibration indicates the measured ΔP should be 37 cm of H_2O. At the study site this ΔP leads to a flow rate of 0.7 ℓ min^{-1}, a 17% increase.

The second comparison between the SMPS and CPC measurements used the local impactor flow calibration and the results are shown in Figure 5. In this comparison, the SMPS and CPC agree to within 10% for particles greater than 40 nm; however, below 40 nm the SMPS concentrations are still greater than those of the CPC and the discrepancy increases with decreasing particle size. The error bars on the plot are the combination of the standard deviations of CPC concentration over the SMPS measurement period, i.e., 300 s, and an estimated instrumental uncertainty in the SMPS of 2% due primarily to flow uncertainty. These uncertainties are added in quadrature.
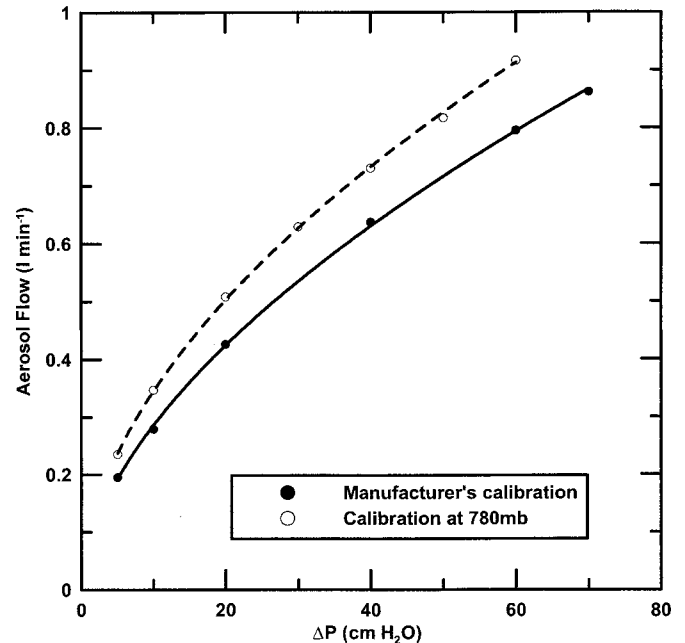

Figure 4. Comparison of TSI flow calibration and that performed at 780 mbar, the study site, for the 0.0457 cm impactor.
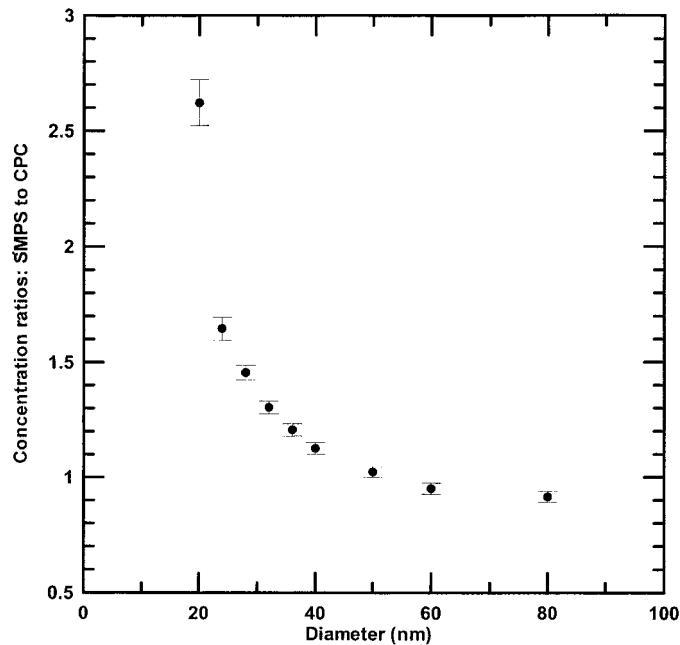
Figure 5. SMPS to CPC concentration ratios with new impactor flow calibration and setup as shown in Figure 3 but without the ADI neutralizer before the buffer chamber.

Figure 6. SMPS to CPC concentration ratios with new impactor flow calibration and setup as shown in Figure 3, with the ADI neutralizer included and TSI 3077 neutralizer removed from the SMPS system.

