Measurement of atmospheric nanoparticle size distribution using
the Radial Differential Mobility Analyzer (RDMA)

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ABSTRACT

Atmospheric nanoparticles, defined as particles having a spherical equivalent diameter smaller than 50 nanometers (nm), have become a major interest to atmospheric scientists. It is believed that these particles form an integral part of important atmospheric processes such as cloud formation, precipitation and chemistry. Our goal, therefore, was to gain a greater understanding of their formation and fate using a radial differential mobility analyzer (RDMA), a novel instrument compared to established instrumentation used for this purpose.

To achieve this task, a scanning mobility particle sizer (SMPS) was assembled with an aerosol charger, an RDMA, a condensation nucleus counter (CNC), a blower system, a power supply box, and a computer-based data acquisition system as its components. It was then deployed at NCAR’s Marshall Field Site, a rural location 5 miles southeast of Boulder, Colorado. Size distributions were compared to a SMPS system with a TSI nano-DMA also deployed at the site to evaluate its performance. Intercomparison of these two systems showed a close correspondence in the measured sizes of aerosols, however the RDMA-based SMPS concentrations were found to be 11 times greater than that of the nano-DMA SMPS.

Continuous monitoring of size distributions in the diameter range 6-170 nm was performed during the period 30 July – 1 August, 2004. These measurements were then compared to locally measured sulfur dioxide (SO$_2$) concentrations and meteorological parameters. Results from these measurements show close correlations between nanoparticle concentrations, SO$_2$, and wind velocity.

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1. INTRODUCTION

Nanoparticles, defined as particles with a spherical equivalent diameter smaller than 50nm, can be found everywhere in the atmosphere in varying concentrations. Although much progress has been made recently detecting and modeling the behavior of atmospheric nanoparticles, the root of their occurrence is not completely understood, warranting further research. Therefore, the prospective goal of this research project was to gain a greater understanding of the formation and fate of atmospheric nanoparticles using a potentially more sensitive method, a scanning mobility particle sizer system equipped with a radial differential mobility analyzer (RDMA), than established instrumentation.

There are a number of reasons for wanting to understand nanoparticles in greater detail. One reason is their effect on human health. Studies have found that for a given mass concentration, particles in the 20nm diameter range have a much greater impact on the lung function of laboratory test animals than ~200nm particles (Oberdorster et al., 1995). And concerning the formation and growth of atmospheric nanoparticles, in a recent review Kulmala et al. acknowledged that these processes impact the climate specifically by “increasing the number concentration of cloud condensation nuclei.” On a global scale, the most important particle formation process is homogeneous nucleation, which is defined as the formation of thermodynamically stable particles from the condensation of gaseous precursors. Though it is understood that nucleation rates are higher in urban areas, coastal areas and industrial plumes than in rural areas (Kulmala et al., 2004), the processes and conditions responsible for formation and growth are not fully comprehended.

The need for more data on the life cycle and conditions suitable for formation and growth of nanoparticles calls for a portable instrument which allows measuring nanoparticles in a wide variety of locales. Size distributions that are extracted from these measurements help decipher the role of nanoparticles in atmospheric processes such as cloud formation, precipitation, and the scatter and absorption of solar radiation and influence future global climate change models. We believe that use of the radial scanning mobility particle sizer (radial SMPS), consisting of a bipolar charger, RDMA and condensation nucleus counter provides the necessary measurements in the near future for achieving the goal of understanding atmospheric nanoparticle formation and fate.

Atmospheric sampling was conducted at NCAR’s Marshall Field site over a three day period. This site was chosen so that results from this experiment could be compared to that of an existing nano-DMA based Scanning Mobility Particle Sizer at the site. The data was also compared to meteorological parameters and measurements of ambient SO$_2$ to determine if any correlations exist with those variables. Some correlations were observed between the concentration of nanoparticles, the concentration of SO$_2$ and the wind direction.

2. METHODS

The size distribution of atmospheric nanoparticles is measured using a scanning mobility particle sizer composed of an aerosol charger, a radial differential mobility analyzer (RDMA), a blower system, a power supply box, a commercial condensation nuclei counter (CNC) and a computer-based data acquisition system.
2.1 Flow Diagram of Scanning Mobility Particle Sizer

A better understanding of the SMPS system may be obtained first by noticing the complete setup available in the flow diagram. This schematic maps the sheath and aerosol flow and the electrical signals that are transmitted during operation. Each component of the SMPS will be described in separate sections in the following text.

