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SIMULTANEOUS DETERMINATION OF INDIVIDUAL AMBIENT PARTICLE SIZE, HYGROSCOPICITY AND COMPOSITION

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Simultaneous determination of individual ambient particle size, hygroscopicity and composition

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[1] A new system for simultaneous determination of individual particle size, hygroscopicity, and composition of internally and externally mixed aerosols is presented. An HTDMA is used to select particles according to their size and hygroscopicity for compositional analysis by a single particle mass spectrometer. The capability of the system is demonstrated on a laboratory generated aerosol consisting of polystyrene latex spheres coated with a layer of ammonium nitrate to represent an internally mixed aerosol with controllable hygroscopicity that is externally mixed with pure ammonium nitrate particles. Results are presented from an ambient study illustrating the sensitivity of the system and the capability to provide detailed information on individual atmospheric particles within a short sampling time. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques. **Citation:** Buzorius, G., A. Zelenyuk, F. Brechtel, and D. Imre, Simultaneous determination of individual ambient particle size, hygroscopicity and composition, *Geophys. Res. Lett.*, *29*(20), 1974, doi:10.1029/2001GL014221, 2002.

1. Introduction

[2] Virtually every property of atmospheric aerosols is a strong function of Relative Humidity (RH). Changes in particle size and phase with relative humidity modify heterogeneous atmospheric chemistry, cloud and fog formation processes, and visibility. As climate models improve, they must incorporate the dependence of aerosol radiative effects on RH. Because of the important role that water vapor plays in determining aerosol effects it is critical to develop the understanding that is required to reliably represent water vapor-particle interactions in models.

[3] The response of individual particles to changing RH depends on the particle chemical composition. With increasing RH particles containing hygroscopic salts and acids grow and become solution droplets, whereas particles composed of soot, or crustal materials may not grow significantly with increasing RH. In 1978 *Liu* and co-workers attempted to take advantage of the relationship between composition and hygroscopic growth by developing the Humidified Tandem Differential Mobility Analyzer (HTDMA), which was designed to provide a real-time measure of particle growth as a function of RH. This unique capacity of the HTDMA has since made it the method of choice for quantifying the RH effect on aerosol size [*Rader and McMurry*, 1986].

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[4] However, to uncover the underlying driving force for the observed RH effect, an additional measurement capable of providing information on particle chemical composition is needed. In 1994 *Pitchford and McMurry* deployed an HTDMA system in parallel with an impactor in an attempt to investigate the relationship between hygroscopicity and composition. The study demonstrated a clear correlation between composition and hygroscopicity; however, the measurements could not distinguish the relative roles of internally and externally mixed aerosols in controlling the observed hygroscopic growth. This deficiency was addressed in a following study [*McMurry et al.*, 1996] where the HTDMA selected the aerosol by size and hygroscopicity for single particle Electron Microscopy (EM) analysis of particle shape and composition. Systematic differences in particle composition and shape that correlated with growth factors were observed. While HTDMA coupled with EM provides the needed information it is labor intensive and very slow and the data could not be obtained in real-time.

[5] Recent developments in Single Particle Mass Spectrometry (SPMS) make it an ideal tool to study the composition-dependent hygroscopicity in real-time. In this paper an experimental setup is presented where the HTDMA is used as an aerosol size and hygroscopicity segregator for individual particle chemical composition analysis by the Brookhaven National Laboratory Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS). The performance of the system is tested with a laboratory generated aerosol consisting of ammonium nitrate particles and Polystyrene Latex (PSL) spheres coated with ammonium nitrate (PSL/AN). We demonstrate that the system is capable of real-time atmospheric measurements and some preliminary results from field measurements are presented.

2. Experimental

[6] A schematic of the experimental setup is shown in Figure 1. An externally mixed aerosol was generated by atomizing an ammonium nitrate solution containing 204 ± 10 nm in diameter PSL spheres (Duke Scientific Corporation). The resultant aerosol included Pure Ammonium Nitrate (PAN) particles and a relatively small number of PSL/AN particles representing an externally and internally mixed aerosol with distinct hygroscopic properties. The pure ammonium nitrate particles are more hygroscopic, while the PSL/AN particles provide for a lower but variable hygroscopicity that can be adjusted by changing the thickness of the ammonium nitrate coating.

