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"Implementation of an Improved Nanometer Aerosol Size Analyzer (nano-ASA) for Near Field Flight Experiments"

A Nanometer Aerosol Size Analyzer (nASA) for Rapid Measurement of High-Concentration Size Distributions

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ABSTRACT

We have developed a fast-response Nanometer Aerosol Size Analyzer (nASA) that is capable of scanning 30 size channels between 3 and 100 nm in a total time of 3 seconds. The analyzer includes a bipolar charger (Po^{210}), an extended-length Nanometer Differential Mobility Analyzer (Nano-DMA), and an electrometer (TSI 3068). This combination of components provides particle size spectra at a scan rate of 0.1 second per channel free of uncertainties caused by response-time-induced smearing. The nASA thus offers a fast response for aerosol size distribution measurements in high-concentration conditions and also eliminates the need for applying a de-smearing algorithm to resulting data. In addition, because of its thermodynamically stable means of particle detection, the nASA is useful for applications requiring measurements over a broad range of sample pressures and temperatures. Indeed, experimental transfer functions determined for the extended-length Nano-DMA using the Tandem Differential Mobility Analyzer (TDMA) technique indicate the nASA provides good size resolution at pressures as low as 200 Torr. Also, as was demonstrated in tests to characterize the soot emissions from the J85-GE engine of a T-38 aircraft, the broad dynamic concentration range of the nASA makes it particularly suitable for studies of combustion or particle formation processes. Further details of the nASA performance as well as results from calibrations, laboratory tests and field applications are presented below.
INTRODUCTION

An aerosol size analyzer for measuring high-concentration nanoparticles with a fast measurement cycle is desirable for many practical applications, e.g., process monitoring of nanoparticle-powder production or studies of particle emissions from combustion sources. One of the immediate applications is to characterize the particle emission from aircraft engines. Aircraft are prolific sources of both soot and sulfate particles to the upper troposphere and lower stratosphere (Fahey et al., 1995; Anderson et al., 1998; Miake-Lye et al., 1998). These particles may have a negative impact upon the climate through direct absorption/reflectance of solar radiation; by altering cirrus cloud formation, reflectance, or duration; or by providing additional surface area upon which heterogeneous chemical processes such as ozone destruction can occur. In order to assess the impact of these aircraft-generated particles to the atmosphere, and to develop a model for aircraft emissions, one of the important features of these particles, the size distribution, must be well characterized.

The differential mobility analyzer (DMA) is used to measure particle size distributions in the sub-micron and nanometer size ranges (Liu and Pui, 1974; Knutson and Whitby, 1975). It has been widely applied in a variety of aerosol studies, including the classification of monodisperse aerosols and the measurement of submicron aerosol size distributions. The DMA classifies particles within a narrow range of electrical mobilities from the charged fraction of an aerosol stream. The selected electrical mobility of particles is determined by the DMA geometry, flow rate, and the applied DMA voltage. If the charge on the selected particles is known, a unique relationship exists between the particle electrical mobility and diameter. Although the DMA performs well in the sub-
micron size range, its performance deteriorates with decreasing particle sizes because of particle diffusion in the classification region of DMAs. In order to minimize the particle diffusion problem, a new generation of DMAs was developed specifically for the nanoparticle size range. An example is the Nano-DMA constructed by Chen et al. (1998). Designed using the numerical model developed by Chen and Pui (1997), the Nano-DMA was evaluated experimentally using the Tandem Differential Mobility Analyzer (TDMA) technique (Stolzenburg, 1988; Stratmann et al., 1997).

DMA systems select a monodisperse size range of particles by applying a voltage across a laminar flow stream, directing particles of a specific electrical mobility onto the sample exhaust slit. Particles of higher or lower mobilities are either deposited on the electrode surfaces or carried out of the instrument in the excess flow stream. Instruments of this type are called electrical mobility analyzers. In the first generation of such instruments, the DMA voltage was varied in discrete steps, holding the value constant at each particle size channel for seconds to minutes before re-setting it to pass particles with the next range of electrical mobilities. Instruments employing this technique typically require 20 minutes to obtain 16 particle size channels of information.

