Calibration Uncertainties in the Droplet Measurement Technologies Cloud Condensation Nuclei Counter

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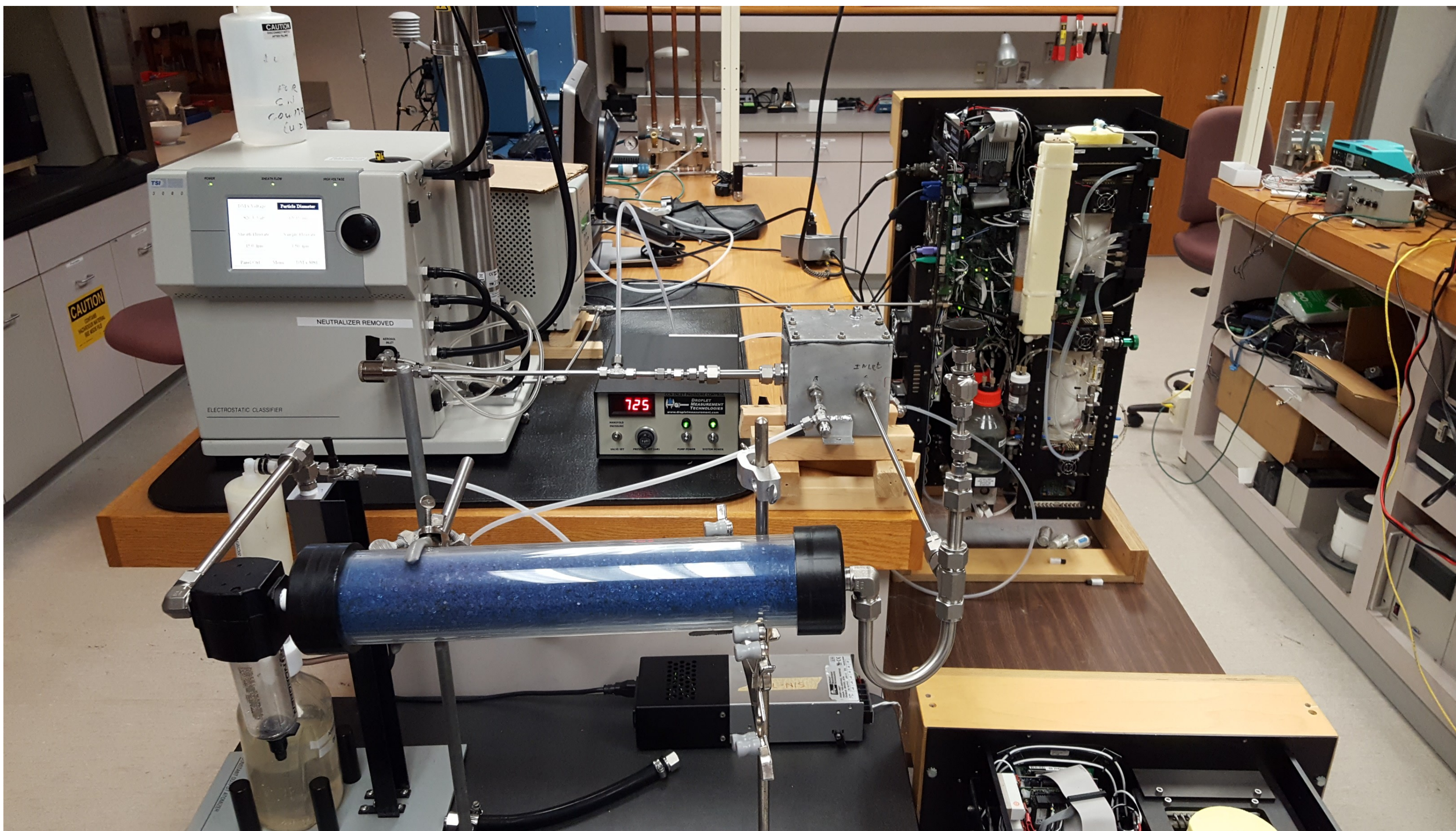
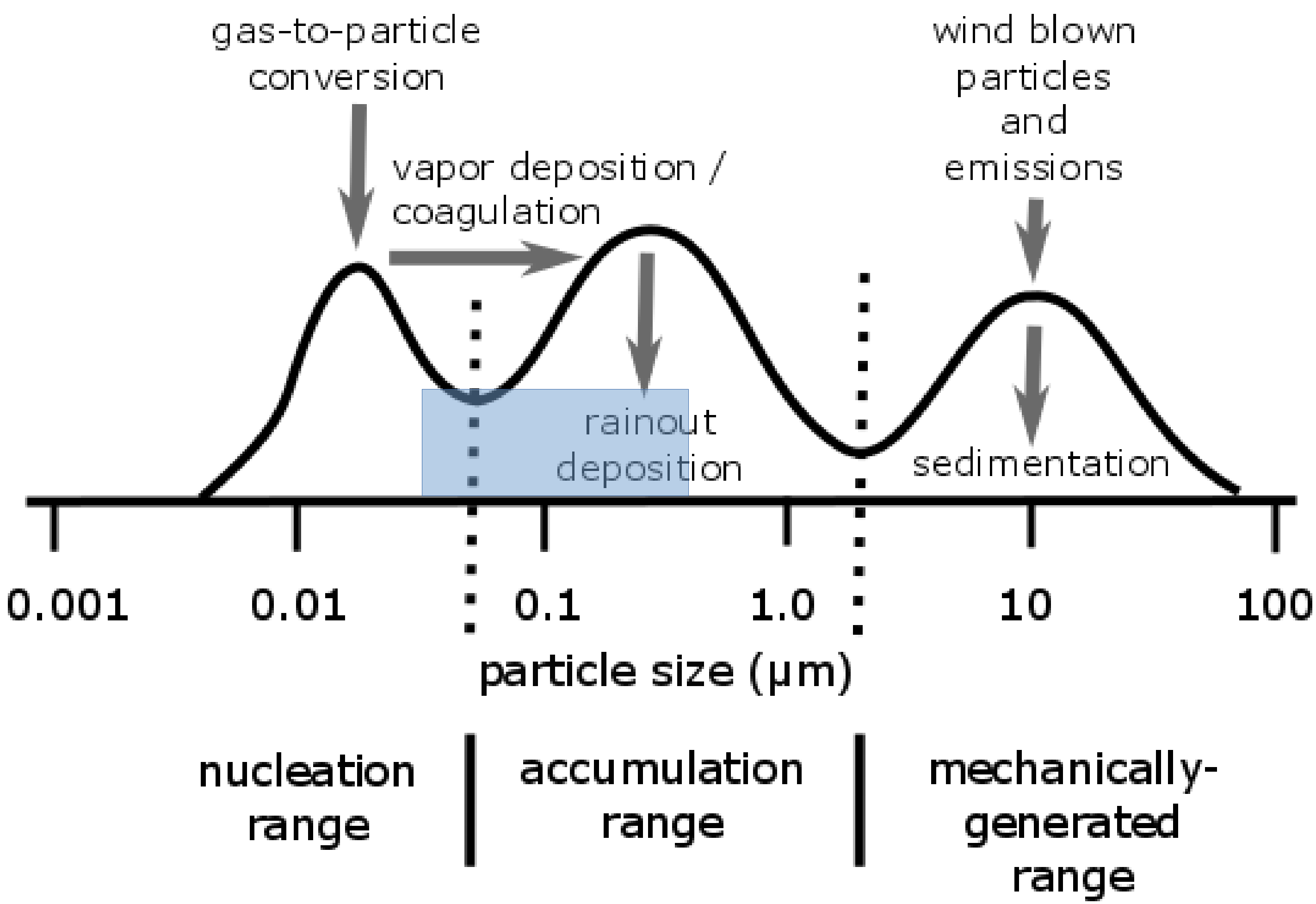


Aerosol Effects

- Understanding the planetary radiation budget depends on understanding of the aerosol climate effects.
- Two Main Aerosol Climate Effects:
  - Direct Effect
  - Indirect Effect
- Indirect effect is particularly important because clouds are the most important contribution to global reflection of incoming solar radiation (Twomey, 1974).
- A subset of aerosols known as Cloud Condensation Nuclei (CCN) are responsible for the aerosol indirect effect.

CCN

- CCN primarily exist in the accumulation mode of aerosols, which are generally larger than 40 nm in diameter.