The discrepancy observed in the second comparison may be due to wall loss en route to the CPC as well as inefficient charge neutralization by the TSI 3077 neutralizer in the SMPS. All particles exiting the EC of the aerosol generation system are charged, and thus there may be enhanced wall loss downstream due to charge effect. This loss will be dependent on differences in exposure to ion sources. The TSI 3077 neutralizer is one of the SMPS components that has previously been identified as a source of difference. Covert et al. (1997) reported on the charging efficiencies of three aerosol charge neutralizers. They found that the TSI 3077 neutralizer was less efficient in bringing charged aerosol to charge equilibrium for particles below 50 nm and at flow rates of 1.0 ℓ min^{-1} and above, while the ADI neutralizer was efficient in bringing aerosol greater than 10 nm to charge equilibrium, even at a flow rate of 6.0 ℓ min^{-1}. In the experimental setup above, the charged classified particles exiting the EC (monodisperse aerosol) were passed to the SMPS and CPC. If these charged aerosols were not brought to charge equilibrium upon exiting the TSI 3077 neutralizer in the SMPS, then a higher than anticipated fraction of charged aerosol would enter the SMPS classifier. Since the SMPS processing software assumes the aerosol to be in charge equilibrium the reported concentrations would be higher. Also, the classified aerosols measured by the external CPC are charged. It is possible that particle loss en route to this CPC may be enhanced although conductive tubing was used. A longer tube was used for the CPC to match diffusional loss expected through the tube to the SMPS. Both these effects are consistent with the observed discrepancy.
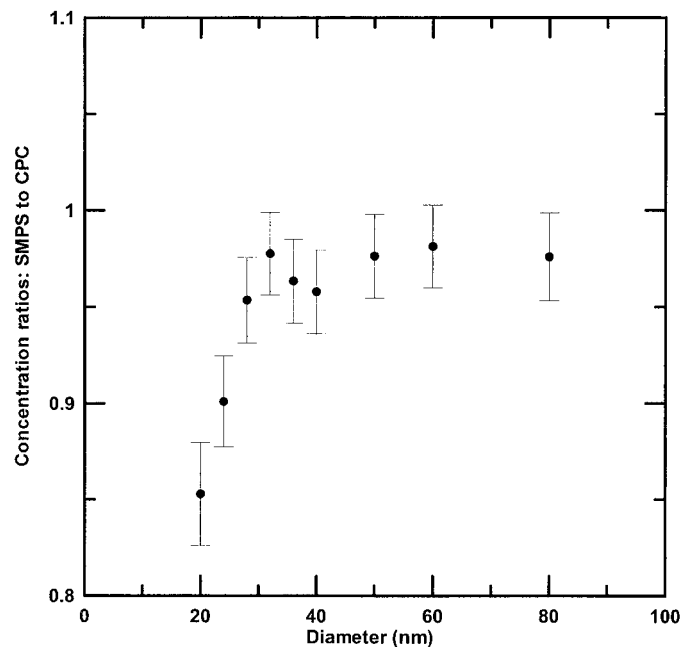
To reduce the influence of charge on particles en route to the external CPC and to provide aerosol in charge equilibrium to the SMPS, the diluted classified aerosol was first passed through the ADI neutralizer (shown within dotted rectangle in Figure 3) for the third comparison between the SMPS and CPC. For this comparison, the TSI 3077 neutralizer (also shown within dotted rectangle in Figure 3) was removed from the SMPS system, as the particles entering the SMPS were already neutralized by exposure to the ADI neutralizer. The results of the third comparison are shown in Figure 6. Better agreement is observed between the SMPS and CPC concentration; however, a disparity still exists for 20 and 24 nm aerosol, but in this case SMPS concentration is less than CPC concentration by >10%.

The SMPS is equipped with an aerosol impactor to remove particles larger than ∼420 nm so error can be avoided during data inversion. It is also equipped with a flow equalizer to allow lower aerosol flow through the EC by adding diluent filtered air upstream of the CPC. Since our interest here was with classified aerosol below 100 nm, the impactor and aerosol flow equalizer were not necessary and were removed for the fourth comparison. This meant that the aerosol was sampled by the SMPS at the CPC flow of 1.0 ℓ min^{-1} and that the sheath air in the SMPS was increased to 10.0 ℓ min^{-1} to maintain the 10:1 sheath-to-aerosol flow ratio. The results of the fourth comparison (Figure 7), indicates good agreement between SMPS and CPC for all sizes tested. It is interesting to see that better agreement is obtained without the use of the impactor and the flow equalizer. The increase in flow through the SMPS would reduce diffusional loss
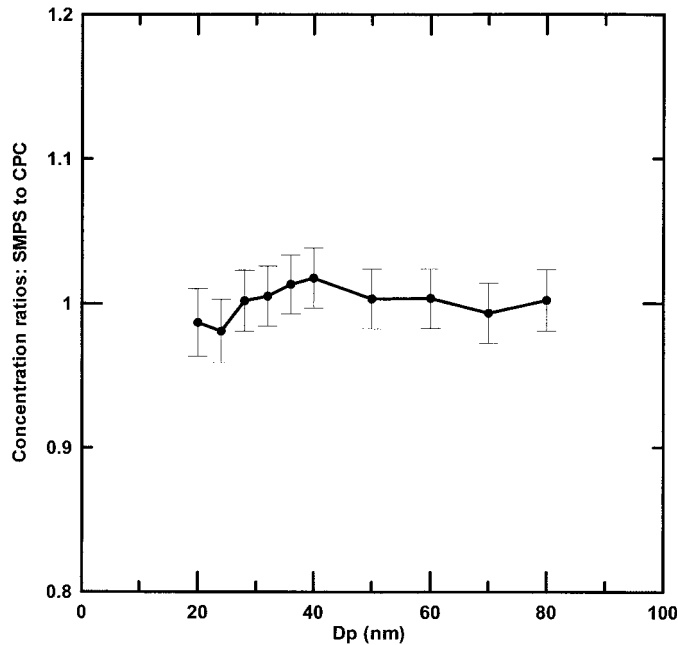
Figure 7. SMPS to CPC concentration ratios using setup as shown in Figure 3 with the ADI neutralizer included but with the TSI 3077 neutralizer, impactor, and the flow equalizer removed from the SMPS system.

