Collection Efficiencies of Ammonium Nitrate, Ammonium Sulfate and Mixed Organic/Ammonium Sulfate Particles as a Function of Relative Humidity for an Aerodyne Aerosol Mass Spectrometer

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Aerosol Mass Spectrometer (AMS)

100% transmission (60-600 nm), aerodynamic sizing, linear mass signal.

Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles.

Experiment Outline

- Performed both hydration (deliquescence) and dehydration (efflorescence) experiments.
- Solutions of $\text{NH}_4\text{NO}_3$, $(\text{NH}_4)_2\text{SO}_4$, and organics prepared in nanopure water.
- AMS ran in alternating mode: 5 min averages
- Vaporizer: $T = 580^\circ \text{C}$
- Volumetric Flow Rate: $1.3 \text{ cm}^3 \text{ s}^{-1}$
- m/z ratios for $\text{NH}_4\text{NO}_3$: 15, 16, 17, 18, 28, 30, 46
- m/z ratios for $(\text{NH}_4)_2\text{SO}_4$: 15, 16, 17, 18, 28, 48, 64, 80, 81
- m/z ratios for organics: 44
Ammonium Nitrate Hydration Experiment

Ammonium Nitrate Particles
$D_{d,m,\text{dry}} = 199$ nm

Collection Efficiency (%) vs. Sampling Line Relative Humidity (%)

Deliq. RH (DRH)
Ammonium Sulfate Hydration Experiment

Ammonium Sulfate Particles
Ddma,dry = 199 nm

Collection Efficiency (%) vs. Sampling Line Relative Humidity (%)
Conclusions: Hydration Experiments

- CE for NH$_4$NO$_3$ are ~ 100% and do not demonstrate a dependence upon RH. (In most cases, the CE values were >100%; this is believed to be associated with the AMS software particle counting procedure.)
  - Consistent with early findings: pure NH$_4$NO$_3$ particles are associated with water, even below the predicted deliquescence point (e.g. Tang, 1980). Because of this, the particles should be spherical in shape and focused in the lens with a high degree of efficiency resulting in high CE values (less bounce?).
- CE for (NH$_4$)$_2$SO$_4$ do demonstrate a strong dependence on RH. At RH < deliquescence relative humidity (DRH), the CE values are 20-30%, but when RH > DRH, the CE values rise quickly and approach 100%.
  - (NH$_4$)$_2$SO$_4$ particles have well defined deliquescence and efflorescence points, 80% and 36% respectively (Tang, 1980). Therefore, (NH$_4$)$_2$SO$_4$ particles can form dry nonspherical particles at low RH which have a lower focusing efficiencies and CE (more bounce?).
- CE for (NH$_4$)$_2$SO$_4$ drop at RH values approaching 100%
  - Particles become larger due to the addition of water and the larger particles can be lost in the critical orifice of the AMS inlet which will result in lower CE values.
  - This can happen to any particle type and is a function of initial particle size, RH, and the species present in the particle.
Ammonium Nitrate Particles
D_{dma,dry} = 343nm
D_{dma,dry} = 199nm

Effl. RH (ERH), “for contaminated NH₄NO₃”
Ammonium Sulfate Dehydration Experiment

Collection Efficiency (%) vs. Sampling Line Relative Humidity (%)

Ammonium Sulfate Particles

\( D_{\text{DMA,dry}} = 343\text{nm} \)
\( D_{\text{DMA,dry}} = 199\text{nm} \)

Effl. RH (ERH)
Conclusions: Dehydration Experiments

- CE for NH$_4$NO$_3$ particles were ~ 100% and did not exhibit a RH dependence when the experiment was initiated with 199 nm dry particles.
  - When the experiment was initiated with 343 nm dry particles, there was a RH dependence (i.e. at high RH, the CE values began to drop below 100%) which can be attributed to the growth of particles and the loss of these particles in the critical orifice of the AMS inlet.
- CE for (NH$_4$)$_2$SO$_4$ exhibit a strong dependence on RH, but not the expected dependence.
  - Based on the efflorescence relative humidity (ERH) of 36%, it was anticipated that the CE for (NH$_4$)$_2$SO$_4$ would approach 100% at RH > ERH, and then drop to those values observed in the hydration experiment at RH < ERH.
  - When the experiment is initiated with 199 nm dry particles, CE values drop to ~40% at RH values (i.e. RH = 80%) considerably higher than the ERH. At the ERH, it appears there is another drop in the CE values to ~25-30%.
  - Strong indication that the RH in the inlet system is considerably lower than the RH in sampling line. This lower RH could result in the particles loosing water faster than what would be expected based upon the sampling line RH.
  - When the experiments are initiated with 343 nm particles, the (NH$_4$)$_2$SO$_4$ particles become to large at higher RH and are lost in the AMS inlet leading to lower CE values.
Summary

• In general NH₄NO₃ particles have collection efficiencies (CE) approaching 100% and do not vary as function of RH.

• CE values for (NH₄)₂SO₄ particles do vary as a function of RH, and range from 20% at low RH to near 100% at higher RH values. This implies a correction factor of 5 for sulfate field data obtained at RH < ERH (36%), but in practice the correction factor is ~ 2. This discrepancy may be due to:
  – field measurements are mainly in the RH range above the ERH and below the DRH where CE is ~ 40%
  – the presence of organic species internally mixed with the sulfate, which could increase the CE for sulfate.