In order to shorten the time required to obtain particle size distributions, Wang and Flagan (1990) introduced the scanning mobility analysis technique that continuously classifies particles in a time-varying electric field using a DMA coupled to a condensation particle counter (CPC) for monitoring downstream particle concentrations. Based on this approach, the measuring cycle was dramatically reduced to 30-90 seconds for 104 particle channels (maximum displayed resolution) to cover the entire measurable size range. Instruments that employ this technique are called scanning mobility particle sizers (SMPSs); use of the
Nano-DMA within SMPS systems enables high-resolution measurements of nanoparticles (Chen et al., 1998).

Though the SMPS systems offer significant advancements over previous aerosol sizing techniques, they possess a number of limitations—primarily imposed by their particle detection technique—that preclude their use in many important applications. For example, most SMPS systems have a DMA exit concentration maximum of $10^5$ particles/cm$^3$ due to the saturation limit of the CPC detectors. In addition, variations of sample pressure and temperatures away from standard values introduce significant errors in SMPS determined size distributions because of the effect these changes have on the detection efficiency of the CPC systems.

Thus, because of the need for a fast measuring cycle, higher concentration capability, and access to broader sampling conditions, we have developed the nanometer aerosol size analyzer (nASA) which replaces the CPC detector of present SMPS systems with an electrometer. The system consists of a Po$^{210}$ bipolar charger, an extended-length Nano-DMA, and an aerosol electrometer (TSI 3068). The extended-length Nano-DMA was modified from the Nano-DMA to cover a wider particle size range from 3 nm to 100 nm at a sheath flow of 15 lpm. The effective column length of the extended Nano-DMA is 12 cm compared to 5 cm for the Nano-DMA.

The nASA was calibrated, using the TDMA method, at both 748 and 201 Torr pressures to facilitate its use in airborne studies of aircraft aerosol emissions. Through the extensive calibrations and new data reduction software, the system achieves the scanning rate of 3 seconds for 30 size channels covering 3 nm to 100 nm particle size range at the sheath flow
rate of 15 lpm. The measurable size range can be extended by varying the DMA sheath flow rate.

Finally, the nASA was used in an instrument inter-comparison workshop conducted at the NASA Langley Research Center for measuring aerosol emissions from a J85-GE turbo-jet engine mounted on a T-38 aircraft. Selected results are presented to demonstrate the capability of the nASA.

SYSTEM ASSEMBLY

Figure 1 shows the system assembly of nASA. It consists of a radioactive bipolar particle charger, an extended-length Nano-DMA, and an aerosol electrometer. The charger uses a Po\textsuperscript{210} radioactive source and is designed to yield an optimum Nt product--where N is the ion concentration and t the residence time for obtaining the equilibrium charge distribution according to the criteria of Liu and Pui (1974) --for the selected range of sample flow rates. The extended-length Nano-DMA with an effective collection rod length of 12 cm is used for particle classification. At a sheath flow rate of 15 lpm, the measurable particle size range is from 3 to 100 nm for the maximum voltage of 8kV. As described below, a re-circulating loop containing high-efficiency particle filters and a small, DC-powered, sealed blower connects the excess flow port to the sheath flow port. By varying the voltage to the blower, the sheath air flow rate is controlled over the range from 6 to 20 lpm. The temperature and pressure inside the re-circulating loop are monitored with a thermocouple and a solid-state pressure transducer, respectively. To avoid possible overheating problems, a cooling fan is installed within the instrument case to effectively transfer the excess heat and maintain the flow at ambient temperature.
The most important distinction between the nASA and current SMPS systems is its use of an electrometer as the particle concentration detector instead of a condensation particle counter (CPC). First used by Whitby and his colleagues (Whitby and Clark, 1966; Liu et al., 1978) as a detector on an early electrical aerosol analyzer, the Faraday-cup/electrometer provides several advantages as an output sensor for a DMA. Since particles classified by the DMA are all electrically charged, particle number concentrations are readily derived from the measured current provided the current flow generated by the particles is sufficiently higher than the electrometer background noise level. Also, use of an electrometer makes it possible to measure DMA-exit particle concentrations exceeding $10^5$ particle/cm³ which is the upper concentration limit of the TSI ultrafine condensation particle counters (UCPC, TSI model 3025). The maximum concentration that can be detected by the present electrometer is $10^{10}$ particles/cm³. This difference arises from the fact that the UCPC counts the signal pulse of individual particles within a set time period to obtain the particle concentration while the electrometer senses the total charges of particles passing through the detector. In addition, variations of sample pressure and temperatures away from standard values change the detection efficiency of CPCs and introduce significant counting errors for particles with the sizes near the CPCs' lower detection limits. These factors are particularly important for studies of exhaust plumes and the formation and growth of particles in response to environmental factors.