![Flow Diagram of RDMA-based SMPS](image)

*Figure 1. The flow diagram of RDMA-based SMPS*

2.2 Aerosol Charger

The aerosol charger, the first component for sampling particles, is of the bipolar charger design. It consists of a metal cylinder with radioactive $^{210}$Po inside that ionizes ambient gas molecules. As particles enter this cylinder, they obtain negative or positive charge from the gas molecules until equilibrium of charge distribution is achieved (Wiedensohler, 1988). Most of the atmospheric nanoparticles are neutral, but some exist with either $\pm 1$ or (to a much smaller degree) $\pm 2$ charges.

2.3 Radial Differential Mobility Analyzer (RDMA)

The radial differential mobility analyzer, RDMA, is a powerful tool for the analysis of atmospheric nanoparticles. It has the potential to measure particles as small as 3 nm in spherical equivalent diameter, the lower detection limit of the CNC. As mentioned above, charged particles enter the RDMA, and it is required that the particles be charged because they must be influenced by an electric field created by a high voltage current delivered to the upper plate of the RDMA; the lower plate is grounded. This electric field accounts for one of two forces acting on the travels of the aerosol particles through the instrument.
The other force acting on the nanoparticles is drag. Particle-free sheath air enters the RDMA tangentially into the circular channel passing through a ring made of porous material that evenly distributes it into a uniform flow field. Finally, the aerosol flow is also introduced tangentially into the inlet channel of the RDMA and, because of internal RDMA design (a sharp edged ring and curved edge forming 0.8mm wide gap), merges with the sheath flow, turbulent free (Zhang et al. 1995). Airflows exit the RDMA through opposite sides of the instrument. The sheath flow exits through the upper plate and is recycled in the closed loop and the aerosol flow exits through the lower plate and into the CNC. Figure 2 shows a picture of the RDMA connected in-line with the blower system.

Thus, a balance between the pull of an attracting electric field and hindrance of an axial sheath flow isolate particles of a specific mobility to the RDMA’s exit. Sweeping the voltage across the disks allows for the measurement of size distribution, determined to be 6-170nm by our operating conditions. Upon leaving the RDMA, the particles enter the condensation nucleus counter (CNC).

Figure 2. RDMA with blower, H.E.P.A. filter and tubing.

2.4 The Blower System

The sheath airflow system of the SMPS is provided by a small blower mounted on the side of the RDMA. As stated above, the sheath airflow acts as a drag force on the charged particles as they pass through the RDMA. A High Efficiency Particulate Air (HEPA) filter is attached to the blower to remove particles from the sheath air and metal tubing is used to both complete the sheath flow system and to provide a pressure gradient in order to characterize the flow rate of the sheath air. Two pressure taps on either side of the tubing connect to a Honeywell pressure sensor that is located within the power supply box. The blower’s power comes from an adjustable 0–12 VDC circuit, which allows the flow to be manually controlled using a potentiometer. The airflow system and pressure sensor were tested and calibrated with a Gilibrator bubble meter that volumetrically measures the flow rate.

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2.5 Power Supply Box

The power supply box has four main purposes: to supply the high voltage to the RDMA electrodes, to supply power to the blower which provides a constant sheath airflow, to supply power to the pressure sensor used to monitor the flow rate, and to house peripheral connectors to enable remote sensing and data collection output. Refer to figure 3 for a drawing of the electrical circuit of the power supply box.

![Power Supply Box Diagram](image)

Figure 3. The power supply box internal circuitry.

2.5.1 Air Circulation Fan

A fan is needed in the power supply box to cool the blower controller circuit. The fan subsystem consists of a 12VDC fan and a 12V 7812 voltage regulator. It is wired to be independent of all other circuits within the power supply box and operates when the DC supply is applied to the box.

2.5.2 The Blower and Pressure Sensor Circuit

The blower and pressure sensor circuits are wired to a power switch allowing simultaneous activation. The blower circuit uses a LM350 adjustable voltage regulator which when coupled with a resistor of calculated resistance provides the exact voltage output. The equation for calculating the resistance is as follows:

\[
V_{out} = V_{ref} \left( 1 + \frac{R_2}{R_1} \right)
\]

where: \( V_{out} \) represents output voltage.
`V_{ref}` represents 1.25V developed internally
`R_1` represents a resistance of 240Ω
`R_2` represents the resistance to be calculated.

