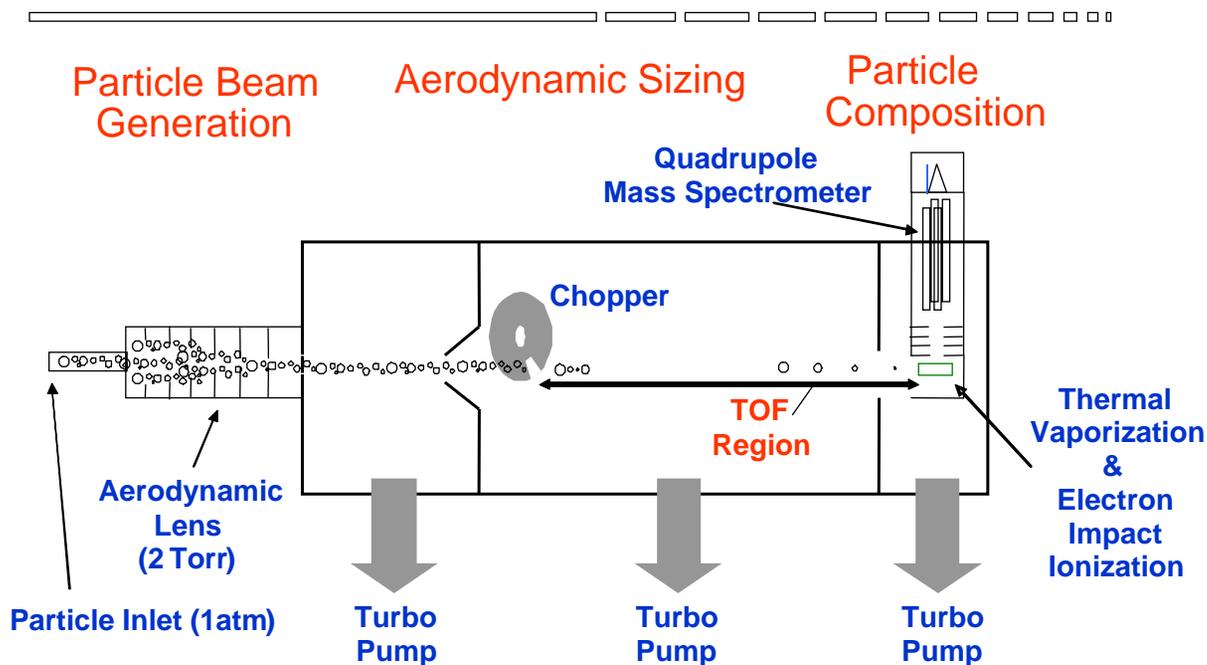


Collection Efficiencies of Ammonium Nitrate, Ammonium Sulfate and Mixed Organic/Ammonium Sulfate Particles as a Function of Relative Humidity for an Aerodyne Aerosol Mass Spectrometer

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Aerosol Mass Spectrometer (AMS)



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

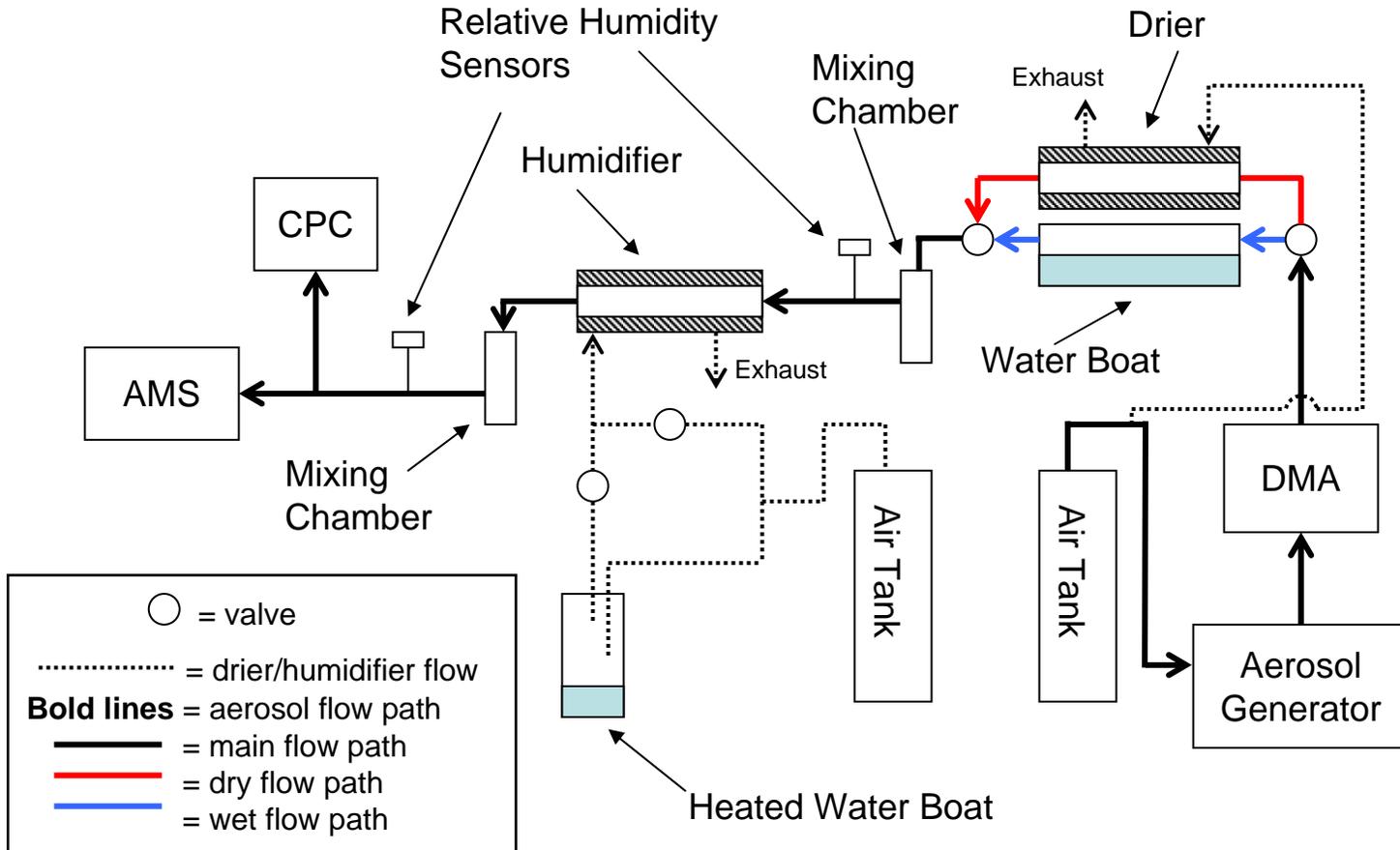
Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles.