INSTRUMENT CALIBRATION

Calibration of extended-length Nano-DMA

The TDMA technique and the experimental setup shown in Figure 2 was used to calibrate the transfer function of the extended-length Nano-DMA.
Nanoparticles were supplied by an evaporation-condensation, silver aerosol generator (Scheibel and Porstendörfer, 1983). In this system, 1.5 lpm of clean air is passed through a ceramic tube furnace containing a ceramic boat loaded with powdered silver metal. The resulting silver-vapor-laden air stream is quenched with a 15 lpm flow of cool air and polydisperse silver nanoparticles are formed via rapid condensation. By varying the furnace temperature setting, the generator can produce polydisperse particles with peak diameters ranging from 10 to 80 nm.

Output from the generator (1.5 lpm) was passed through a bipolar charger (Po210) and then introduced into the first DMA in the TDMA setup. The monodisperse aerosol flow of 1.5 lpm exiting from the first DMA was then either introduced into the second DMA, or fed into a TSI 3025A Ultrafine Condensation Particle Counter (UCPC) to measure the particle concentrations. The same UCPC was also used to measure the concentration of the monodisperse aerosol flow exiting from the second DMA.

In the present application, the bypass aerosol port of the extended-length Nano-DMAs was not used. To facilitate precise control of the sheath flow rate, a re-circulating flow loop between the excess and the sheath flow ports was constructed for each of the Nano-DMAs. In the loop, a sealed blower was driven by a DC voltage supply. Two high efficiency filters were used to ensure particle-free flow before it was re-used as the sheath flow, and to prevent the blower and heat exchanger from particle contamination. One filter was installed at the entrance of the sheath flow. The other filter was used immediately at the exit of the excess flow port. A heat exchanger was installed in each loop to ensure no heat accumulation in the re-circulation flow. For the atmospheric pressure
condition, a sheath flow of 15 lpm was chosen for the tandem Nano-DMA.

The voltage applied on the first DMA was kept constant at a value selected to produce the desired test particle size. At the ambient pressure, the test particle sizes were adjusted between 3 nm and 52 nm. By varying the voltage applied on the second DMA, the particle concentration exiting from the second DMA was recorded continuously. The ratio of the particle concentrations between the exiting and the entering aerosols of the second DMA as a function of varied voltage is the result of the convolution of transfer functions of two DMAs. By using the de-convolution schemes described by Fissan et al. (1996), the transfer function of the DMAs, which represents the transmission efficiency of particles having a specific electrical mobility, can be obtained with the assumption that its functional form is triangular in shape.