[7] The output from the atomizer is dried to below 30% RH before being introduced into the first Differential Mobility Analyzer (DMA, Model 3081, TSI Inc., Minn., MN), marked as DMA1 in Figure 1 to produce low RH

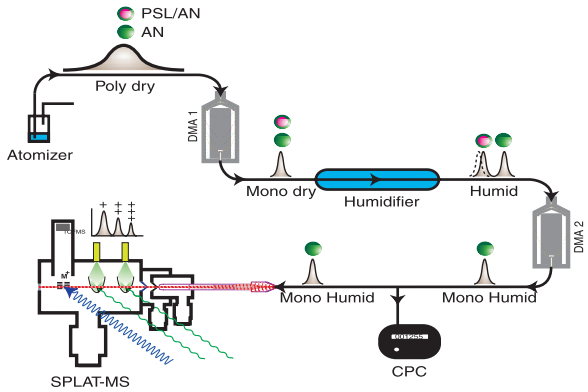

Figure 1. Experimental setup.

monodisperse aerosol. In the present experiment particles of various diameters from 160 nm to 225 nm were produced. Since the PSL sphere size is fixed, selecting the aerosol size by DMA1 sets the thickness of the ammonium nitrate coating and hence the hygroscopicity of the internally mixed PSL/AN particles.

[8] The monodisperse output from DMA1 was humidified to between 91% and 96% RH before it was introduced into the second DMA (DMA2 in Figure 1). Throughout the experiment the DMA2 sheath-air humidity was matched to the RH of the monodisperse aerosol flow and temperatures throughout the system were maintained near 26°C.

[9] The resultant size distribution of the humidified aerosol was obtained by exponentially ramping the voltage in DMA2 [*Wang and Flagan*, 1990] to cover the size range from $0.75*d_{dry}$ to $2.7*d_{dry}$; where d_{dry} is the diameter of the monodisperse aerosol selected by DMA1. To decrease smearing effects the particle counter sampling flowrate was increased to 2 lpm [*Buzorius*, 2001]. Once the humidified aerosol size distribution was determined and the two observed modes, corresponding to PAN and PSL/AN particles were identified, DMA2 was set to transmit the droplet sizes corresponding to the maximum number of either of the modes to SPLAT-MS.

[10] The technical details of SPLAT-MS will be described in a separate publication, here we mention a few salient points. It is important to note that because the inlet to the mass spectrometer is operated at 2 torr a significant fraction of the water present in the aerosol evaporates prior to aerodynamic sizing by SPLAT-MS, consequently the observed aerodynamic diameters are a function of the selected sizes by DMA1 and DMA2, the evaporation dynamics within SPLAT-MS and the particle density. Drying the aerosol before its introduction into SPLAT-MS could eliminate this complication. Moreover, by comparing aerodynamic and mobility diameters for the same particles it should be possible to derive the density of individual particles.

[11] A notable feature of the experimental setup is that the aerodynamic sizing by SPLAT-MS makes it possible to distinguish between the singly and multiply charged particles (denoted by "+", "++" and "+++" in Figure 1) that are selected by the HTDMA. This means that the experiment is conducted on three sizes simultaneously.

[12] The overall performance of the HTDMA system was tested using ammonium sulfate particles, for which the observed growth factor agreed within 4% with that reported in literature [*Tang and Munkelwitz*, 1994; *Brechtel and Kreidenweis*, 2000].

3. Results

[13] Figure 2 shows several number concentration distributions obtained by scanning DMA2 for the condition where DMA1 selected 160 nm, 180 nm, 200 nm, 212.5 nm and 225 nm particles and the RH in DMA2 was between 91% to 96%. As expected, setting DMA1 to select 160 nm particles (black line in Figure 2) assured that the aerosol contained no 204 ± 10 nm PSL spheres, and only the hygroscopic mode with a peak at 272 nm could be observed.