Jayne et al., *Aerosol Science and Technology* 33:1 -2(49-70), 2000.

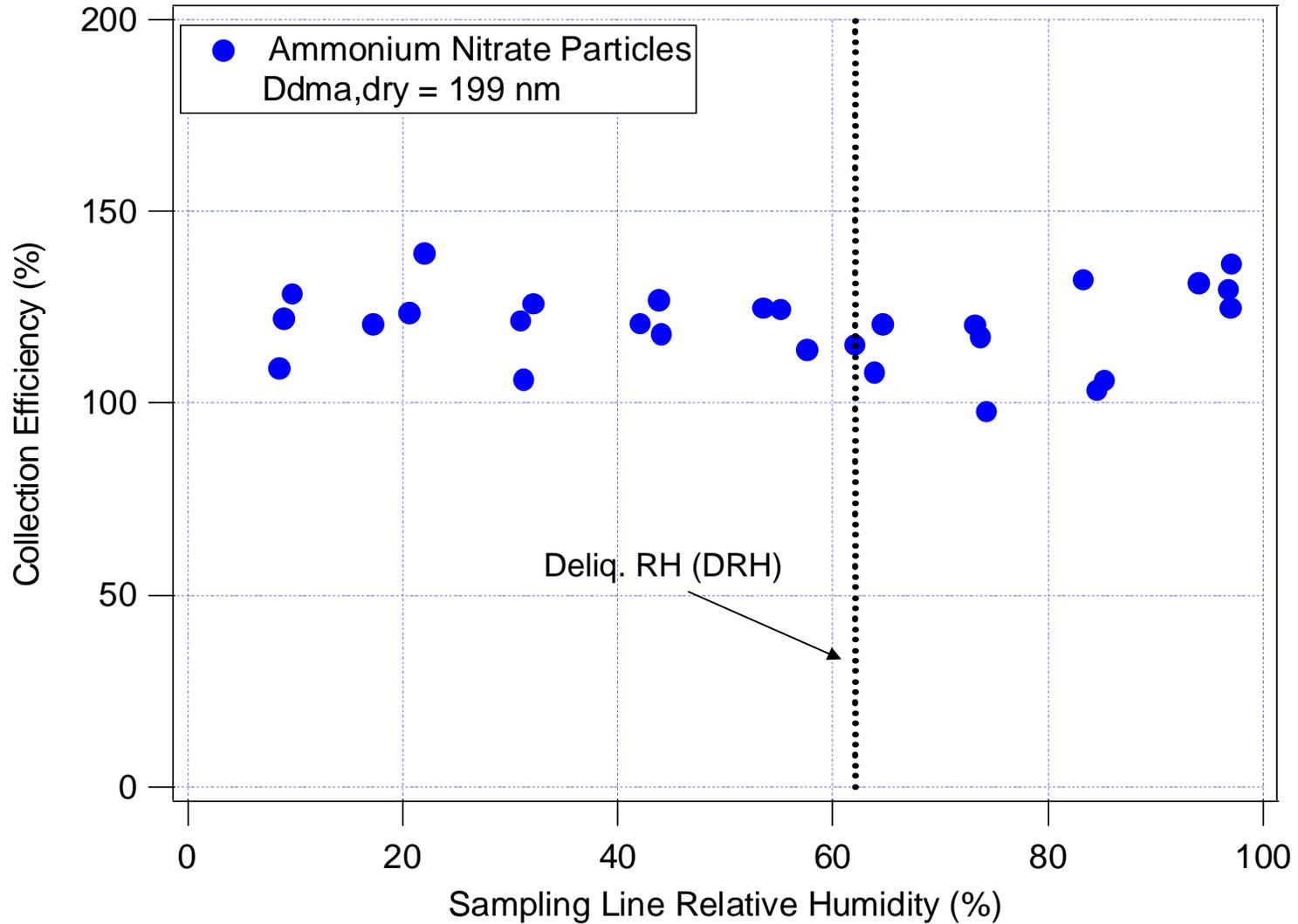
Experiment Outline

- Performed both hydration (deliquescence) and dehydration (efflorescence) experiments.
- Solutions of NH_4NO_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 NH_4NO_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