For the pressure of 201.2 Torr, the experimental setup was similar to that shown in Figure 2 with some minor modifications to maintain the desirable pressure and to introduce particles into the low-pressure environment. These modifications were (1) a critical orifice was placed in front of the bipolar charger so that a low-pressure environment was achieved in the TDMA system, and (2) the volumetric flowrates used in this calibration were 0.8 lpm for the aerosol flow, and 10 lpm for the sheath flow. In this low-pressure calibration, a TSI 3068 Aerosol Electrometer was used as the particle detector instead of the TSI 3025A UCPC. The reason for switching the particle counters is that the performance of the UCPC is unstable at this low-pressure condition. The experimental procedures in this test were identical to those described before. The test particle size ranged from 10 to 80 nm. The reason that we did not perform tests for particles smaller than 10 nm was due to the significant particle loss through the critical orifice.
During the calibration, the equal length of the tubes for sampling particles upstream and downstream of the 2nd DMA were used to maintain the same level of particle losses in tubing. Simple experiment was also performed to determine the actual particle losses in tubes with connectors and valves used. These losses were determined by measuring particle concentrations upstream and downstream of each sampling line with challenge particles classified by a Nano-DMA (Chen et al., 1998). The difference between two sampling lines is normally within 10%. For the atmospheric pressure, the actual loss through the upstream sampling line is 30% at 6 nm and the value decreases with increasing particle sizes. For the pressure of 201.2 Torr, it is 35% at 19 nm.

Figures 3 and 4 show the transfer function height and width of the extended-length Nano-DMA at the pressures of 748.1 and 201.2 Torr respectively. As expected, the height of the transfer function for the particle size of 51 nm is close to the theoretical value of 1.0 at the pressure of 748.1 Torr. When the particle size decreases, the height of the transfer function decreases due to the particle diffusion of smaller particles. Furthermore, the height of the transfer function drops sharply when the particle sizes are smaller than 10 nm. At 3 nm, the height is about 0.4. For the low-pressure test, the effect of particle diffusion is more significant than that at the ambient pressure. The height is about 0.8 for diameter of 80 nm at low pressure. The height reduces sharply for particle size smaller than 22 nm, and is about 0.29 at 10 nm.

The width of the DMA transfer function at 201.2 Torr pressure approaches a different value than that for the 748.1 Torr calibration, primarily due to the fact that different volumetric flowrate ratios of aerosol flow to sheath flow were used at the two pressures. Similar to
the cases of the height of the DMA transfer function, the width at low pressure is wider than that at the ambient pressure, especially for particle sizes smaller than 10 nm. For the pressure of 201.1 Torr, the width approaches a constant value as the particle size increases. However, this value is greater than the value of 0.8 that is predicted for the selected flow settings (Knutson and Whitby, 1975). This could possibly be due to particle diffusion or sheath flow fluctuations caused by the variations in the blower speed.

**Delay Time Calibration**

The voltage scanning procedure and data inversion algorithms described by Wang and Flagan (1990) were used in the nASA system. Software to control the instrument and perform on-line data reduction was developed using the National Instruments Labview programming package. To accurately perform a rapid scan of nASA, the time required to transport particles from the monodisperse exit port of the Nano-DMA to the detection sensor of the electrometer must be precisely determined. Knowledge of this delay time allows detected particle concentrations to be accurately correlated to the scan voltage, and hence size channel, of nASA.

Because standard PSL particles of <100 nm in diameter are not available, the procedure of Endo et al. (1997) could not be used to determine the nASA delay time. Instead, this factor was determined using a monodisperse silver aerosol classified by a DMA. Polydisperse silver particles were produced using the tube furnace described above, then fed into a modified TSI 3071 Electrostatic Classifier to select a monodisperse silver aerosol with a particle diameter of 61 nm. The modified TSI 3071 Electrostatic Classifier utilizes a short DMA with a
collecting length of 11.11 cm, instead of the standard DMA of the column length of 44.44 cm. The reason for using the DMA with the shorter length was that this DMA has a better resolution and less diffusion loss than those of the standard DMA (Liu and Pui, 1975). The particle size of 61 nm was chosen based on the considerations that (1) the effect of particle diffusion at this size is significantly reduced, and (2) the size is around the middle of the measurable size range of nASA operated at the sheath flow of 15 lpm.

The monodisperse silver aerosol generated by this method was then introduced into the nASA to calibrate for the delay time. The delay time was determined by adjusting the time in the control software such that the peak size of the displayed size distribution matched the challenge particle size.