[14] The thickness of the ammonium nitrate layer on the PSL particles is directly related to the diameter selected by DMA1. As the size increases so is the AN layer thickness, increasing the soluble volume fraction in the internally mixed particles and their hygroscopic growth. PSL containing particles were first observed when DMA1 was set to select 180 nm particles, as illustrated in Figure 2 by the low amplitude mode at 190 nm representing PSL/AN particles with a very thin ammonium nitrate coating. The more hygroscopic mode containing PAN particles was centered at 311 nm for the same DMA1 and RH settings. The subsequent distributions obtained with DMA1 selecting 200 nm, 212.5 nm and 225 nm also exhibited two distinct modes.

[15] When DMA1 was set to select particles 212.5 nm in diameter the average nitrate volume fraction was 0.10 ± 0.05 and the observed growth factor of the PSL/AN particles was 1.1, compared with a growth factor of 2.0 for the PAN particles. Increasing the selected size to 225 nm increases the AN volume fraction in the PSL/AN particles to 0.25 ± 0.05 and their growth factor to 1.5. Note that the above growth factors relate to the size established at 30% RH by DMA1.

[16] The observed number concentrations downstream of DMA2 for different diameters were used to select the appropriate voltage setting of DMA2 to transmit the max-

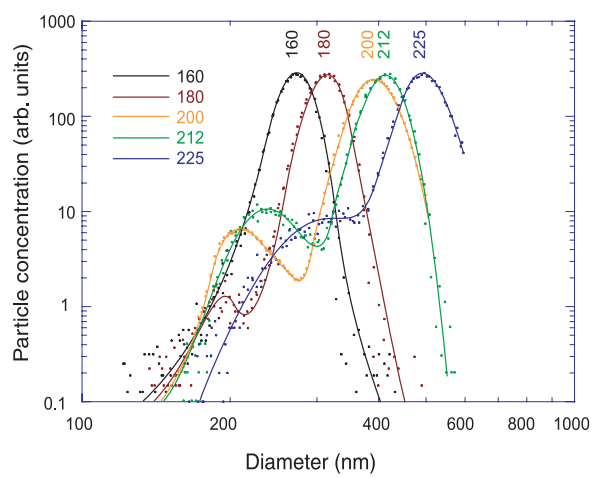

Figure 2. Number concentration downstream of DMA2. Abscissa is the diameter that would be transported through DMA2 with highest probability.

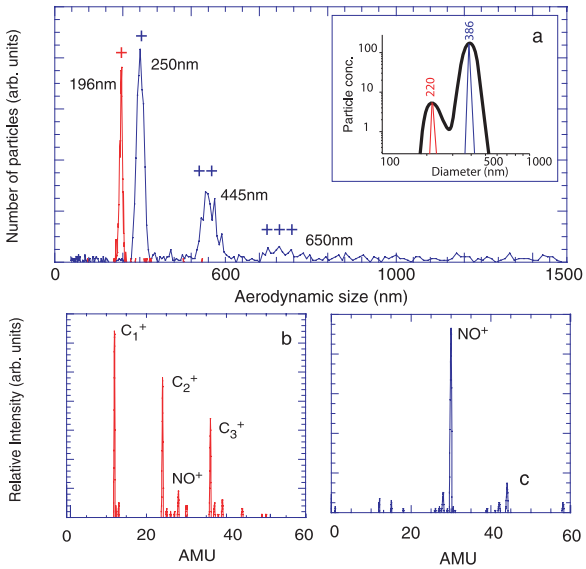

Figure 3. SPLAT-MS results on humidified (dry-200 nm) test aerosols; (a) aerodynamic size, (b) mass spectrum of less hygroscopic particles, (c) mass spectrum of more hygroscopic particles.

imum number of either PAN or PSL/AN particles to SPLAT-MS.