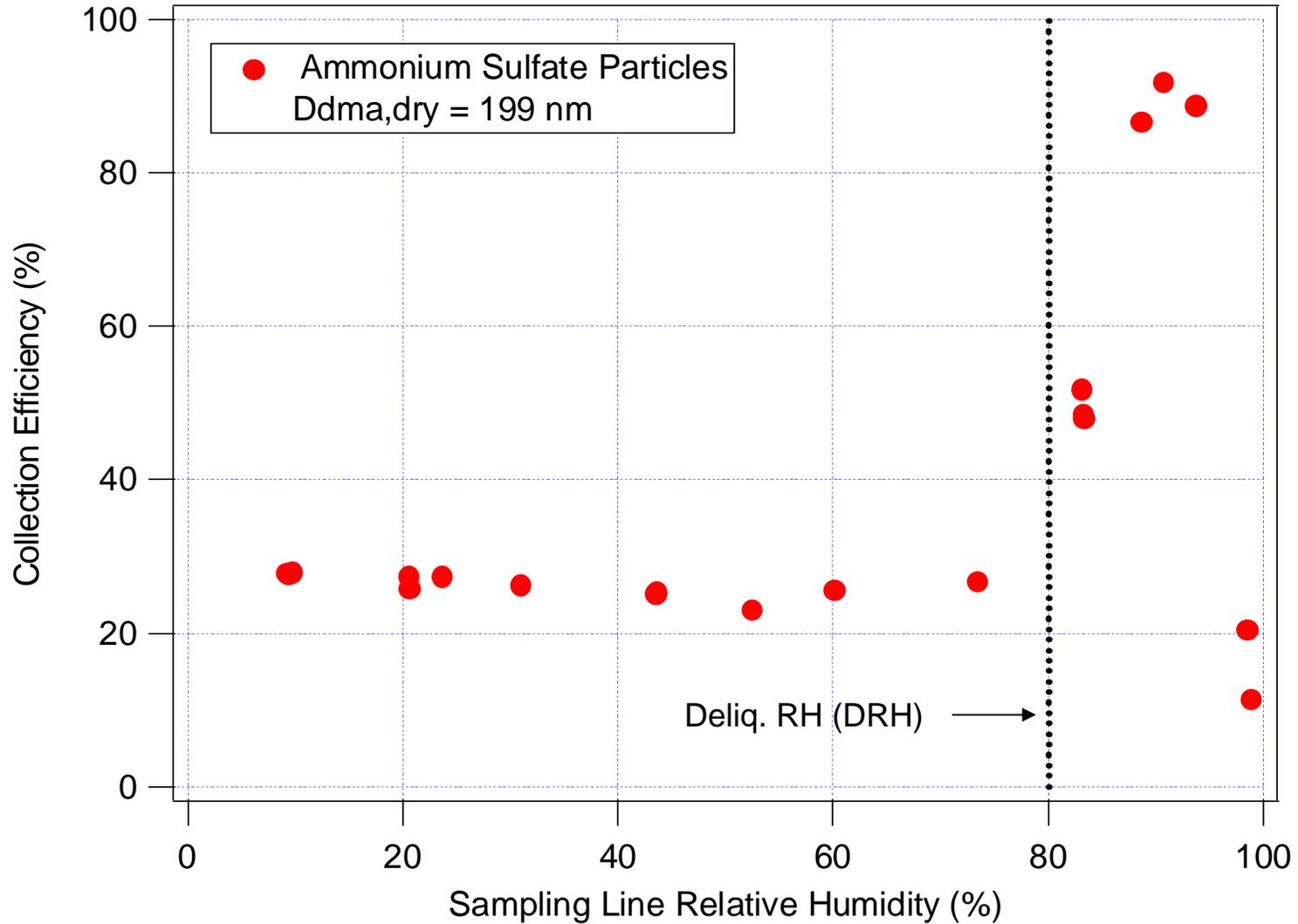
Experimental Setup



Ammonium Nitrate Hydration Experiment



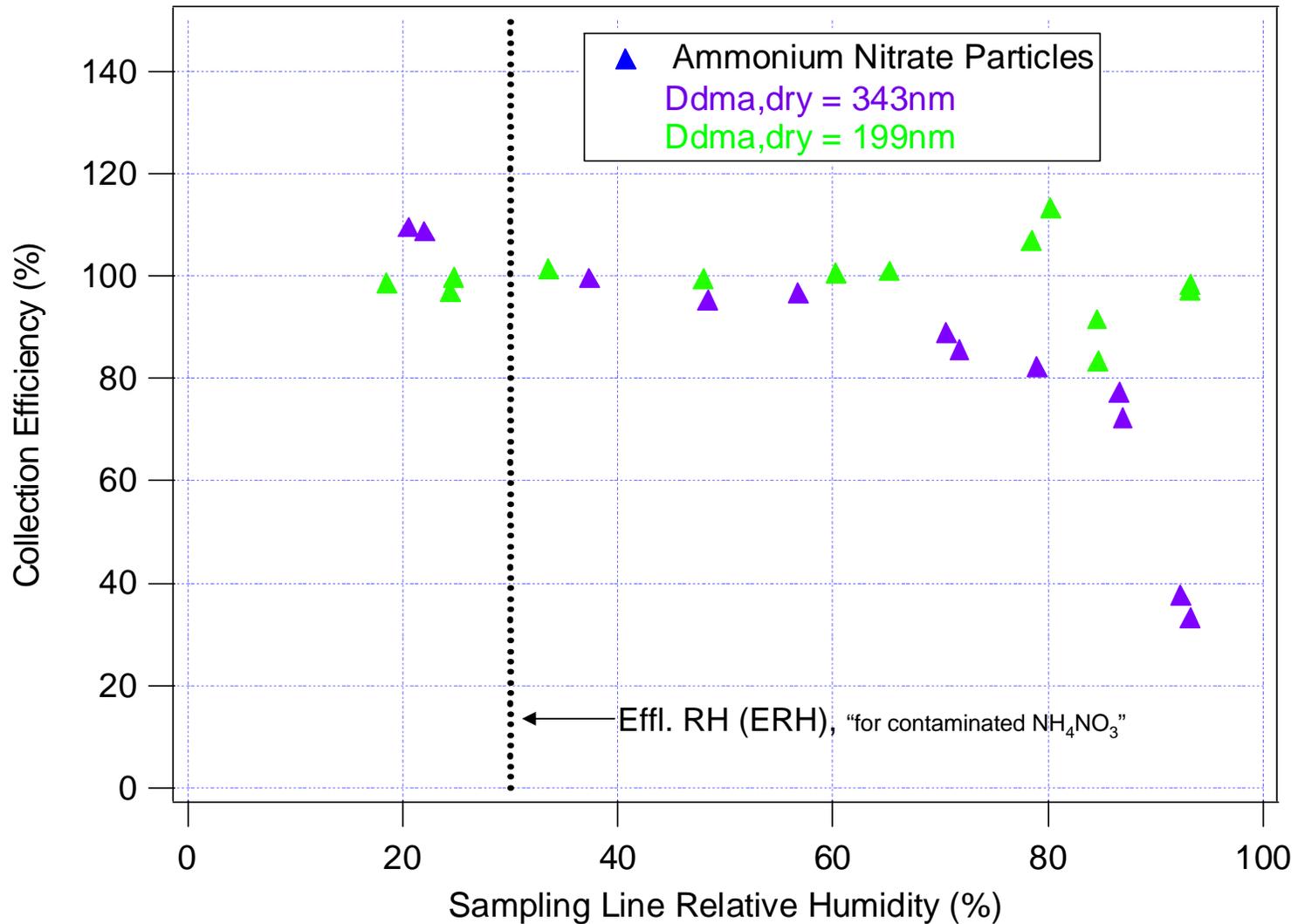
Ammonium Sulfate Hydration Experiment



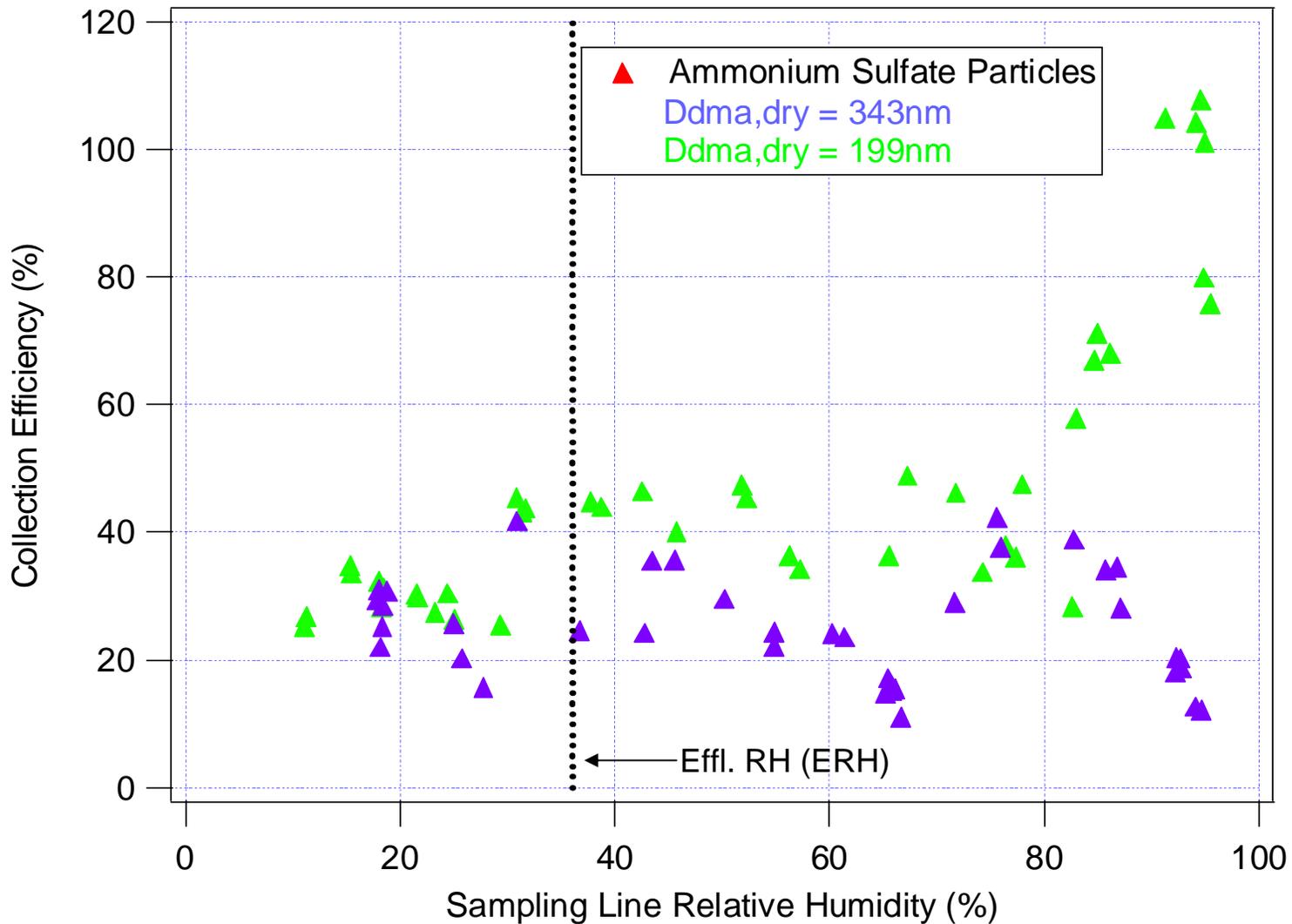
Conclusions: Hydration Experiments

- CE for NH_4NO_3 are $\sim 100\%$ 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_4NO_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 $(\text{NH}_4)_2\text{SO}_4$ do demonstrate a strong dependence on RH. At $\text{RH} < \text{DRH}$, the CE values are 20-30%, but when $\text{RH} > \text{DRH}$, the CE values rise quickly and approach 100%.
 - $(\text{NH}_4)_2\text{SO}_4$ particles have well defined deliquescence and efflorescence points, 80% and 36% respectively (*Tang, 1980*). Therefore, $(\text{NH}_4)_2\text{SO}_4$ particles can form dry nonspherical particles at low RH which have a lower focusing efficiencies and CE (more bounce?).
- CE for $(\text{NH}_4)_2\text{SO}_4$ 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 Dehydration Experiment



Ammonium Sulfate Dehydration Experiment



Conclusions: Dehydration Experiments

- CE for NH_4NO_3 particles were $\sim 100\%$ 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 $(\text{NH}_4)_2\text{SO}_4$ 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 $(\text{NH}_4)_2\text{SO}_4$ would approach 100% at $\text{RH} > \text{ERH}$, and then drop to those values observed in the hydration experiment at $\text{RH} < \text{ERH}$.
 - When the experiment is initiated with 199 nm dry particles, CE values drop to $\sim 40\%$ at RH values (i.e. $\text{RH} = 80\%$) considerably higher than the ERH. At the ERH, it appears there is another drop in the CE values to $\sim 25\text{-}30\%$.
 - 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 losing water faster than what would be expected based upon the sampling line RH.
 - When the experiments are initiated with 343 nm particles, the $(\text{NH}_4)_2\text{SO}_4$ particles become too large at higher RH and are lost in the AMS inlet leading to lower CE values

Summary

- In general NH_4NO_3 particles have collection efficiencies (CE) approaching 100% and do not vary as function of RH.
- CE values for $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{RH} < \text{ERH}$ (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 $\sim 40\%$
 - the presence of organic species internally mixed with the sulfate, which could increase the CE for sulfate.
- Both NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ particles have low collection efficiencies at high RH if the particle diameter exceeds the maximum transmittable diameter of the critical orifice.

