Development and Characterization of an Aircraft Aerosol Time-of-Flight Mass Spectrometer

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This supporting information section contains: 12 pages and 4 figures.
**Supplemental Discussion**

**Increased Submicron Particle Size Range.**

The scattering efficiency $E_s$ is defined as the ratio of the number of particles detected in the sizing region per unit time $N_s$ (particles $\cdot$ minute$^{-1}$) to the total number of particles entering the aerodynamic lens during the same time period, where

$$E_s = \frac{N_s}{CQ_i} \quad (1)$$

$C$ is the number concentration as measured by the condensation particle counter (CPC, model 3010, TSI Inc., MN) or aerodynamic particle sizer (APS) spectrometer (model 3321, TSI Inc., MN) (particles $\cdot$ cm$^{-3}$) and $Q_i$ is the volumetric flow rate (cm$^3$ $\cdot$ minute$^{-1}$) of the inlet system.

The scattering efficiency of UF-ATOFMS over the size range of 95 – 700 nm was 0.5 – 62%. Differences between the A-ATOFMS and UF-ATOFMS may result from differences in tuning of the aerodynamic lens alignment and scattering lasers. The A-ATOFMS curve was generated from a fixed tuning position, i.e. the system was set to a good overall position, and not optimized for each particle size, as was completed for the UF-ATOFMS. The modeled transmission performance based on the simulation program by Wang et al.$^1$ is shown for comparison. The modeled total transmission is above 97% for particles 50 – 500 nm and falls off sharply to ~10% for particles larger than 500 nm. As the $E_s$ is a convolution of total transmission and scattering detection, we expect the A-ATOFMS scattering efficiency to be lower than modeled, particularly for the smaller sizes (< 100 nm) near the limit of detection by the scattering lasers. Interestingly, the observed transmission is greater than simulations for sizes larger than 700 nm, likely due to inaccuracy in the model. Previously, Liu et al.$^2$ found measured transmission efficiencies to be greater than predicted for particles >350 nm (vacuum aerodynamic diameter) at an ambient pressure of 585 torr. As a result, Liu et al.$^2$ suggest that the
transmission efficiency of particles >400 nm is controlled by the orifice assembly in the aerodynamic lens system. Further, Jayne et al.\textsuperscript{3} observed high transmission efficiencies for particles >350 nm, which Liu et al.\textsuperscript{2} attribute to the skimmer cone just after the aerodynamic lens exit in the ATOFMS. Thus, it is suggested that the higher measured transmission efficiency for particles greater than \textasciitilde 700 nm is controlled by the orifice assembly at the entrance to the aerodynamic lens system and the skimmer cone following the lens exit.

Previously, for the nozzle-inlet ATOFMS, instrument busy time, that is the time during which the instrument is processing the size and/or chemical composition information for a particular particle and therefore cannot continue to detect particles during this time, was found to be 5-95\% of the nominal sampling time.\textsuperscript{4} For SOAR-1, representative A-ATOFMS, UF-ATOFMS, and nozzle-inlet ATOFMS hit and sized particle distributions for night, morning, and evening one hour time periods are shown in Figure 2. During the peak time period for the A-ATOFMS (night), size information was collected for 148,266 particles, and chemical composition information for 20,566 particles by the A-ATOFMS. In comparison, during the peak time period for the UF-ATOFMS (afternoon), size information was collected for 21,875 particles and chemical composition information for 5,611 particles by the UF-ATOFMS. During the peak time period for the ATOFMS (morning), size information was collected for 14,842 particles, with chemical composition information for 4,100 particles by the ATOFMS. During these time periods of interest, 47-72\% of the particles observed by the nozzle-inlet ATOFMS were in the size range of 1.0-2.5 µm, showing the utility of the ATOFMS for the study of supermicron particles, such as dust and sea salt.

The overall shapes of the ambient hit particle distributions compare well with those of the sized particles, demonstrating an overall lack of size biasing in the hit particles from 50-1000
nm. For the A-ATOFMS, small divergences in the shapes of the sized and hit particle
distributions below 100 nm and above ~300 nm are likely due to increased deflection of ultrafine
particles in the ionization region and divergence of particles from the focused particle beam due
to the size and shape-dependent transmission of particles through the aerodynamic lens system.5,
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To further compare the size ranges of the A-ATOFMS, UF-ATOFMS, and nozzle-inlet
ATOFMS, ultrafine and submicron hit particle counts were scaled to 1 hr average SMPS data
using the following size bins were used: 50.5-100.1, 100.1-124, 124-149, 149-172, 172-199,
505-543, 543-584, 584-627, 627-673, 673-724, 724-778, 778-836, and 836-866 nm. Scaling
conversions between aerodynamic and mobility diameter have been completed previously by
making assumptions regarding particle density and shape.7 However, while significant size
differences can exist between aerodynamic diameter (ATOFMS) and mobility diameter (SMPS)
for certain chemical particle types, Spencer et al8 found that chemically diverse particle types
observed by ATOFMS during SOAR had similar effective densities due to the abundance of
secondary species, such as organic carbon, sulfate, and nitrate. It is assumed in this paper that
scaling ultrafine and submicron ATOFMS data directly to SMPS data yields negligible sizing
errors for comparison of total particle counts between ATOFMS instruments.