CCN Climate Effects

- Cloud properties are related to CCN concentration with an increase resulting in:
  - Increased Cloud Droplet Concentration
  - Decreased Cloud Droplet Diameter
  - Increased Cloud Reflectance
  - Longer Cloud Lifetimes (Lindsey and Fromm, 2008)
- There is uncertainty in quantifying the effects of CCN.
- Aerosol effects on cloud albedo are the most uncertain of quantified radiative forcing changes since pre-industrial times (IPCC AR5, 2014).

CCN Uncertainties

- The foundation of the uncertainty in the aerosol indirect effect stems from the uncertainty in the number of CCN (Pierce and Adams, 2009).
- Research community agrees that better CCN measurements are a necessary step in improving our understanding of aerosol cloud interactions (Lance et al., 2009; Roberts et al., 2010).
- CCN measurement uncertainties are not fully understood and the density of CCN measurements is very low.

Research Objective: Quantify the Uncertainties in CCN Measurements.

Supersaturation and Activation

- An air parcel is supersaturated when there is more water vapor in the air than at thermodynamic equilibrium.
- Supersaturation occurs in the atmosphere due to rising motions that cool an air parcel and increase its relative humidity beyond 100 %.
- The supersaturation required for a particular CCN to form a droplet (activate) is known as the critical supersaturation.

Kappa-Köhler Theory

- The equation developed by Petters and Kreidenweis (2007) is:

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right)$$

  - Where kappa >0.2 can be calculated from the expression:

$$\kappa = \frac{4A^3}{27 D_d^3 \ln^2(S_c)}$$

  - And A is defined as:

$$A = \frac{4\sigma_{s/a} M_w}{RT\rho_w}$$

where, ρ_w = density of water

M_w = molecular weight of water

$\sigma_{s/a}$ = surface tension of the solution/air interface

R = universal gas constant

T = temperature

D = diameter of the droplet

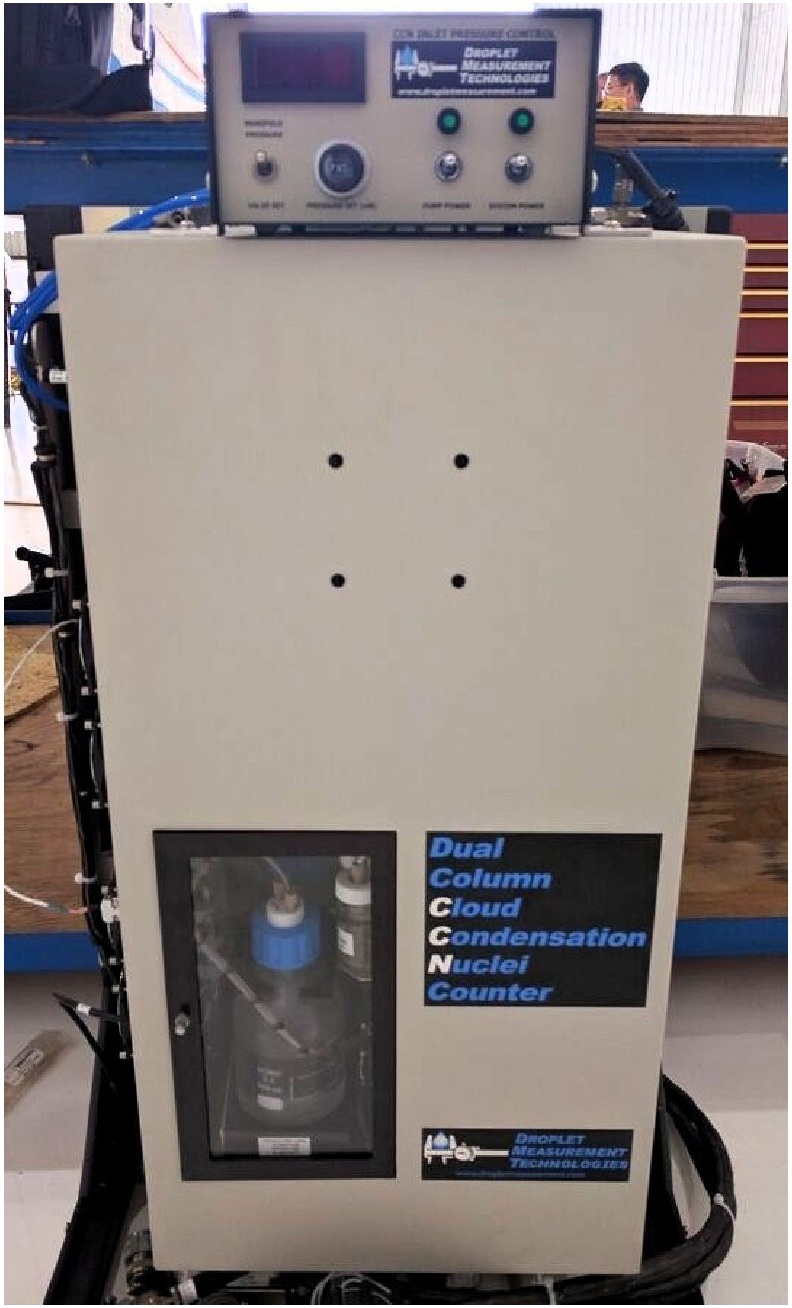
D_d = dry particle diameter

S_c = critical supersaturation corresponding to the dry diameter

- Kappa for ammonium sulfate is 0.61.

CCN Measurements

- CCN measurements are made possible by our understanding of Köhler theory.
- Since CCN are much smaller than the wavelength of visible light it is necessary to grow them to detectable sizes.
- In general, CCN counters create supersaturated conditions inside their droplet growth chamber where aerosols can activate and grow into droplets that are a detectable size.
- Since CCN activate based on size and chemical composition, only some aerosols will activate and be counted at a particular supersaturation.
- Being able to regulate supersaturation and count grown droplets gives the ability to measure the supersaturation spectrum.

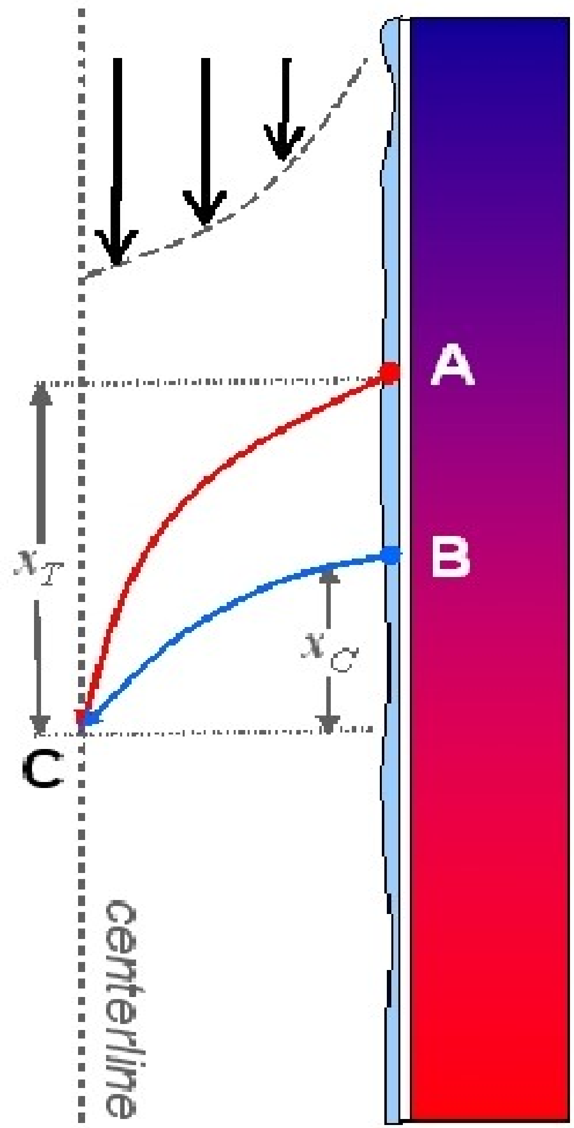


Droplet Measurement Technologies CCN Counter

- Commercially available, most widely used CCN counter in the world (~230 instruments).
- Using the same instrument aids in the comparability of measurements.
- Calibration Affects Comparability:
  - CCN counter calibrations are not trivial
  - Calibration uncertainties and methodology affect measurement uncertainty
- Rose et al., 2008 has comprehensively studied the calibration uncertainties but not how uncertainties change with pressure.