• Both NH₄NO₃ and (NH₄)₂SO₄ particles have low collection efficiencies at high RH if the particle diameter exceeds the maximum transmittable diameter of the critical orifice.
Mixed Organic/Ammonium Sulfate Experiments

- Looked at three organic compounds; idea was that presence of organics would cause ammonium sulfate (AS) particles to retain water at RH values below the DRH of AS and increase CE at lower RH values.
  - Ammonium Acetate (AA)
  - Ammonium Oxalate (AO)
  - Citric Acid (CA)
- AA and AO provided no useful results
  - AA – no noticeable organic peaks detected; perhaps acetate was evaporating before reaching heater?
  - AO – m/z 44 was present, but DRH for AO > 94%, higher than AS; therefore AO should not cause the particles to retain water below DRH of AS.
Experiments with Citric Acid

- Citric acid (CA) has a continuous growth curve, analogous to ammonium nitrate (*Peng et al. 2001*)
  - Anticipated that presence of CA would allow the mixed particles to retain water below DRH of AS
- Conducted both hydration and dehydration experiments with 200 and 300 nm particles
CE for Particles Containing Ammonium Sulfate and Citric Acid/Ammonium Sulfate

- 300nm 10% CA
- 200nm 50% CA
- 200nm NO CA
- 300nm 50% CA
- 300nm, pure CA (dehydration)
- 200nm, 10% CA RH=94.5
- 200nm, pure CA RH=96.7

CE vs RH diagram with various particle sizes and conditions.
Conclusion: Mixed Citric Acid/Ammonium Sulfate Particle Experiments

- Presence of CA did not increase the CE as expected.
- Particles containing small amounts of CA (10%) behaved analogous to AS.
- Particles containing 50% CA behaved analogous to pure CA.
- Pure CA particles had low CE and did exhibit a small RH dependence.
- Overall, CA particles do not behave as anticipated.
Collection Efficiencies as a Function of Vacuum Aerodynamic Diameter

![Graph showing collection efficiencies as a function of vacuum aerodynamic diameter. The x-axis represents vacuum aerodynamic diameter in nanometers (nm), ranging from 10 to 1000 nm. The y-axis represents collection efficiency in percentage (%), ranging from 0 to 160%. The graph includes data for experimental data, FLUENT model data, and data for Ammonium Nitrate and Ammonium Sulfate. The data is sourced from John Jayne, Aerodyne.]
Conclusions: Size Experiments

- The collection efficiencies for NH$_4$NO$_3$ were always greater than $\sim$ 75%, which is in agreement with our previous findings.
- Fluent Model predicts that there should be a drop in CE for large spherical particles which we also observe (it is assumed the “dry” NH$_4$NO$_3$ particles are still associated with some water, and therefore are spherical).
- The collection efficiencies for dry (NH$_4$)$_2$SO$_4$ are $\sim$ 20%, over the size range tested, which is consistent with our previous results.
Ammonium Nitrate Growth

Ammonium Nitrate Particles
- ○ hydration expts.
- ▲ dehydration expts.
- — Tang, 1980

Ddma,dry = 343 nm
Ddma,dry = 199 nm

Sampling Line Relative Humidity (%)
Ammonium Sulfate Growth

Dv/Dv,dry (Tang, 1980)

Ddma,dry = 343 nm
Ddma,dry = 199 nm
Ddma,dry = 100 nm

Sampling Line Relative Humidity (%)
Conclusions: Particle growth

- The relative change in Dva is not as large as the relative change in Dv.
  - Because the Dva depends on the particle density and physical size, increases in physical size are somewhat offset by decreases in particle density as more H₂O is absorbed. When the density approaches one, the Dva increases because the Dv increases.

- The deliquescence and efflorescence points are not as distinct in the AMS growth curves compared to the Tang data.
  - Other experiments (discussed previously) indicate that phase changes probably depend on the conditions within the critical orifice and lens.
Ammonium Sulfate Water Content

-1.0  -0.5  0.0  0.5  1.0

Mwater/Mtotal

100  80  60  40  20  0

Sampling Line Relative Humidity (%)

Tang, 1980

Ammonium Sulfate Particles
- hydration expts.
- dehydration expts.

Ddma,dry = 343 nm
Ddma,dry = 199 nm
Ddma,dry = 100 nm
Conclusions: Water Content

- The AMS measurements of H$_2$O content are lower than expected.
  - The low pressure within the AMS instrument (critical orifice followed by aerodynamic focusing lens and a vacuum chamber) is likely causing some H$_2$O to evaporate from the particles (i.e., the RH within the AMS is significantly lower than the RH within the sampling line).
- Particle growth and water content appear to be dependent on initial particle dry size, and the smallest particles do not “grow” as much as the larger particles.
  - While the evaporation rates are probably comparable, the relative amounts of H$_2$O lost from the smaller particles will be greater than from larger particles.
- Although the AMS can measure increases in particle water content at high RH, the quantification of particle water is limited by evaporation in the AMS, accurate subtraction of gas phase H$_2$O and H$_2$O due to fragmentation of molecules containing water (H$_2$SO$_4$), and knowing the ionization efficiency of H$_2$O relative to nitrate.