Figure 8. Concentration ratios between CPC-B and CPC-A with TSI 3077 or ADI neutralizer ahead of CPC-A inlet for charge-equilibrated (filled circles) and nonequilibrated classified aerosol.

in the SMPS and may explain the improvement seen in the fourth comparison.

It is evident that by efficient neutralization of classified aerosol to a charge equilibrium state before measurement by an SMPS and an external CPC, quite good agreement can be achieved (Figure 6). A further improvement for particles below 25 nm was obtained by eliminating the aerosol flow equalizer and impactor in the SMPS (Figure 7). However, the question still remains as to whether the enhanced SMPS concentration (Figure 5), is due only to inefficient charge neutralization by the TSI 3077 or whether it is also due to losses of charged classified aerosol en route to the CPC. The following experiments address these questions.

CPC Comparison on Charge Neutralized and Non-Neutralized Aerosol

The effects of charge neutralization and charge neutralizers were further investigated in three comparisons. First, aerosol exiting the EC was charge neutralized by passing it through the ADI neutralizer before routing it to CPC-B, the external CPC, and CPC-A, the CPC from the SMPS system. A TSI 3077 neutralizer was placed ahead of CPC-A. In this case the concentration from the two CPCs agrees to within ±5% (filled circles in Figure 8). This observation is as expected and indicates that any aerosol loss downstream of the ADI neutralizer is the same for these neutralized aerosol even though the aerosol on one path were passed through a second neutralizer. Second, the ADI neutralizer was
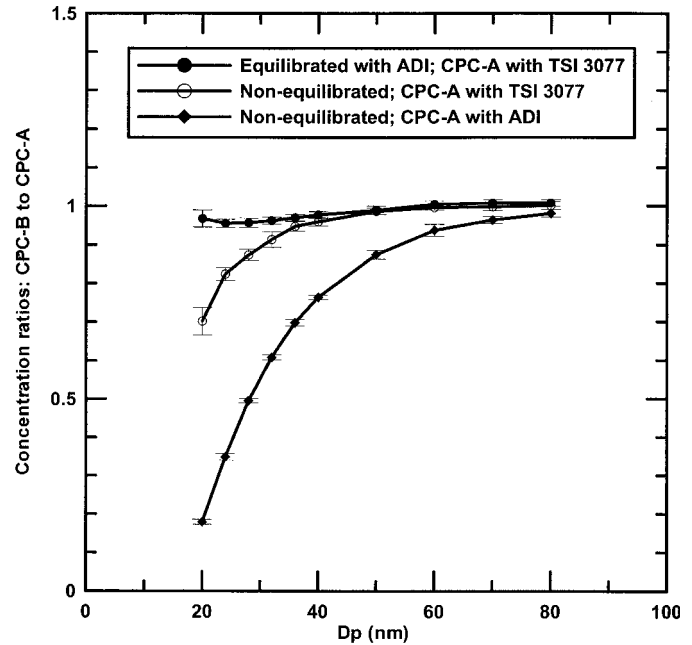
removed so charged classified aerosol was routed directly to CPC-B and through a TSI 3077 neutralizer to CPC-A. The tube length to CPC-B was the same as the tube length to the TSI 3077 neutralizer. The concentration comparison indicates significant loss of particles below 40 nm sampled with CPC-B compared to CPC-A with a TSI 3077 neutralizer ahead of it (open circles in Figure 8). The loss increases as particle size decreases. Third, the TSI 3077 neutralizer on CPC-A was replaced with the ADI neutralizer. The resulting concentration difference was even larger (filled diamonds in Figure 8), and affects particles as large as 80 nm. Since particle loss in the last two comparisons is expected to be the same up to the point where the aerosol enters CPC-B and the charge neutralizer on CPC-A, any differences must result from differences in aerosol loss within the two CPCs for charge neutralized and non-neutralized aerosol. The second and third experiments indicate clearly that there is loss of charged aerosol in CPC-B. Differences between CPC-B and CPC-A for the different charge neutralizers indicate changes in the number of particles counted by CPC-A. Assuming the aerosol loss in CPC-B is due to charged aerosol, CPC-A measurements will increase as the efficiency of the neutralizer increases. Figure 8 suggests that the ADI neutralizer is more efficient and affects a larger size range of particles. This difference in efficiency of the two neutralizers is in agreement with Covert et al. (1997). Since the tube length to CPC-B was the same as the tube length to the neutralizers, the loss must have occurred in CPC-B. Particle-free air that was passed through the ADI neutralizer and fed to both CPCs indicated no particles were being measured, thereby