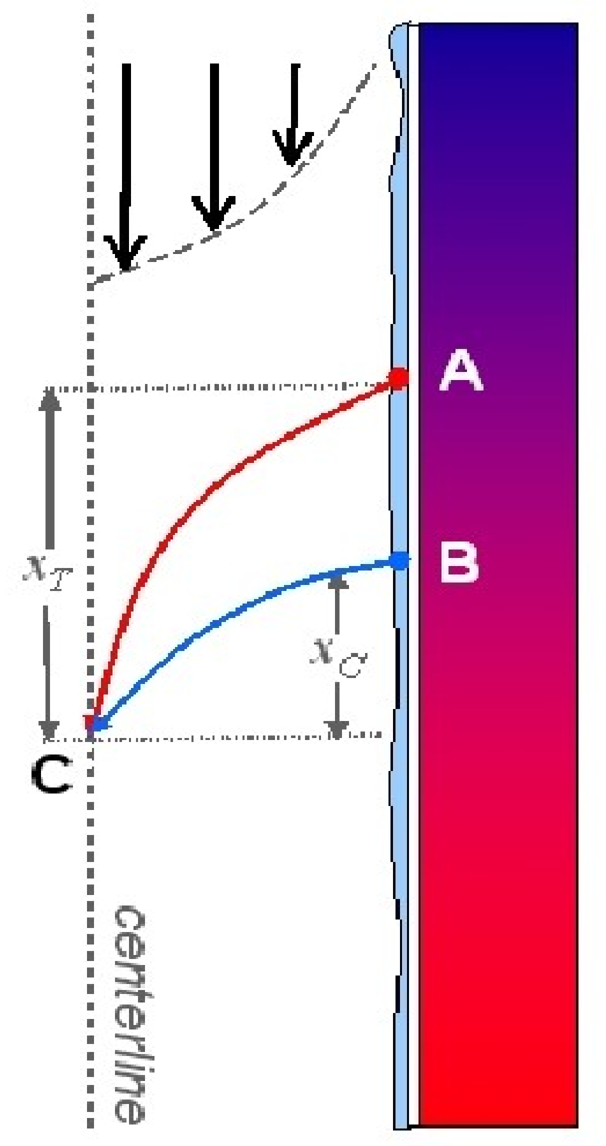
Supersaturation in the DMT CCN Counter

- The DMT CCN counter is a dynamic vertical thermal gradient diffusion chamber.
  - A temperature gradient is applied while flow is continuous through the droplet growth chamber.
- Constant supersaturation is maintained inside the chamber which cause CCN to activate and grow so they can be measured with an optical particle counter (OPC).
- The inner walls of the chamber are kept wet using an alumina bisque liner and continuous water supply.
- Water vapor diffuses more quickly in air than heat. As they both diffuse toward the center of the chamber, there is more water vapor than in thermodynamic equilibrium creating a supersaturation.



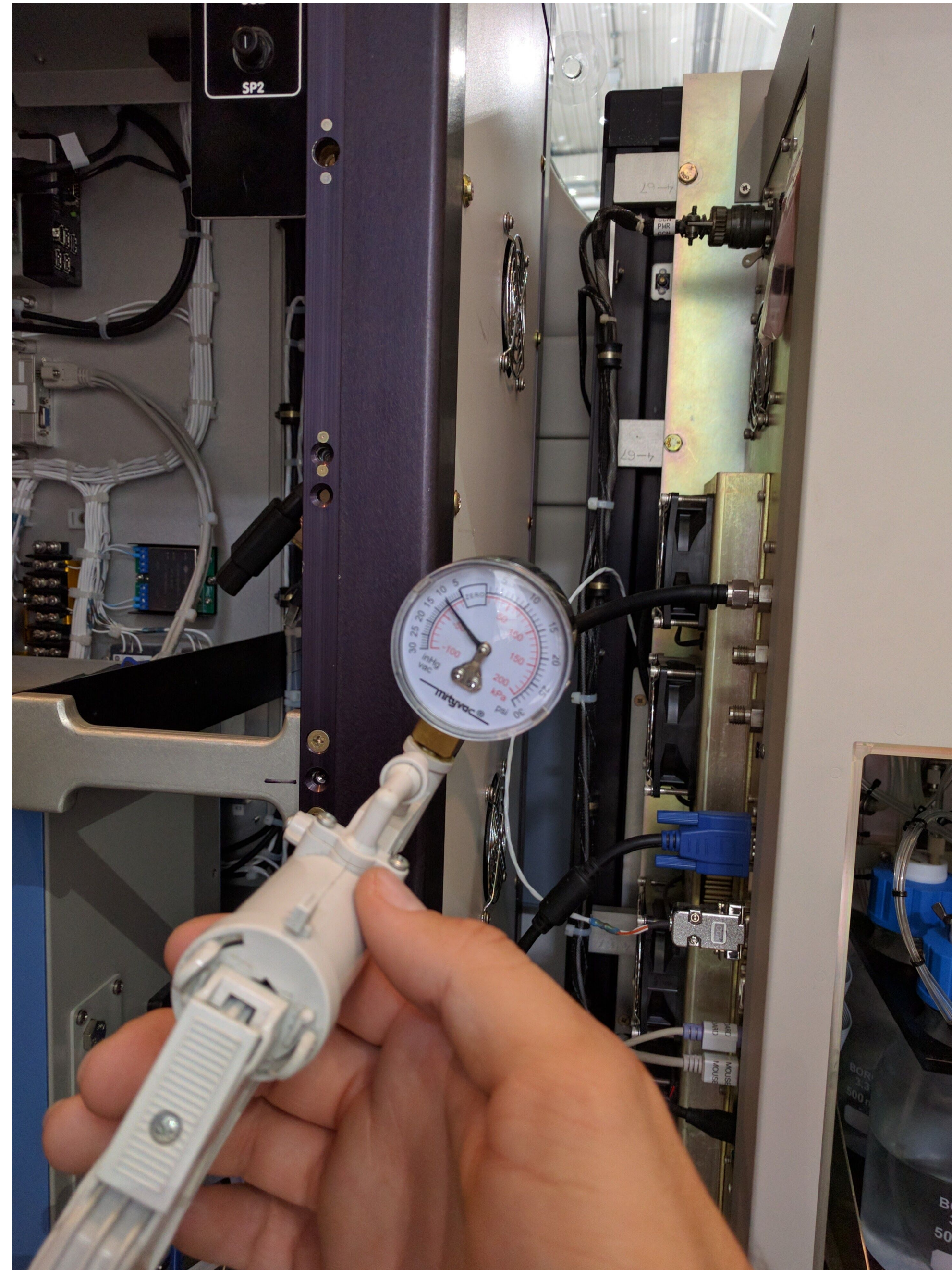
Droplet Measurement Technologies CCN Counter

- Supersaturation is constant along the centerline of the chamber
  - Supersaturation can be varied from 0.1-2.0 %
- The supersaturation at the centerline of the chamber depends on the temperature difference between the top and bottom of the chamber, pressure in the chamber, and flow rate
- Flow rate effects
  - Increase of 0.029% per 0.1 L/min at 1020 mb
  - Increase of 0.042% per 0.1 L/min at ~650 mb