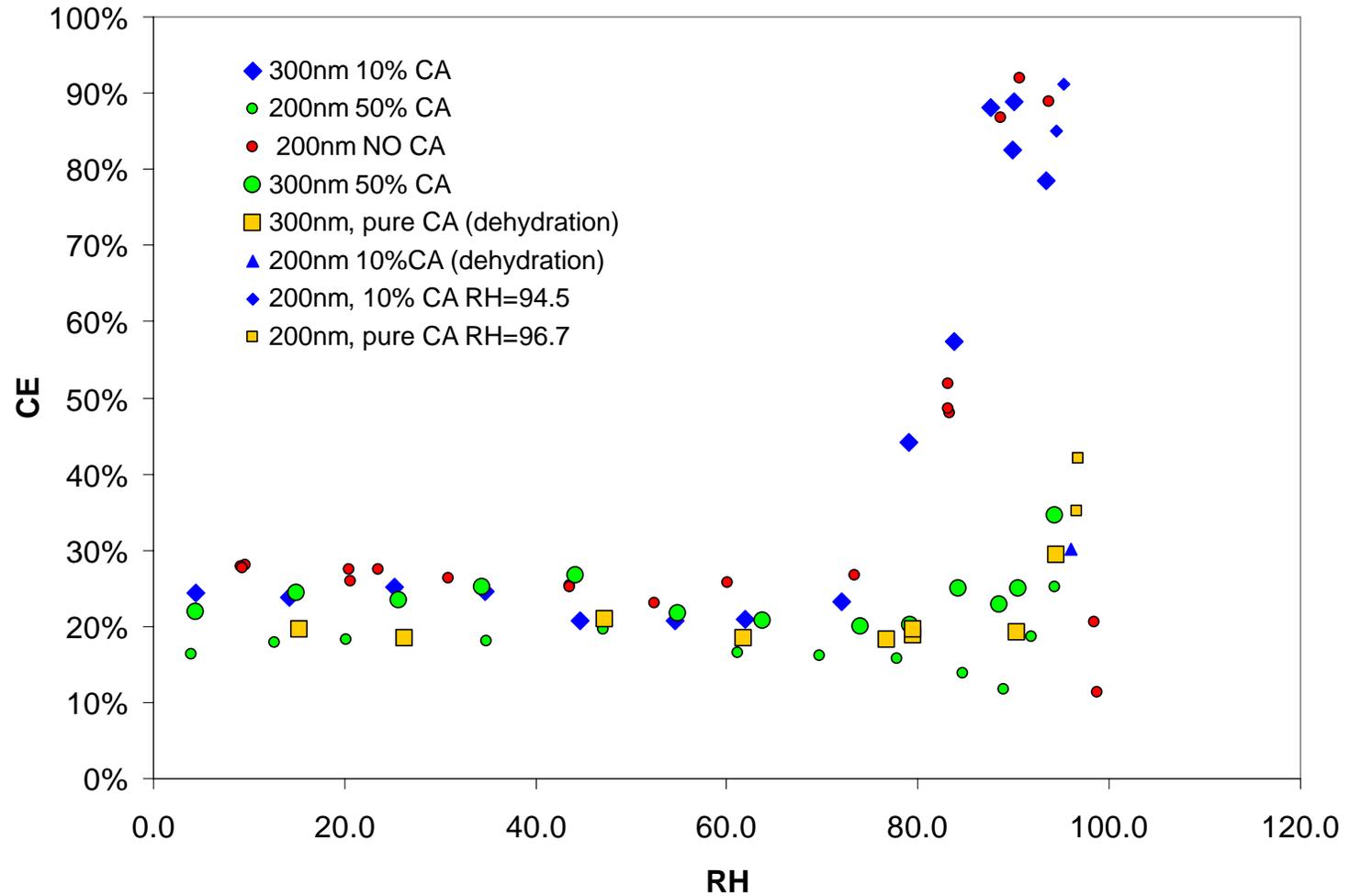
Mixed Organic/Ammonium Sulfate Experiments

- 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

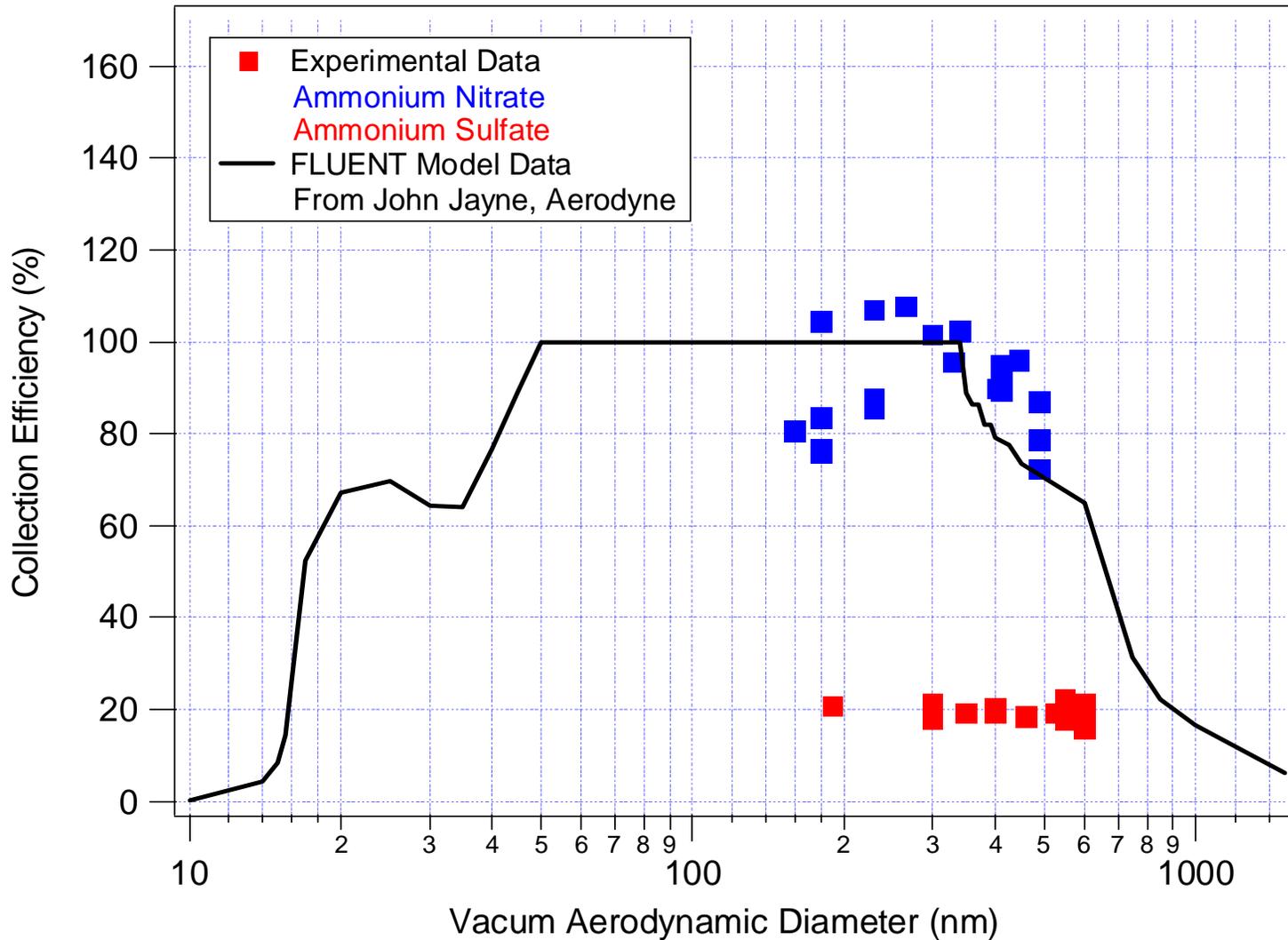
CE for Particles Containing Ammonium Sulfate and Citric Acid/Ammonium Sulfate