eliminating the possibility that ion-induced nucleation may be occurring in the CPCs.

SUMMARY AND CONCLUSION

The latest generation of SMPS instruments from TSI has been improved in terms of recirculating flow control and ease of use; however, care is needed when operating the SMPS at pressures different from the factory calibration pressure. For this study, performed at 780 mbar, the aerosol impactor flow was 17% higher than the flow indicated on the front panel when set to $0.6 \, \ell \, min^{-1}$. This causes an error in concentration measurement. If the impactor is used in the SMPS then it is essential that the impactor be calibrated to meet the conditions of the study site.

With correct aerosol impactor flow, a higher aerosol concentration was still observed with the SMPS than with an independent identical CPC for size-classified particles below 40 nm. When the classified aerosol was treated with an ADI ^{210}Po neutralizer before delivering it to SMPS and CPC, without the TSI 3077 neutralizer in the SMPS, much better agreement was observed. Even better agreement, concentration differences less than a few percent for particles as small as 20 nm, was observed with the impactor and flow equalizer removed from the SMPS, Figure 7. This result confirms expectations for equivalent results from the two instruments if they are both sampling from the same charge equilibrated aerosol population. Weber et al. (2001) compared the mass estimated from SMPS measurements to that estimated using a particle-into-liquid sampler ion chromatography PILS-IC, while Sioutas et al. (1999) compared the mass estimated from SMPS measurements to mass collected on Teflon filters. Both studies found the SMPS to give a higher mass concentration for particles below about 200 nm. This difference is similar to the results described here, although the difference in our study occurred only for particles smaller than 80 nm. According to the experiments described here, the higher mass estimated by the SMPS in Weber et al. (2001) could be due to inefficient neutralization of classified aerosol in the SMPS and/or inefficient sampling of charged aerosol in the comparison measurements. Other causes such as particle shape (Kelly and McMurry 1992) and internal structure (Weis and Ewing 1999) may contribute to the uncertainties in mass estimation as well and cannot be ruled out. The source of the difference reported in Sioutas et al. (1999) is not clear, as the atomized spherical polystyrene latex particles were not preclassified and were equilibrated with a ^{210}Po neutralizer before being measured by a SMPS.

Significant losses of charged particles were observed directly within a CPC when measurements of these particles were compared with charge-neutralized particles. This comparison illustrated differences between the TSI 3077 ^{85}Kr and ADI ^{210}Po neutralizers. The ADI ^{210}Po neutralizer was more effective in bringing the classified aerosol to charge equilibrium and was effective for all particle sizes tested. The TSI 3077 was not effective for particles below 70 nm and its efficiency deteriorates rapidly below 50 nm. Care must be taken in choosing a bipolar ion source, because some can induce ion nucleation in the CPC as for example with the 20 mCi ^{210}Po from NRD (Model P-2031) (C. Brock, private communication). The ^{210}Po and ^{85}Kr sources used here had much lower source strength. Proper charge equilibration of classified aerosol is important not only for accurate concentration measurement with an SMPS, but also for accurate concentration measurement with a CPC for particles below 80 nm. This study shows that neutralization of charged particles is important in the calibration of condensation-based particle counters. For CPC calibration the appropriate concentration reference is most often obtained from classified aerosol measured by an aerosol electrometer; however, if classified aerosol were to be directed to a CPC without charge equilibration, a significant amount could be lost in the CPC. This is also important in the calibration of cloud condensation nucleus counters or other aerosol instruments, if the reference concentration is measured by a CPC and the classified particle diameter is <80 nm.

Discrepancies between the SMPS and CPC concentrations of size-classified aerosol stem from both inefficient charge neutralization by the TSI 3077, giving an enhanced SMPS concentration, as well as from loss of charged aerosol in the CPC. Efficient neutralization of classified aerosol to charge equilibrium reduced the SMPS concentration and increased the CPC concentrations by minimizing losses in the CPC. This reduced the concentration discrepancy. Further reduction of the discrepancy was obtained by eliminating the aerosol impactor and equalizer to produce a near one-to-one comparison between the SMPS and CPC.

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