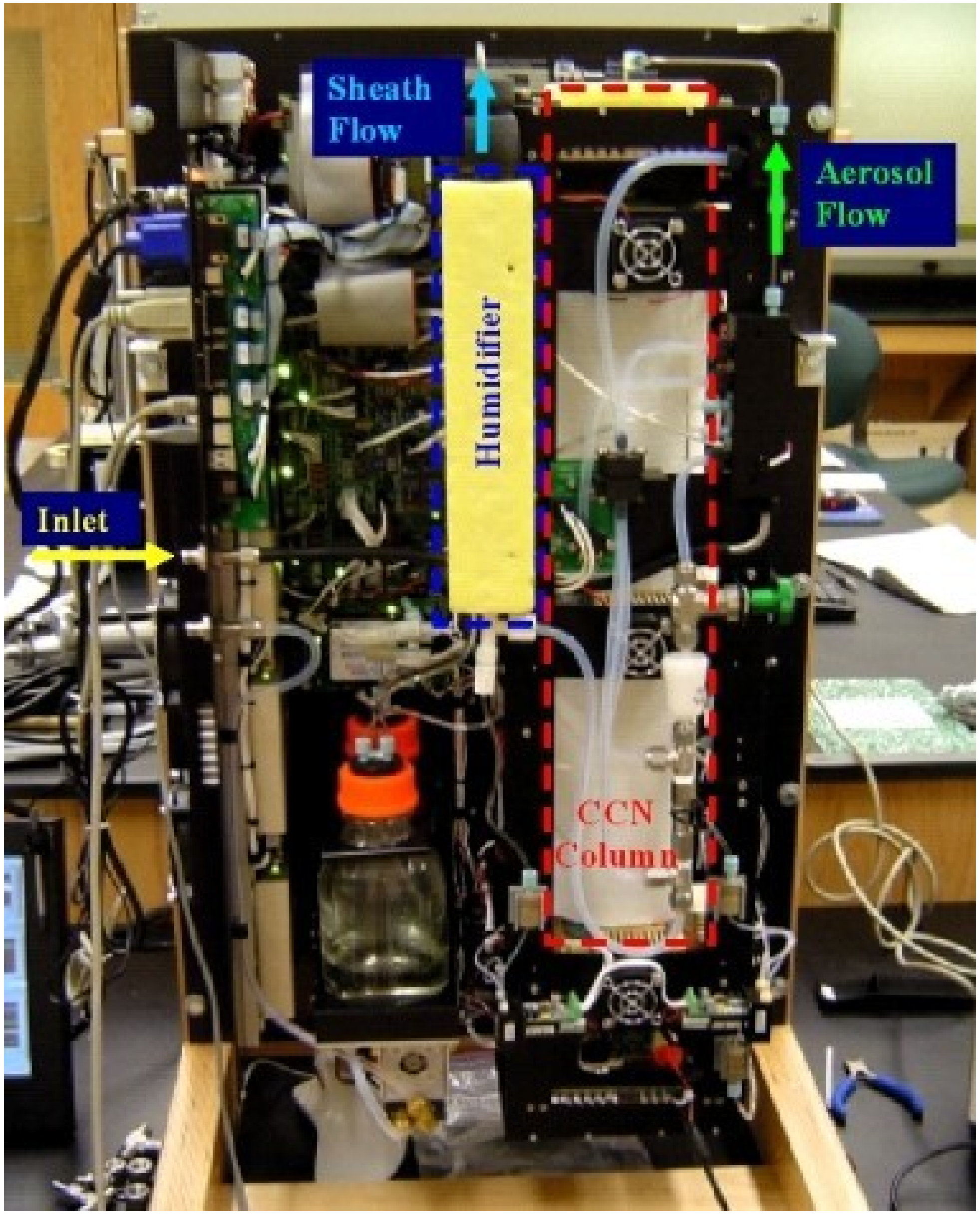
Performance Checks

- Leak testing upon shipping or physical changes
  - Using a handheld vacuum pump
  - Once pressure equalizes around 10 in Hg start a timer (no more than – 1.0 in Hg in 5 minutes)
  - Common leak spots are water bottle caps, sheath filter, or plastic screws
- With a filter on the inlet there should be zero counts
- 1st Stage monitor
  - Must remain below 0.40 V or OPC is possibly fogged
  - Numerous methods for correcting