[17] The insert in Figure 3a repeats the data shown in Figure 2 for the case when DMA1 was set to transmit 200 nm particles. The position of the red and blue vertical lines indicate the growth factors of the particles selected by DMA2 to be transmitted for analysis by SPLAT-MS; red for PSL/AN and blue for PAN particles. The body of Figure 3a shows two aerodynamic size distributions observed by SPLAT-MS in red and blue corresponding to the red and blue lines in the insert. When DMA2 was fixed to transmit PAN (blue) the aerodynamic size distribution observed by SPLAT-MS clearly shows three modes corresponding to singly, doubly and triply charged particles. The red size distribution, corresponding to PSL/AN, shows a single narrow peak at virtually the same size as that selected by DMA1 consistent with particles containing only a small amount of ammonium nitrate and with a density close to 1 g cm^{-3}. No multiply charged particles were observed when DMA2 selected the less-hygroscopic PSL/AN particles because multiply charged particles containing PSL would necessarily have a very thick ammonium nitrate coating; the resulting particles would be just as hygroscopic as PAN particles and consequently would not be selected by DMA2 at this voltage.

[18] Figures 3b and 3c show mass-spectra of singly charged particles in red and blue, corresponding to PSL/AN and PAN particles, respectively. Each spectrum is an average of approximately 200 individual particle spectra corresponding to sampling times of 1–2 minutes. The red spectrum of the less hygroscopic particles is dominated by a progression of carbon atoms, labeled C_1^+, C_2^+, and C_3^+, associated with the carbon-based polymer composition of the PSL spheres. A very small ammonium nitrate signature is seen as the NO^+ peak at a mass-to-charge (m/z) of 30. Since DMA1 in this experiment was set to select 200 nm and the PSL spheres are 204 ± 10 nm in diameter the thickness of the ammonium nitrate layer must be on the order of a few nanometers only. The blue spectrum (Figure 3c) of the more hygroscopic particles in exhibit a large NO^+ peak indicating that the particles were composed of ammonium nitrate.

[19] Figure 4 is a composite of four averaged mass spectra all of which correspond to PSL/AN particles representing 4 different selected dry sizes by DMA1 and with DMA2 set to transmit the maximum number of particles in the less hygroscopic mode. As before, the peaks labeled C_1^+, C_2^+, and C_3^+ are due to the presence of PSL while the NO^+ peak, also shown in the insert in an expanded view, is attributed to nitrate. The four spectra represent raw data and no rescaling was applied. The amplitude of the PSL peaks remains constant from one spectrum to the next consistent with a fixed size PSL sphere. In contrast, the amplitude of the NO^+ peak, corresponding to ammonium nitrate, increases as the size of the particles selected by DMA1 increases. This trend is consistent with the fact that the larger PSL/AN particles have thicker ammonium nitrate layers (quantitative analyses of the relationship between peak intensity and nitrate mass is beyond the scope of this brief letter). Similarly, as shown in Figure 2, the thicker the ammonium nitrate layer is, the more hygroscopic the particle is.

[20] To illustrate the applicability of the HTDMA/SPLAT-MS system to the ambient atmosphere we present here an example of results from experiment carried out at Cheju Island, Republic of South Korea during the Aerosol Characterization Experiment (ACE) Asia.

[21] The ambient aerosol experiment followed the same procedure described above for the laboratory-generated particles. The size distribution presented in Figure 5a was obtained by setting DMA1 to select dry ambient particles 250 nm in diameter (black dotted triangle), humidifying the monodisperse output to above 90% RH and scanning DMA2 with the number density of particles exiting DMA2 indicated. During this run the 250 nm ambient aerosol exhibited 'less' and 'more' hygroscopic modes with growth factors of 1.1 and 1.4, respectively. The red and blue triangles in Figure 5a indicate the ranges of sizes sampled by SPLAT-MS.

[22] Sixty-one mass spectra were obtained over a period of 12 minutes of data collection when DMA2 was set to transmit particles from the more hygroscopic mode. Anal-

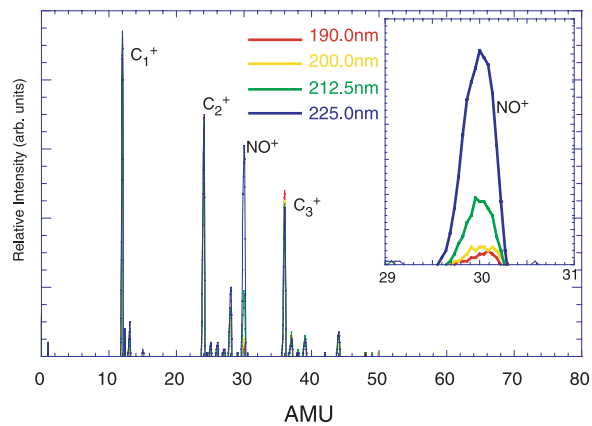

Figure 4. Mass spectra of less hygroscopic particles with different thickness of AN layer on them.