The DC power leaving the LM350 circuit was then connected to the positive lead on the blower, and the ground lead was connected to DC return (0V). A potentiometer was connected in line with the adjustable pin lead of the LM350 allowing variability of the blower speed. In order to know the voltage required for a specific blower speed, a test point was wired to the blower circuit that would allow voltage readouts.[JS2].

The pressure sensor, which was connected in parallel with the blower, receives power from a REF01 precision 10V voltage reference chip, which provides 10VDC to the pressure sensor. The pressure sensor receives input from the two outlets situated at each end of the sheath airflow system. A test point is wired to the pressure sensor circuit to read the output voltage when necessary.

2.5.3 The High Voltage (HV) Circuit

The HV circuit is wired to two switches, a potentiometer and a test point. The first switch is an enable-disable switch which turns on the power supply. Local or remote control of the circuit is controlled by the second switch on the power supply box. Under local control, the high voltage that is applied to the RDMA is controlled by a potentiometer on the front panel. A test point is used to verify the voltage applied to the RDMA. The test point output ratio is 1000:1, *i.e.* HV 10,000VDC is displayed as 10VDC. Under remote control, the output voltage of the supply can be controlled by an adjustable 0-10VDC signal from a computer controlled data acquisition card.

The main component of the high voltage circuit is the Ultravolt 10A Series Modular High Voltage Power Supply which is a DC to DC converter, 15VDC to maximum 10kVDC. This Ultravolt circuit and the circuit board were designed in house at the ACD Electronics Lab and provide sufficient high voltage to the RDMA. The circuit board’s 12 pin edge connector was used to wire the HV supply to the power supply box components shown in the table below.

<table>
<thead>
<tr>
<th>PIN</th>
<th>Description</th>
<th>Wired to</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HV monitor</td>
<td>Monitor test point</td>
</tr>
<tr>
<td>3</td>
<td>Enable/Disable</td>
<td>Middle contact of the “HV on” front panel switch, top contact of switch wired to ground.</td>
</tr>
<tr>
<td>5</td>
<td>HV adjust</td>
<td>Potentiometer wiper (the part that moves the pot)</td>
</tr>
<tr>
<td>6</td>
<td>HV reference</td>
<td>Potentiometer 5V side (also grounded to DC return)</td>
</tr>
<tr>
<td>7,8</td>
<td>Power common</td>
<td>To DC return</td>
</tr>
<tr>
<td>11,12</td>
<td>12V</td>
<td>Wired to 7812 to provide 12V DC voltage.</td>
</tr>
</tbody>
</table>

The 10 pin “crimp and poke” connector was then wired to the 50-pin peripheral cable which relays data to the National Instruments DAQCard-1200 card used for data acquisition. The table below describes the signal connections.
Table 3. Signal connections for "crimp and poke" to ribbon cable.

<table>
<thead>
<tr>
<th>IDC PIN</th>
<th>50 PIN #</th>
<th>50 PIN Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10</td>
<td>DAC Output – Voltage output signal for analogue output channel.</td>
</tr>
<tr>
<td>8</td>
<td>1,11,13,50</td>
<td>Grounds for individual components</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>Analogue input</td>
</tr>
</tbody>
</table>

The counter feedback from the CNC was wired to the counter input to the data acquisition card on the 50 pin IDC connector.

2.6 The Condensation Nucleus Counter, CNC\textsuperscript{[s3]}\textsuperscript{[s3]}

The condensation nucleus counter is one of the most important parts of the scanning mobility particle sizer because it is its detecting component. The CNC draws atmospheric nanoparticles in at 300 cm\textsuperscript{3} min\textsuperscript{-1} and exposes them to a supersaturated environment of butanol that will cause them to grow to sizes detectable by light scattering. To achieve this supersaturation, the air flow is passed over a heated pool of butanol then through a cold region where thermal diffusion condenses the alcohol vapor onto the nanoparticles. Just beyond this region, optics collect light scattered off the particles as they pass through a laser beam, counting them as electrical pulses relayed to the computing environment via a BNC connector.