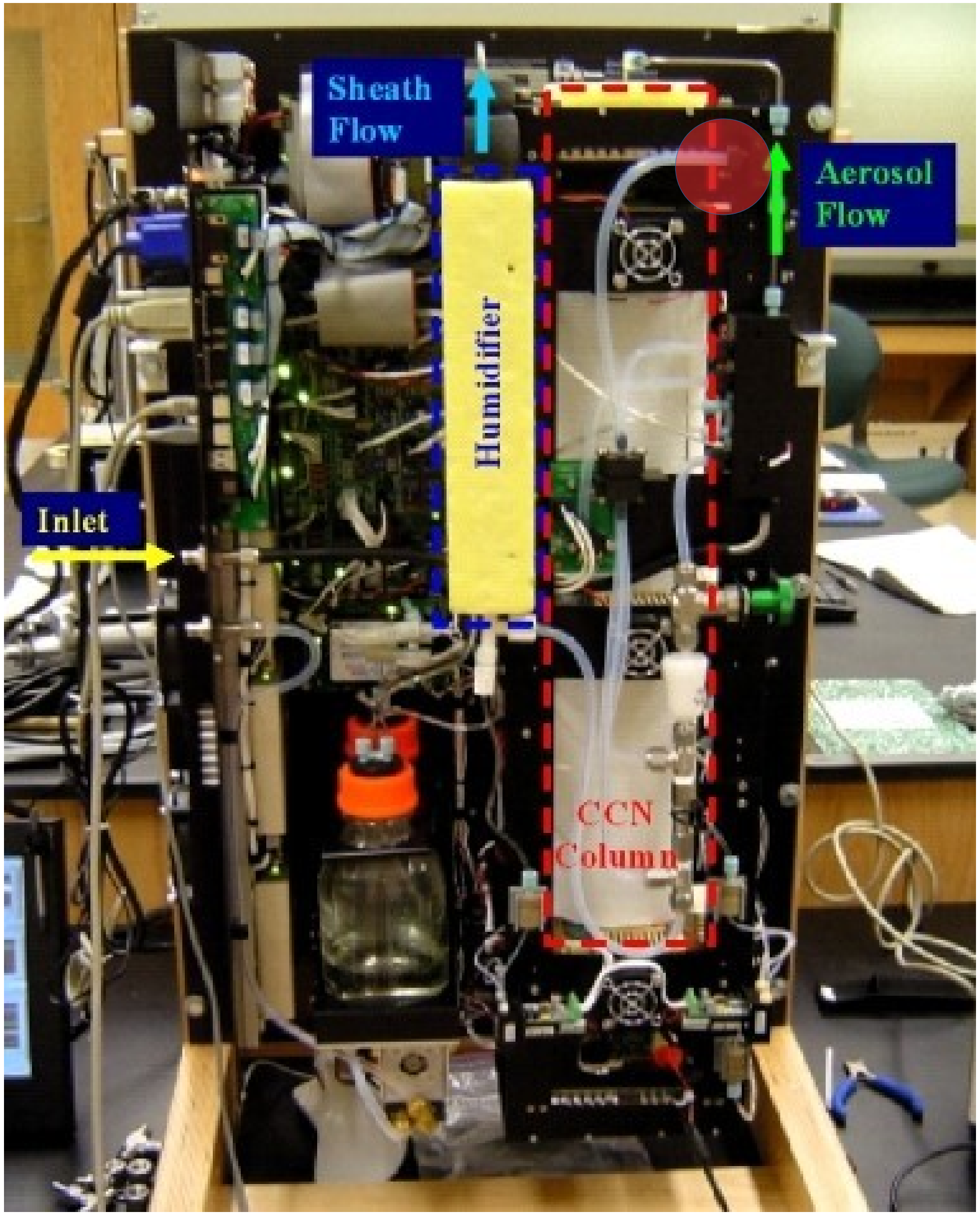
DMT CCN Counter Calibrations

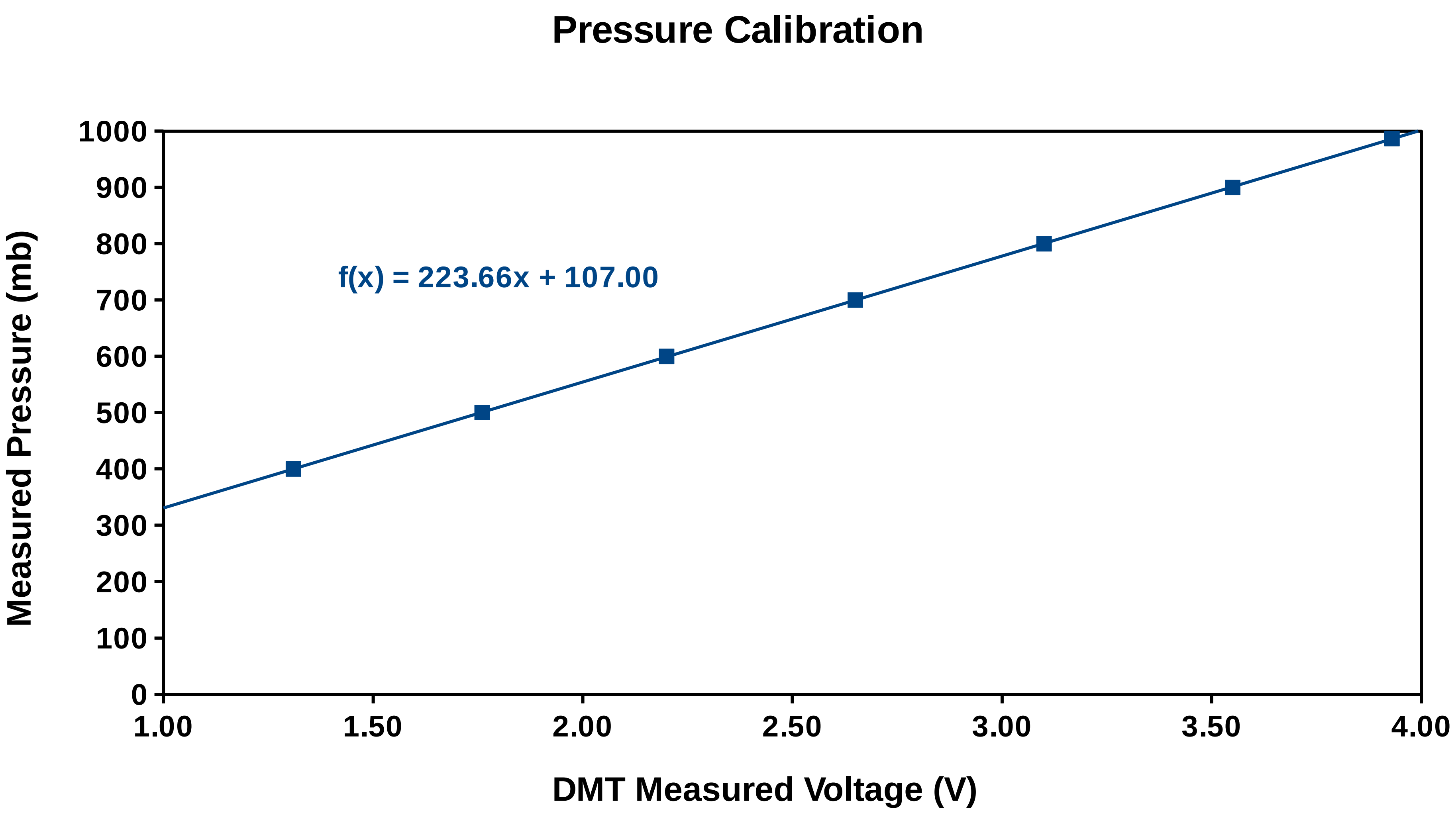
- Three main calibrations
  - Pressure, flow rate, supersaturation
- Pressure calibration
  - Straightforward comparison of voltage to standard measured pressure
  - Important because pressure influences the supersaturation inside the instrument
- Flow rate Calibration
  - Voltage is related to measured flow rate using a standard flow meter
  - Determines accuracy of concentration measurement and constant supersaturation
- Supersaturation calibration requires a complex lab setup and complex processing



Pressure Calibration

- Connect pressure transducer line to a vacuum source and calibration standard
- Set y-int to 0 and slope to 1 in the calibration settings software
- Record 5 corresponding voltages and pressures between 100-1000 mb