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.

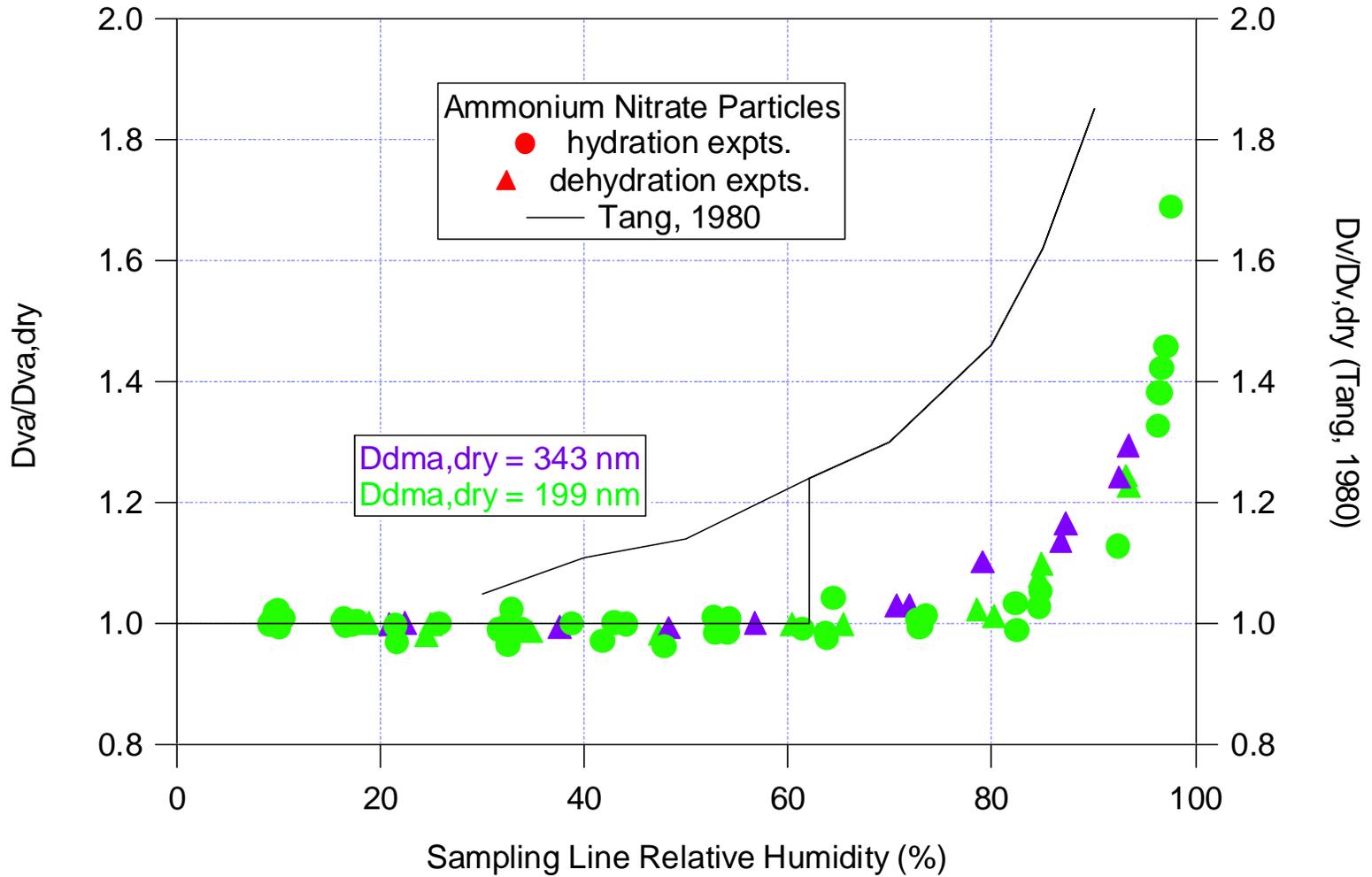
Collection Efficiencies as a Function of Vacuum Aerodynamic Diameter