Fastest Scan Rate Calibration

To examine the fastest scan rate of the nASA, the size distribution of test aerosols were determined using both the stepping and scanning modes of operation. Using the same particle generating system employed for the delay time calibrations, polydisperse silver aerosols with a median diameter of 16 nm were produced and delivered to the nASA system. As demonstrated in Figure 5, the size distribution measured at a scan rate of 0.1 second per particle size channel closely matched that measured at using the stepping mode of operation. In addition, no smearing effect was observed at this rate, which eliminates the need to apply a de-smearing algorithm in the data reduction process (Russell et al., 1995).

T-38 JET ENGINE EMISSION MEASUREMENT
The nASA instrument was developed specifically to address a critical need within the atmospheric science community for rapid measurements of aerosol characteristics within jet aircraft exhaust plumes, either at high altitudes within commercial aircraft flight paths or behind engines running on test stands. The first opportunity to use the nASA in this type of application arose during August 1999, when the National Aeronautics and Space Administration (NASA) sponsored an aerosol instrument intercomparison workshop at Langley Research Center in Hampton, VA (Anderson et al., 2000). Though the primary focus of the workshop was to inter-compare the calibration and sensitivities of CPC and SMPS systems used in NASA-sponsored field projects, a portion of the experiment was devoted to characterizing the aerosol emissions from the J85-GE turbo-jet engine mounted on T-38 aircraft.

For these tests, the T-38 was strapped down to a concrete pad and a weighted sampling probe was positioned on the center-line and at a series of distances downstream from the engine exhaust plane in order to monitor changes in the aerosol emissions as a function of age/temperature. For measurements using the nASA system, ~2.5 lpm of sample air was withdrawn from a small hole on the side of the sampling probe and immediately diluted by a factor of four to one with dry, particle free, nitrogen gas to prevent condensation of water as the hot exhaust gas cooled to ambient temperature. The diluted sample stream was subsequently transported ~5 meters through 0.18 cm I.D. copper tubing to the nASA which was located in the back of a truck parked to the side of the jet-exhaust blast zone. Other CPC and SMPS systems were connected to a 43 to 1 dilution system which withdrew sample from a critical flow orifice located at the base of a 90° bend in the sample probe; these systems were similarly located in trailers and vans.
parked along the perimeter of a 45° cone extending back from the engine exhaust plane.

Objectives of the experiment included determining the size distribution and number density of particles created by the jet engine as a function of engine power. Thus data were collected over a range of engine RPM values from idle (48%) to full military power (100%) and, briefly, full afterburner. Power settings were usually maintained for a period of five minutes to allow the slower response SMPS systems time to obtain two full size scans. During this long period, the nASA system was able to obtain scans at a variety of sample dilution ratios as well as to switch back and forth between processing samples from the primary sampling probe and those from a second probe which was being evaluated for transmission efficiency (Anderson et al., 2000).

Although a more complete presentation and discussion of results from the engine tests will appear in a future publication, Figures 6 and 7 provide a sampling of results using a 4 second measurement cycle of nASA (a total of 40 size channels used). These data show that the engine aerosol emissions shift to larger sizes and become more concentrated as the engine power is increased. They also illustrate the excellent agreement observed between integrated concentrations provided by the nASA system and values determined from a UCPC sampling more dilute sample flow. This agreement provides additional confidence in the performance of the nASA system.

The data obtained by the nASA (and other instruments) in the carefully conducted engine tests differ substantially from previously published information on aircraft soot emissions. For example, Hagen et al. (1992) reported finding median size diameters for soot from jet engines mounted
on test stands ranging from 40 to 60 nm, a factor of 2 larger than the T-38 results of Figure 6. They also found much lower number densities of particles than seen in Figure 7. Although a portion of these differences may be related to engine type and performance characteristic, we believe that a majority of these differences are experimentally induced and arise partly from the higher efficiency of the sampling probe used in the T-38 experiments compared to those used in previous experiments. Additionally, the nASA is substantially more sensitive, than previously employed systems, to the nanometer size range of particles which appear to be a dominant component of exhaust emissions. The ability of the nASA to access this size regime of particles represents an important advancement for accurately assessing the impact of combustion aerosols on atmosphere.