2.7 Data Acquisition and Experiment Control

The software needed to sample in this method has been designed, previously, in Labview\textsuperscript{\textregistered}. This program allows a user to set the range of high voltages applied to the radial DMA electrodes and display the size distribution of the sampled atmospheric nanoparticles. Another program, however, converts the data into a format for a better, contour plot display.

3. EXPERIMENT

In order to evaluate the RDMA-based scanning mobility particle sizer, SMPS, tests were conducted at NCAR’s Marshall Field site which is located approximately 5 miles SE of Boulder, Colorado. The instrument was set up and run alongside an existing nano-DMA based SMPS over a three day period from July 30\textsuperscript{th} – August 1\textsuperscript{st}, 2004. Collected data from both instruments were plotted using Sigma Plot software and compared. The plots were also compared with SO\textsubscript{2} and meteorological data for the three days to observe any correlations. Wind direction was the main focus of the meteorological data as it played the most important role in the transport of the nanoparticles from the source.
4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Concentration Comparison for Particles 20nm or Smaller for both DMA’s

7/31/2004

Total concentration of particles smaller than 20 nm

![Graph showing concentration of particles smaller than 20 nm over time]

Figure 4. The total concentration of particles smaller than 20 nm vs. time (24hr period)

Figure 4 represents the total concentration of particles smaller than 20 nm in spherical equivalent diameter with respect to local time for a 24 hour period for both the nano-based SMPS and the radial-based SMPS. From the plot one can easily see a correlation between the two instruments. Thus the RDMA’s measurements were consistent with the nano-DMA’s with respect to size distributions, but to make the concentration over time overlap so nicely the nano-DMA’s data had to be multiplied by a factor of 11, indicating that one or both of the instruments need their efficiencies to be determined.
4.2 Comparison of Concentration (cm\(^{-3}\)) and Spherical Equivalent Diameter (nm) for both DMA's

![Graphs showing size distributions for RadialSMPS and NanoSMPS](image)

**Figure 5.** Representations of spherical equivalent diameter (nm) and concentration (cm\(^{-3}\)) vs. time (24hrs) for the RDMA-based SMPS and the nano-DMA-based SMPS.

Both graphs in figure 5 represent concentration (cm\(^{-3}\)) and spherical equivalent diameter (nm) vs. local time over a 24 hour period. There was a noticeable difference in the concentrations of atmospheric nanoparticles sampled by both instruments and, as mentioned, evaluations of both instruments should be conducted in order to evaluate their efficiencies. Despite this fact, the patterns represented by both graphs were very similar showing increasing activity between the periods of 8:30am – 12:30pm, 2:00pm – 4:00pm and 5:00pm – midnight. Observations of both plots which represent the two SMPS systems demonstrate the observation of identical atmospheric nanoparticle activity.
Figure 6. Plots of nanoparticle concentration (cm$^{-3}$) and spherical equivalent diameter (nm), concentration of SO$_2$ (ppb) and wind direction (degrees). All plots were against a 24 hr time axis.

Figure (6a) shows the plot of atmospheric nanoparticle concentration (cm$^{-3}$) and spherical equivalent diameter (nm) vs. time. Figure (6b) and (6c) shows SO$_2$ concentration (parts per billion) and wind direction (degrees) vs. time respectively. The time axis of the three graphs were all scaled from 7:00am – midnight; and the degree representations for wind direction are as follows: 0° and 360° = North, 90° = East, 180° = South and 270° = West.

The change in wind direction from westerly, mountain winds to easterly winds correlates with high nanoparticle activity from approximately 8:00am – 4:00pm. It is assumed that westerly winds which descend from the mountains are usually particulate free but as the wind direction changes to blowing from the east high amounts of nanoparticles are transported to NCAR’s Marshall Field site, possibly on account of the pollution of the Denver metropolitan area. Solar dependant reactions such as the production of atmospheric OH$^-$ should be responsible for the conversion of atmospheric SO$_2$ to sulfuric acid (H$_2$SO$_4$). High levels of SO$_2$ during peak sunlight hours are, however, extremely noticeable. This leads to the belief that some other natural occurrence could have altered the atmospheric chemical processes on that day. It is however important to note that H$_2$SO$_4$ coupled with H$_2$O provides the most important binary
nucleation system in the atmosphere, thus the spike in SO₂ concentration may be related to this system (Seinfeld and Pandis, 1998).