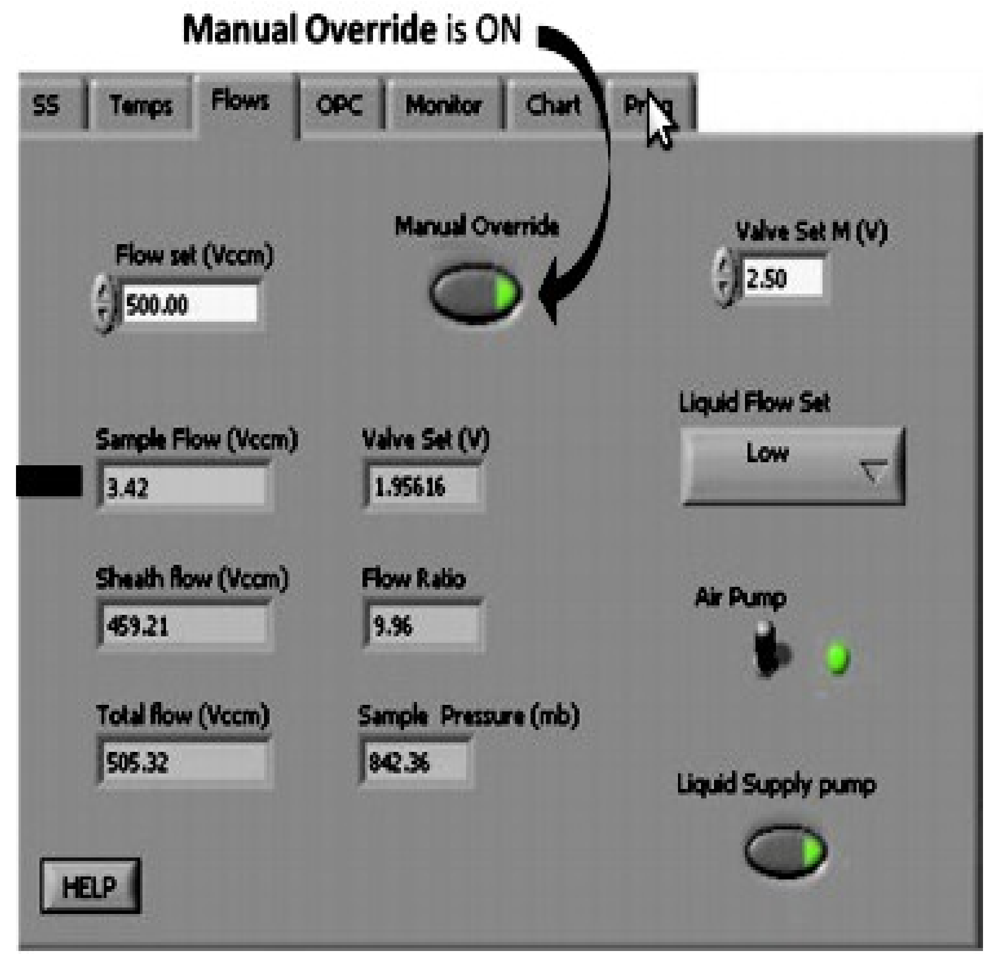


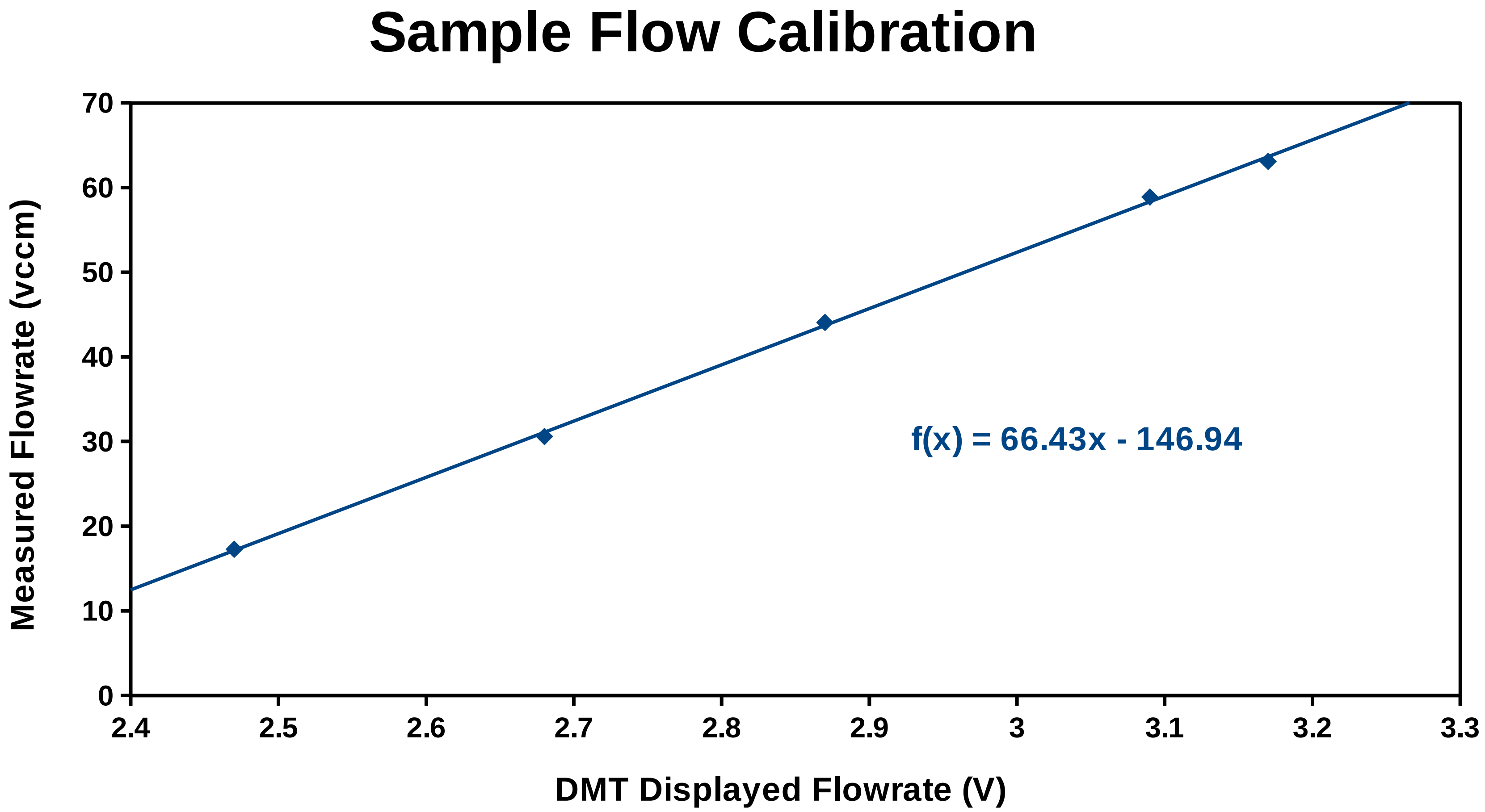


- Pressure Calibration changed by less than 1%
- Don't expect much change in pressure calibrations over time
  - Negligible uncertainty introduced through pressure calibration

Sample Flow Calibration

- Sample flow y-int is set to 0 and slope to 1 in calibration settings software
- Flow standard is connected to the inlet port and the sheath valve is closed
- The Valve Set (V) value is adjusted until flow standard reads approximately 75, 60, 45, 30, and 20 ccm
  - Measured flow and corresponding sample flow voltage measurement are noted

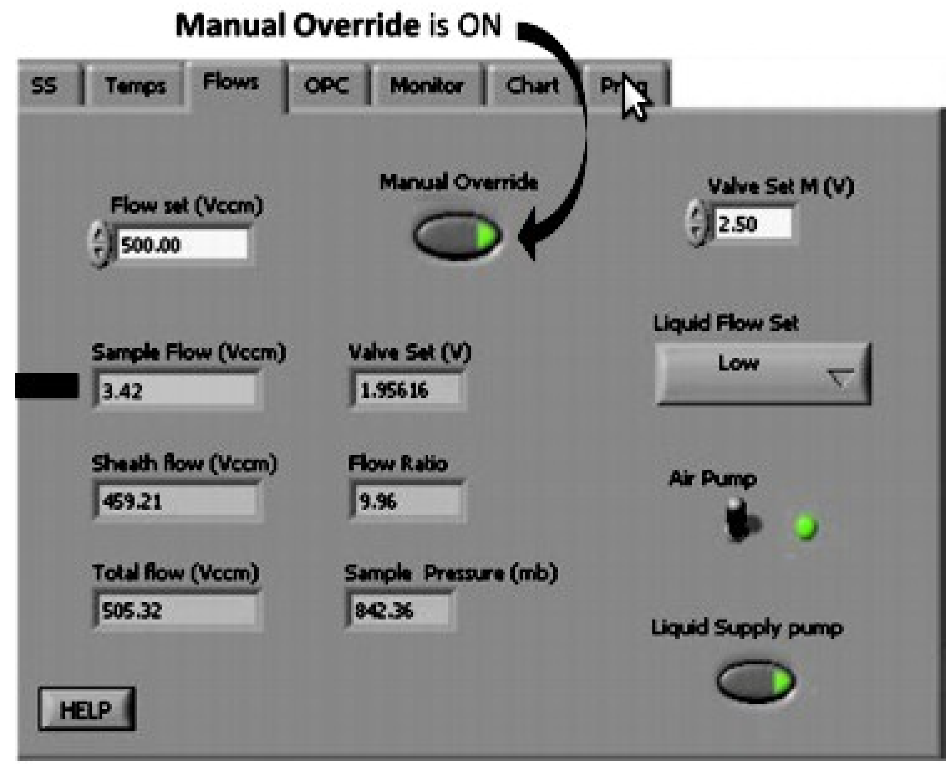


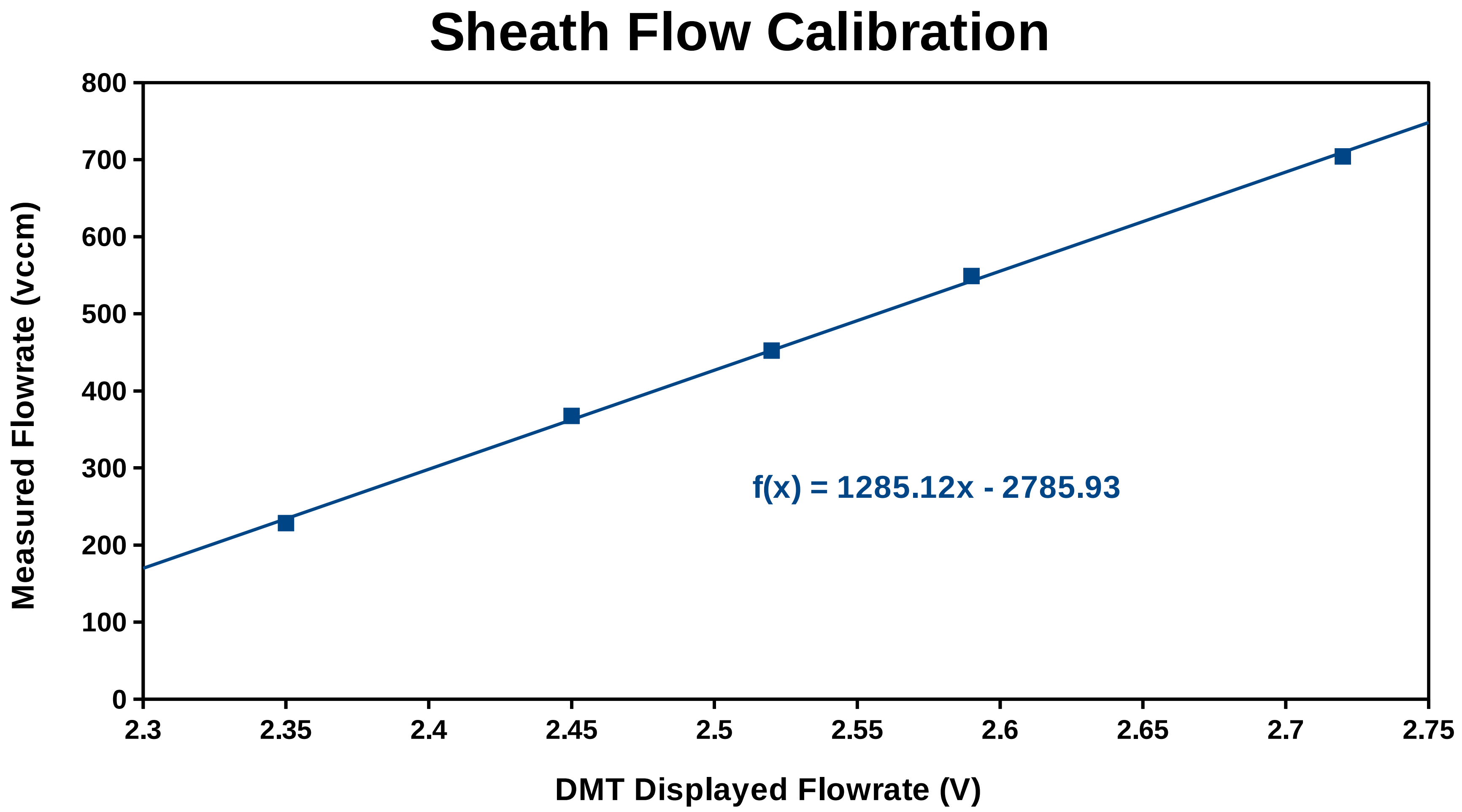


- Uncertainty measurements taken 6 months after calibration
- With a setpoint of 0.045 Lpm, 10 sample average measured flow is 0.04694 Lpm
- 4.3 % error in sample flow