CONCLUSIONS AND FUTURE WORK

A fast-scan Nanometer Aerosol Size Analyzer (nASA) was developed, calibrated at pressures characteristic of surface and high altitude operation, and demonstrated in making fast and accurate assays of combustion aerosol concentrations and properties. The instrument is capable of scanning 30 size channels in 3 seconds without having the smearing problem on size distributions. It has an upper concentration limit that is several orders of magnitude higher than SMPS systems. The use of an electrometer as the particle detector in the nASA also allows processing of samples at pressures and temperatures that are well outside the narrow operational range of the UCPC sensors used in most SMPS systems. These performance characteristics make the nASA ideal for studies of combustion aerosols as well as for use in fundamental investigations of aerosol formation and growth. Indeed, in its initial experimental use, the nASA provided significant new information on the
characteristics of jet engine soot emissions and how these emissions change as a function of engine power and plume age. We envision that its use in future experiments will provide us with much better understanding of how such parameters as engine temperatures, fuel/air mixtures, fuel formulations and contaminants, and environmental factors control the production and characteristics of internal combustion engine particle emissions.

Several improvements are being implemented to the nASA to enhance its performance and ease of use. First, its physical size is being reduced and the capability for controlling the DMA flow rates via computer software is being added. The former improves the portability of the instrument and the latter allows the nASA to measure wider aerosol size ranges. Further, the aerosol electrometer will be upgraded to significantly increase its sensitivity, and the high efficiency, high throughput unipolar charger (a factor of 10-100 higher charging efficiency) developed by Chen and Pui (1999) will be incorporated in the nASA. These upgrades will enable the nASA to measure lower concentration aerosols containing >1000 particles cm\(^{-3}\) (the current lower limit is >10\(^5\) cm\(^{-3}\)). In terms of software development, a de-smearing algorithm, such as the model proposed by Russell et al (1995), will be included. With a good de-smearing algorithm, it should be possible to scan 30 particle size channels in a total time less than 1 second. In addition, the data reduction scheme will be altered to account for the probability of sampling multiply-charged large particles. When fully implemented, these changes should make the nASA instrument suitable for use in monitoring background atmospheric aerosols. We note that it would be particularly suitable for unattended, long-term monitoring experiments because, unlike the SMPS systems that employ CPC particle detectors, the nASA does not need frequent servicing and fluid replenishment.
REFERENCES


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Figure 1. Schematic diagram of the Nanometer Aerosol Size Analyzer (nASA).

Figure 2. Schematic diagram of Tandem Differential Mobility Analyzing system used for calibrating the nASA.

Figure 3. Transfer function height of the extended-length Nano-DMA at 748.1 and 201.1 Torr.

Figure 4. Transfer function width of the extended-length Nano-DMA at 748.1 and 201.1 Torr.

Figure 5. Comparison of the measured size distributions for nASA operating at the stepping and the scanning modes.

Figure 6. Typical fast-scan size distributions measured from a J85-GE turbo jet engine at various engine power settings: (a) 55%, (b) 85%, and (c) 100%. (Sampling probe one meter from the engine; dilution ratio of 4:1 based on the ratio of the dilution flow to sampling flow). The size distributions are corrected for the dilution.

Figure 7. Comparison of the total particle concentration measured by the UCPC and by summing the size distribution channels from the nASA.
Transfer Function Width

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<th>Exp</th>
<th>Best Fit</th>
<th>Pressure, torr</th>
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<th>Q_sh, lpm</th>
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<tr>
<td></td>
<td></td>
<td>201.2</td>
<td>0.8</td>
<td>10</td>
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Particle Diameter, D_p, nm
T. C. = 3.81E7
NMD = 15
σ_e^6 = 2.01
E. P. = 55%
D. R. = 4
P. D. = 1 m
T.C. = 4.63E7
NMD = 20
D.F.P. = 0.5
D.R. = 4
P.D. = 1 m

T-20

Dp (nm)

3.5E7 3.0E7 2.5E7 2.0E7 1.5E7 1.0E7 0.5E7

Dn/Dlog(Dp) (#/cm^3)