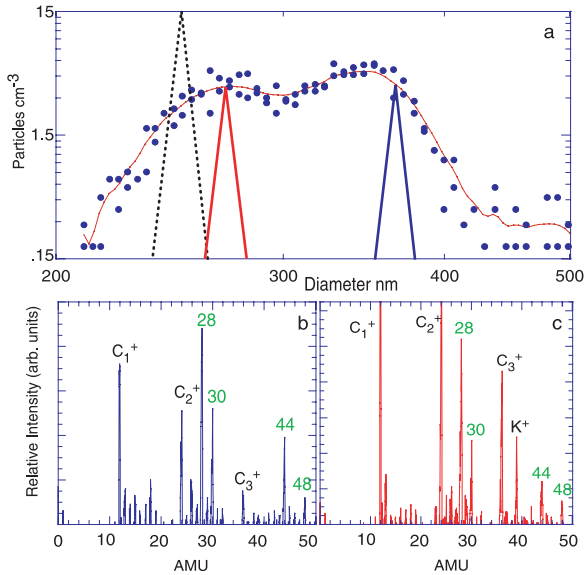

Figure 5. SPLAT-MS results on humidified (dry-250 nm) ambient aerosols; (a) analogues to Figure 2, (b) mass spectrum of more hygroscopic particles, (c) mass spectrum of less hygroscopic particles.

ysis of the mass spectra of these particles showed that 41 (67%) were internally mixed sulfate and organic containing particles, while nine were sulfate-enriched sea salt particles. Therefore, roughly 82% of the more hygroscopic particles exhibited spectra dominated by water soluble compounds. Figure 5b shows an average spectrum, described below, of two atypical particles from the more hygroscopic mode composed of soluble and insoluble organics and a small amount of sulfate.

[23] Spectra of 25 particles from the less hygroscopic mode were recorded during a five minute data collection period. These particles were dominated by crustal material with 21 out of 25 (84%) of the particles containing K with various minerals like Fe, Na, Al, and Si. The majority of the less hygroscopic particles therefore exhibited spectra representative of insoluble compounds. In Figure 5c we present the spectrum of one particle belonging to the less hygroscopic mode with a composition that closely resembles that shown in Figure 5b.

[24] We chose to present the spectra in Figures 5b and 5c, despite the fact that they do not represent the typical composition for the two modes, because they strongly resemble the spectra of the laboratory generated internally mixed particles shown in Figure 3b and 4. In each of these figures, the carbon peaks represent the insoluble fraction and the other labeled peaks correspond to organic acid and sulfate compounds. A comparison between Figures 5b and 5c shows that is the relative fractions of soluble and insoluble components is what determines particle hygroscopicity.

4. Conclusions

[25] We presented an experimental system that provides for simultaneous determination of individual ambient particle size, hygroscopicity and composition. It uses an HTDMA to select particles according to their size and hygroscopicity and a single particle mass spectrometer to characterize their aerodynamic size and their composition. The capability of the system was demonstrated on lab generated internally and externally mixed aerosol consisting of ammonium nitrate coated PSL spheres and pure ammonium nitrate particles.

[26] One of the challenges in this field has been to develop methods that can quantify the relationship between composition and hygroscopicity for internally mixed particles. The results demonstrate that the system is clearly capable of providing detailed information linking individual particle internal composition with their hygroscopic properties. The observations substantiate that the mass spectral peak amplitudes are related to the relative mass fractions of the two components of the internally mixed aerosol.

[27] We were able to demonstrate that the system sensitivity is sufficiently high to allow for experiments on ambient aerosols within a reasonable acquisition time. The ambient data showed that sulfate was present in most of the particles of the more hygroscopic growth mode, while the less hygroscopic mode was mostly of crustal origin.

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