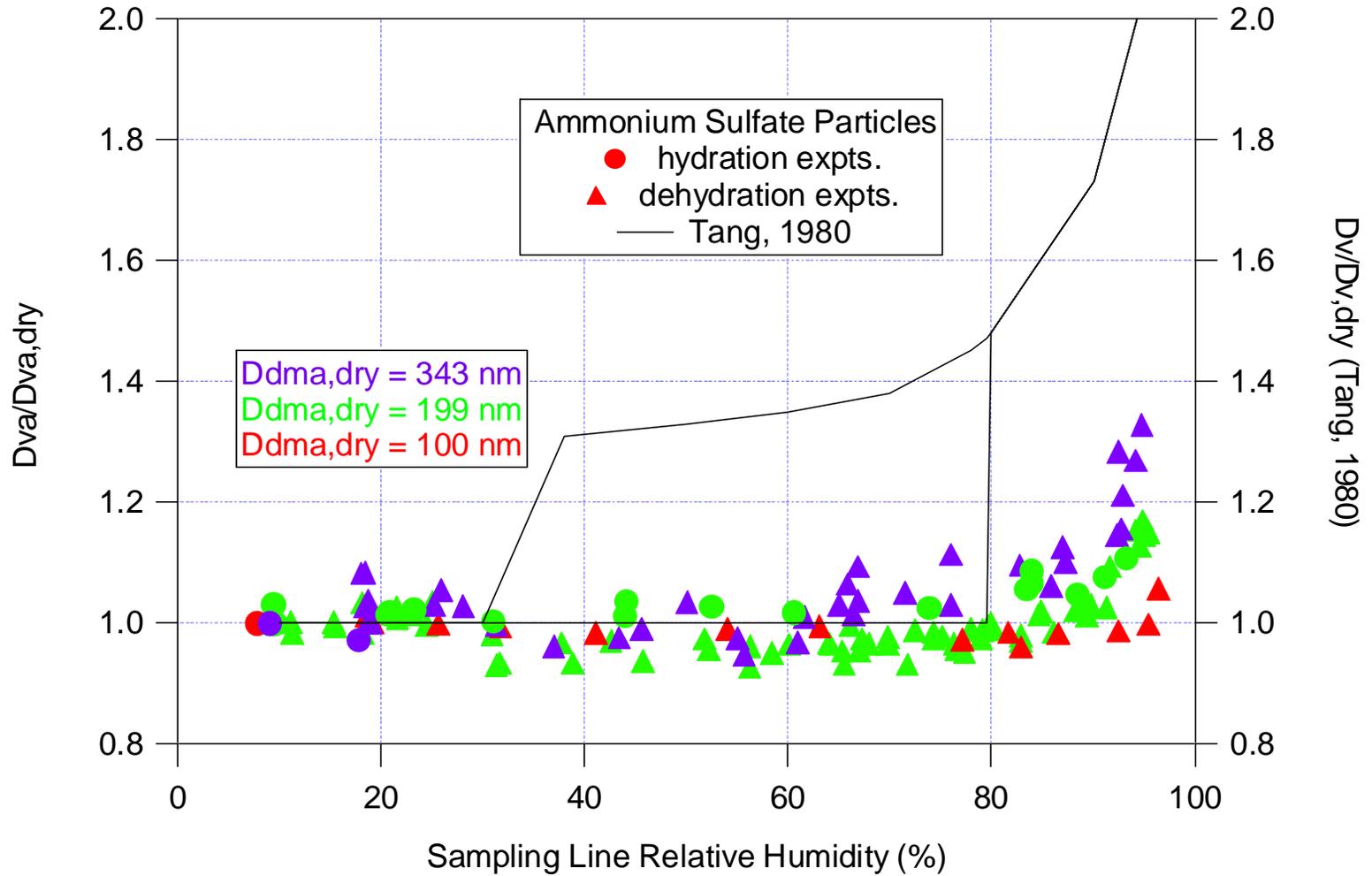
Conclusions: Size Experiments

- The collection efficiencies for NH_4NO_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_4NO_3 particles are still associated with some water, and therefore are spherical).
- The collection efficiencies for dry $(\text{NH}_4)_2\text{SO}_4$ are $\sim 20\%$, over the size range tested, which is consistent with our previous results.