Sheath Flow Calibration

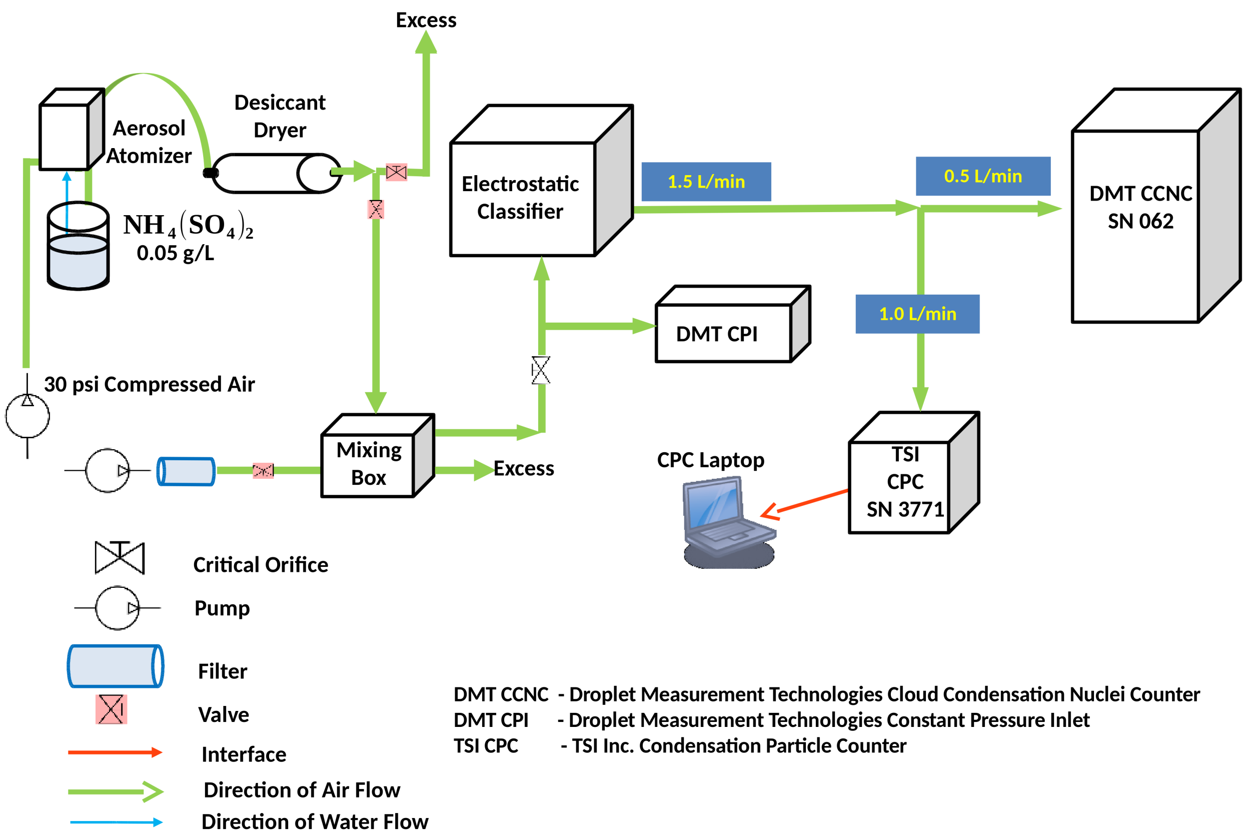
- Flow standard connected to the inlet port
- Sheath flow valve completely open
- The calibration coefficients are set to y-int 0 and slope 1
- The Valve Set (V) is adjusted until flow reads approximately 750, 600, 450, 300, and 200 ccm
  - Measured flow and corresponding sheath flow voltage are noted



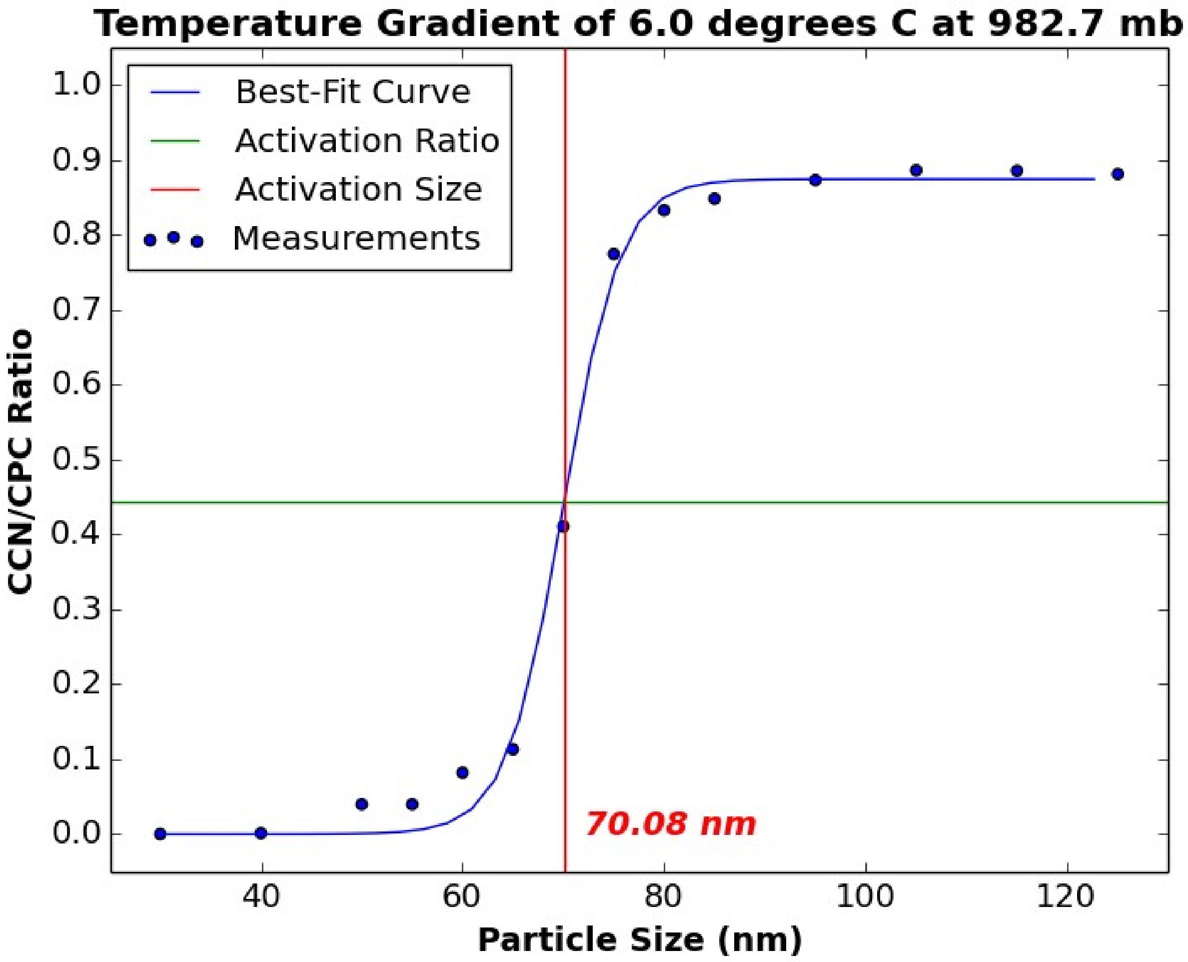


- Uncertainty measurements taken 6 months after calibration
- With a setpoint of 0.4550 Lpm, the ten sample average of measured flow is 0.4434 Lpm
- 2.5 % error in sheath flow