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**Improved Ion Transmission and Mass Resolution.**

For the ion simulations (SIMION 3D 7.0, developed by David Dahl, Idaho National Lab,
Scoville, ID) to compare the A-ATOFMS with the previous coaxial ATOFMS, the following ion
parameters were utilized. 5000 ions starting in random directions had random initial positions
within a spherical volume (radius = 0.3 mm); random initial velocities were assigned from 1100-1400 m/s. The reported resolving power is calculated from all ions arriving at the detector at half height of the m/z peak.

First Dual-Polarity Single-Particle Mass Spectrometry Aircraft-based Measurements.

Ion peak assignments correspond to the most probable ions for a given m/z value, considering the other ion peaks present within the single particle.\textsuperscript{9-13} The organic carbon (OC)-sulfate-nitrate particle (Figure 4a) is characterized by positive ion peaks at m/z 27 (C$_2$H$_3^+$/CHN$^+$), 37 (C$_3$H$^+$), 39 (C$_3$H$_3^+$), 50 (C$_4$H$_2^+$/C$_3$N$^+$), and amine peaks at m/z 59 (CH$_3$)$_3$N$^+$) and 118 (C$_2$H$_5$)$_3$NOH$^+$), in particular. The negative ions are dominated by nitrate and sulfate at m/z -46 (NO$_2^-$), -62 (NO$_3^-$), and -97 (HSO$_4^-$) with organic carbon ion peaks at m/z -26 (CN$^-$), -42 (CNO$^-$), and -43 (CH$_3$COO$^-$). The mass spectra of a biomass/biofuel burning particle (Figure 4b) are characterized by a large potassium ion peak at m/z 39 (K$^+$) coupled with smaller carbonaceous ion peaks at m/z 36 (C$_5^+$) and 37 (C$_3$H$^+$), potassium-sulfate clusters at m/z 175 (K$_2$HSO$_4^+$) and 213 (K$_3$HSO$_4^+$), and a negative ion sulfate peak at m/z -97 (HSO$_4^-$). The dust-nitrate-sulfate particle (Figure 4d) is characterized by intense inorganic positive ion peaks at m/z 23 (Na$^+$), 24 (Mg$^+$), 27 (Al$^+$), 39 (K$^+$), 40 (Ca$^+$), 56 (CaO$^+$), 57 (CaOH$^+$), 96 (Ca$_2$O$^+$), and 165 (Na$_3$SO$_4^+$), in particular. Silicate (m/z -76 (SiO$_3^-$)), nitrate (m/z -46 (NO$_2^-$), -62 (NO$_3^-$), -125 (H(NO$_3$)$_2^-$), and -147 (Na(NO$_3$)$_2^-$), and sulfate (m/z -80 (SO$_3^-$), -96 (SO$_4^-$), and -97 (HSO$_4^-$)) are found in the negative ions of this reacted dust particle.

The particle types shown in Figure 5 and S-4 are briefly described here. The OC-nitrate-sulfate type is characterized by organic carbon, nitrate, and sulfate. The amine-sulfate-nitrate particle type is dominated by amine marker ions, discussed above, as well as organic carbon,
Sulfate, and nitrate. The aromatic particle type is dominated by organic carbon marker ions indicative of aromatic species; the negative ions of this particle type often include chloride and nitrate. The biogenic particle type is dominated by inorganic positive ions, including sodium, potassium, and/or calcium, with nitrate or phosphate in the negative ion spectra. The elemental carbon-organic carbon (ECOC)-nitrate-sulfate type is characterized by both elemental and organic carbon mixed with nitrate and sulfate. The EC-nitrate-sulfate type is dominated by carbon cluster ions, described above, and indicative of elemental carbon mixed with nitrate and sulfate. The biomass-nitrate-sulfate particles are described above and include secondary nitrate and sulfate. The salt-nitrate-sulfate particle type is characterized by sodium and potassium chloride salts with nitrate and sulfate. The nitrate-sulfate type includes particles which only produced negative ion spectra characterized by nitrate and sulfate. The sulfuric acid type includes particles producing only negative ions and characterized by sulfate (m/z -97 (HSO₄⁻)) and sulfuric acid (m/z -195 (H₂SO₄HSO₄⁻)).
References


Supplemental Figure Captions

Figure S-1. Photograph of the A-ATOFMS aboard the NCAR C-130 aircraft.

Figure S-2. A-ATOFMS transmission/sizing efficiency compared to modeled results and observed UF-ATOFMS results.

Figure S-3. A-ATOFMS size calibration curve generated from standard PSL particles. A 5th order polynomial is fit to 95 – 2920 nm. To size ambient particles below 100 nm, a power curve (inset) is used from 95 - 300 nm PSL data.

Figure S-4. A-ATOFMS particle counts with 2-4 minute resolution for A-ATOFMS measurements during ICE-L on December 13, 2007.
Figure S-1.
Figure S-2.

\[ y = -1 \times 10^{-5}x^5 + 0.0052x^4 - 1.1196x^3 + 120.38x^2 - 6480.8x + 140536 \]

\[ R^2 = 0.9983 \]

Figure S-3.

\[ y = 12588.3704 e^{-0.0363x} \]

\[ R^2 = 0.9561 \]
Figure S-4.