Ammonium Nitrate Growth



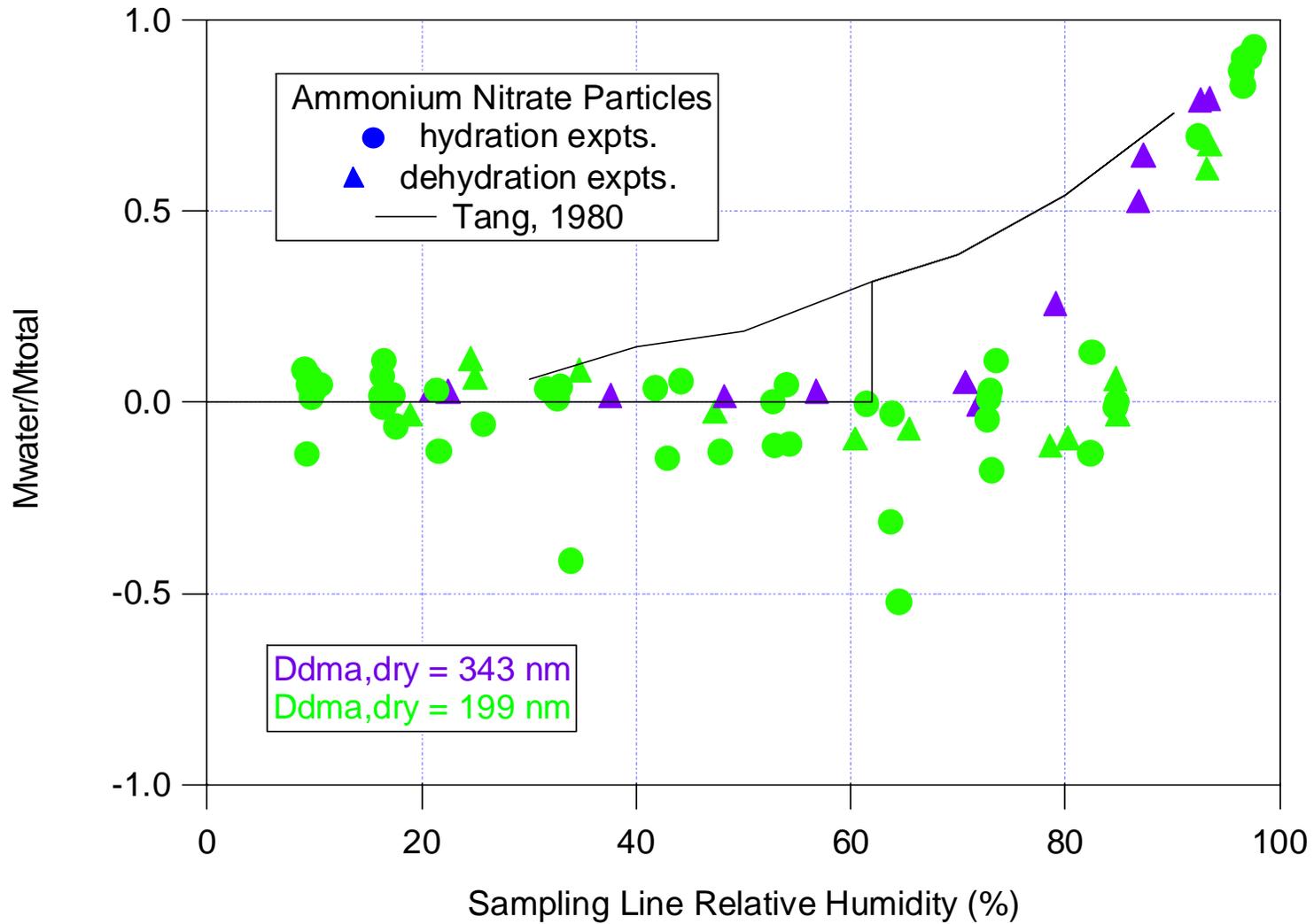
Ammonium Sulfate Growth



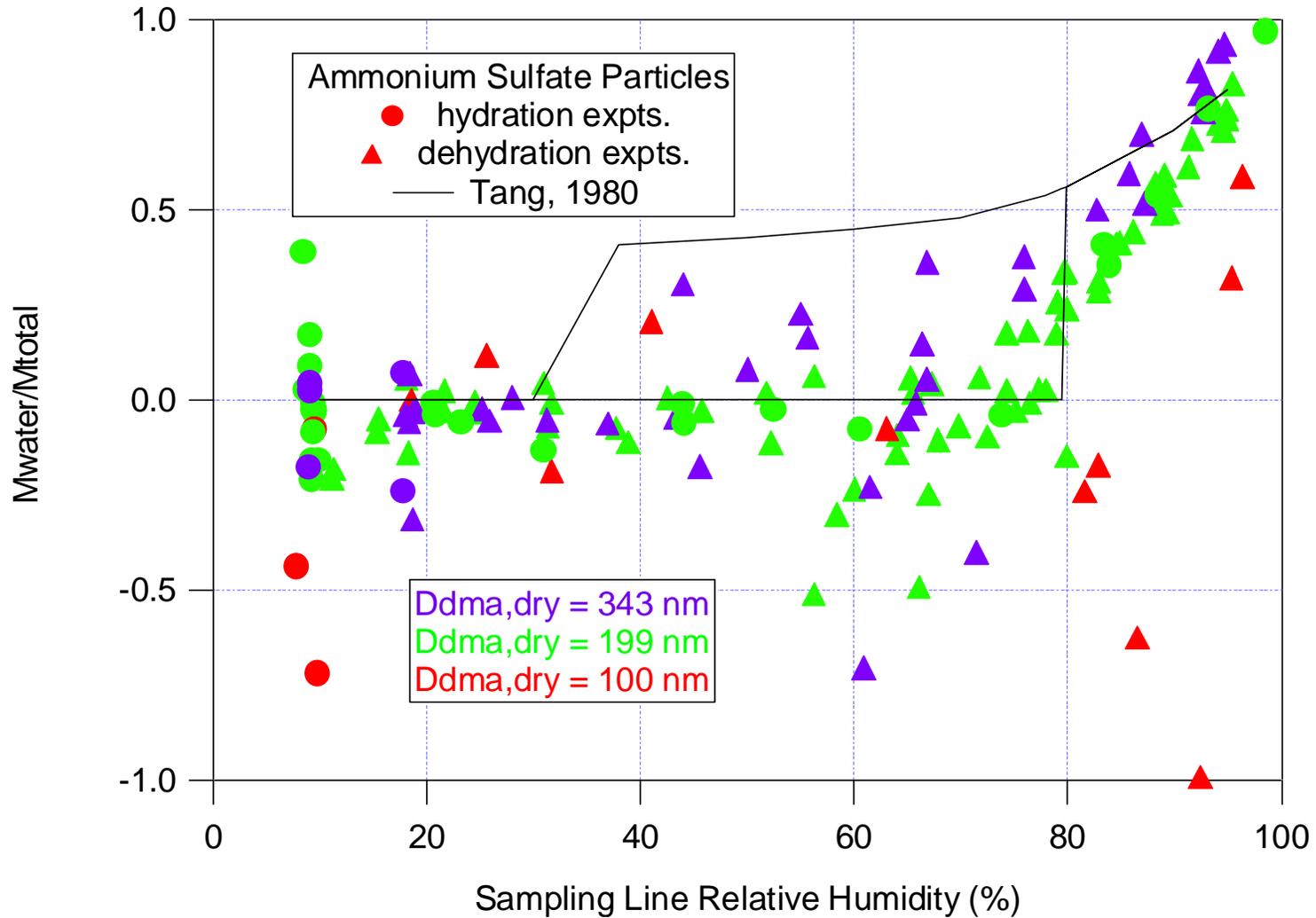
Conclusions: Particle growth

- The relative change in D_{va} is not as large as the relative change in D_v .
 - Because the D_{va} depends on the particle density and physical size, increases in physical size are somewhat offset by decreases in particle density as more H_2O is absorbed. When the density approaches one, the D_{va} increases because the D_v 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 Nitrate Water Content



Ammonium Sulfate Water Content



Conclusions: Water Content

- The AMS measurements of H₂O 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 H₂O 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 H₂O 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 H₂O and H₂O due to fragmentation of molecules containing water (H₂SO₄), and knowing the ionization efficiency of H₂O relative to nitrate.