The atmospheric reactions which produce sulfuric acid are summarized below.

\[
\begin{align*}
SO₂ + OH⁺ + M &\rightarrow HOSO₂⁻ + M \quad (1) \\
HOSO₂⁻ + O₂ &\rightarrow HO₂⁻ + SO₃ \quad (2) \\
SO₃ + H₂O + M &\rightarrow H₂SO₄ + M \quad (3)
\end{align*}
\]

4.5 July 31st, 2004

![Graphs showing nanoparticle concentration, sulfur dioxide concentration, and wind direction over time.](image)

*Figure 77777. Plots of nanoparticle concentration (cm⁻³) and spherical equivalent diameter (nm), concentration of SO₂ (ppb) and wind direction (degrees). All plots were against a 24 hr time axis.*

Figure (7a) represents atmospheric nanoparticle concentration (cm⁻³) and spherical equivalent diameter (nm) vs. time. Figures (7b – 7c) represent SO₂ concentration (ppb) and wind direction (degrees) respectively. The time axis for all three graphs corresponds to a 24 hour time...
period. Comparisons of graph 7a and 7c show correlations between the concentration of nanoparticles and change in wind direction. Westerly winds changed direction to easterly winds and brought in a higher concentration of nanoparticles, which may be attributed to combustion nucleation. Changes in direction at periods 1:00pm – 2:00pm and 4:00pm – 5:00pm correspond to decreased concentrations of nanoparticles during those times.

The levels of SO$_2$ in plot (7b) correspond to two reactions that may be occurring in the atmosphere at the corresponding times. The first reaction is the particle growth by the condensation and coagulation of SO$_2$ molecules on the nanoparticles. The other reaction that occurs is the reaction of SO$_2$ with the OH radical (OH$^-$) to produce sulfuric acid (H$_2$SO$_4$). This reaction is abundant during the daylight hours because the production of OH$^-$ is light dependant.

At 8:00pm local time the levels of SO$_2$ rose from approximately 0 parts per billion (ppb) to 7ppb, corresponding to the decrease in its consuming molecule, OH$^-$, due to lower solar irradiance as the sun sets. Wind direction may also be a factor influencing the lower levels of SO$_2$ since it is not a product of combustion.

4.6 August 1, 2004

Figure 8. Plots of nanoparticle concentration (cm$^{-3}$) and spherical equivalent diameter (nm), concentration of SO$_2$ (ppb) and wind direction (degrees). All plots were against a 24 hr time axis.
The data represented in the plot 8a shows similar trends to the data in plot 7a. At approximately 9:30 am, wind direction changes from west to east bringing with it increased levels of nanoparticles. Erratic wind patterns shown in 8c represent changes in wind direction between 0° and 360°, 90°, 180° which corresponds to north, east and south respectively. A noticeable wind change to westerly winds at approximately 3:00 pm coincides with a decrease in nanoparticle concentration. The increase in SO₂ levels at 9:00 pm corresponds to the reduction in OH levels, and other fluctuations in SO₂ levels correspond to the changes in wind direction from west to north and back to west. Northern winds which usually coincide with increased nanoparticle activity are relatively particle free due to the fact that at night nanoparticle production from both anthropogenic and natural sources is at a minimum.

5. CONCLUSION AND FUTURE WORK

Preliminary results and interpretation of these results have shown that the radial-DMA SMPS is a functional, working system capable of measuring nanoparticles in the range of 3nm – 170nm. Comparison with the nano-DMA based SMPS showed that the concentrations sampled by the RDMA-based SMPS were approximately greater by a factor of 11. In order to validate these results, the efficiencies of both instruments should be evaluated. One of the factors that may be responsible for this great difference in concentration is the losses of the atmospheric nanoparticles to the walls of the tubing to the DMA’s. The RDMA-based SMPS had less than a meter of tubing whereas the nano-DMA based SMPS had close to 2 meters of tubing. Once both instruments have been evaluated and the results of the RDMA-based SMPS are validated more continuous sampling at NCAR’s Marshall Field site should be done.

Another experiment that we plan to do is place the RDMA-based SMPS in a normal-living environment to examine the nanoparticle concentrations that occur in the home. This would give scientists a closer look at the effect of nanoparticles on human health and wellness and the activities that increase or decrease concentration levels.

REFERENCE


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