Lab Setup: Cloud Condensation Nuclei Counter Calibrations

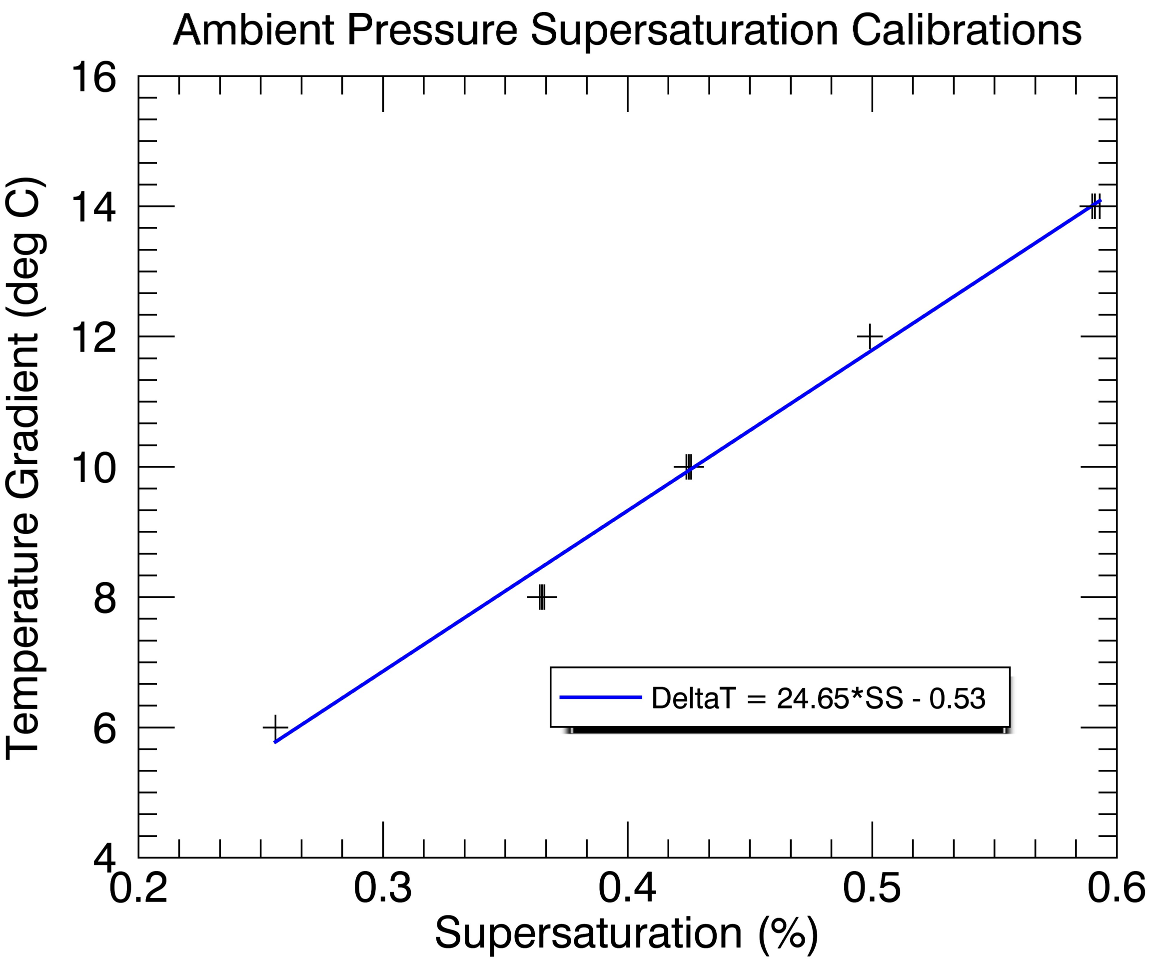


- Generate aerosols of known size and chemical composition
- Introduce into the DMT CCN counter while holding its chamber temperature gradient constant
- CCN are counted while a calibration standard counts all particles simultaneously
- The ratio of CCN concentration to total particle counts is the activated ratio
- Selected sizes are introduced into the CCN counter at regular intervals yielding activated ratios between 0 and 100 percent



Activation size of 70.08 nm results in a calculated supersaturation of 0.256%

- The activation curve is made using a sigmoidal curve fitting routine to fit the data
- The same processing script determines the activation size based on the size at which the activation curve crosses the activated ratio
  - Normalization of ratio data to 1.0 does not significantly impact activation size calculation (< 0.5 %)
- Using kappa-Köhler theory, the critical supersaturation is calclulated
- Critical supersaturation is calculated at 5 different instrument temperature gradients (6, 8, 10, 12, and 14 K).
- Process is repeated three times at each of three pressures: 700, 840, and 980 mb



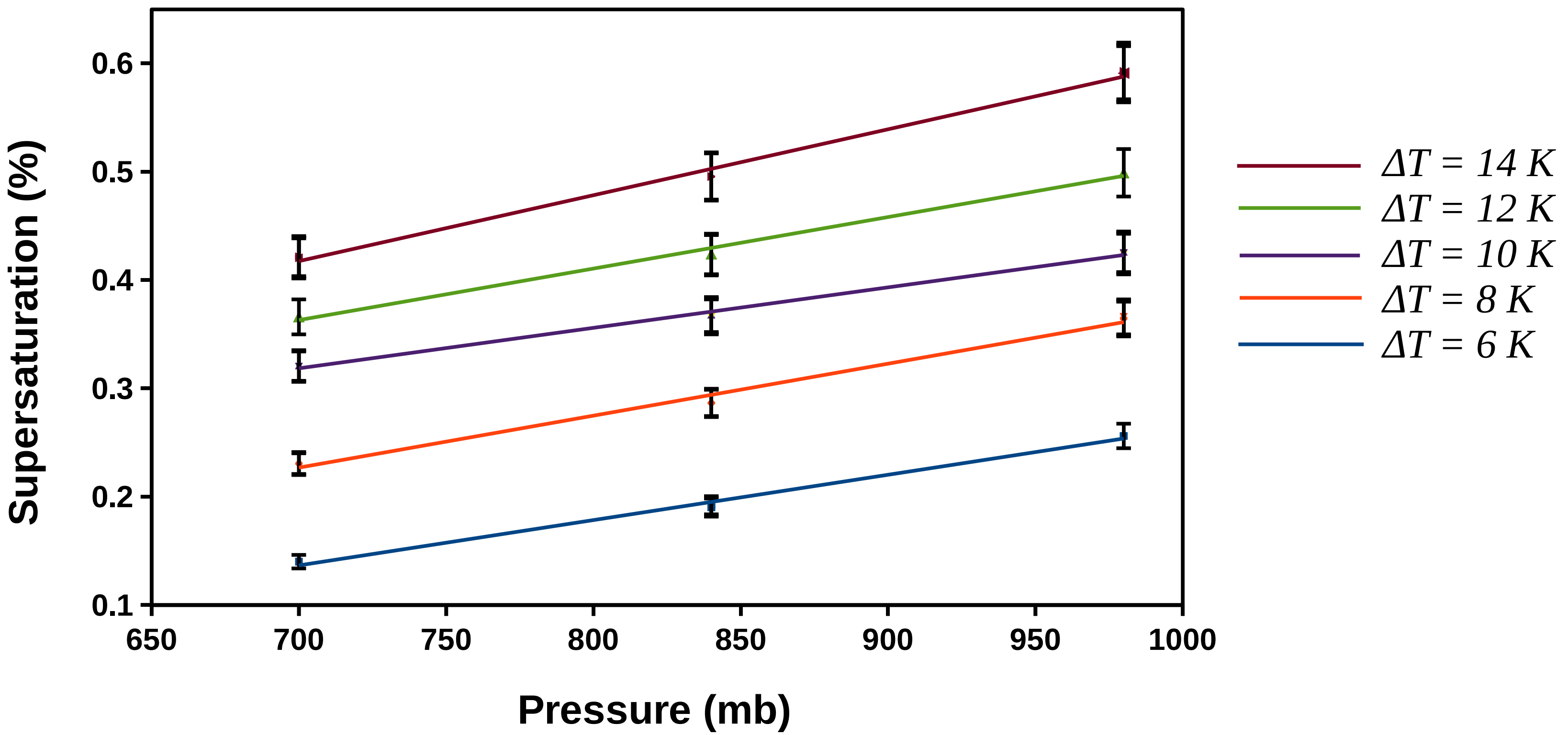
- Calculated supersaturation is plotted with its corresponding temperature gradient and fitted linearly
- The fit equation coefficients are used as the instrument's calibration coefficients

- The uncertainty in supersaturation is determined using the relative deviation of three supersaturation calibrations for each temperature gradient.
  - 0.1-0.3 % uncertainty
- The overall supersaturation calibration uncertainty is calculated from the relative error of the three calibrations at a given pressure
  - 2.3, 3.1, and 4.4 % uncertainty for 980, 840, and 700 mb calibrations respectively

Summary of Uncertainties

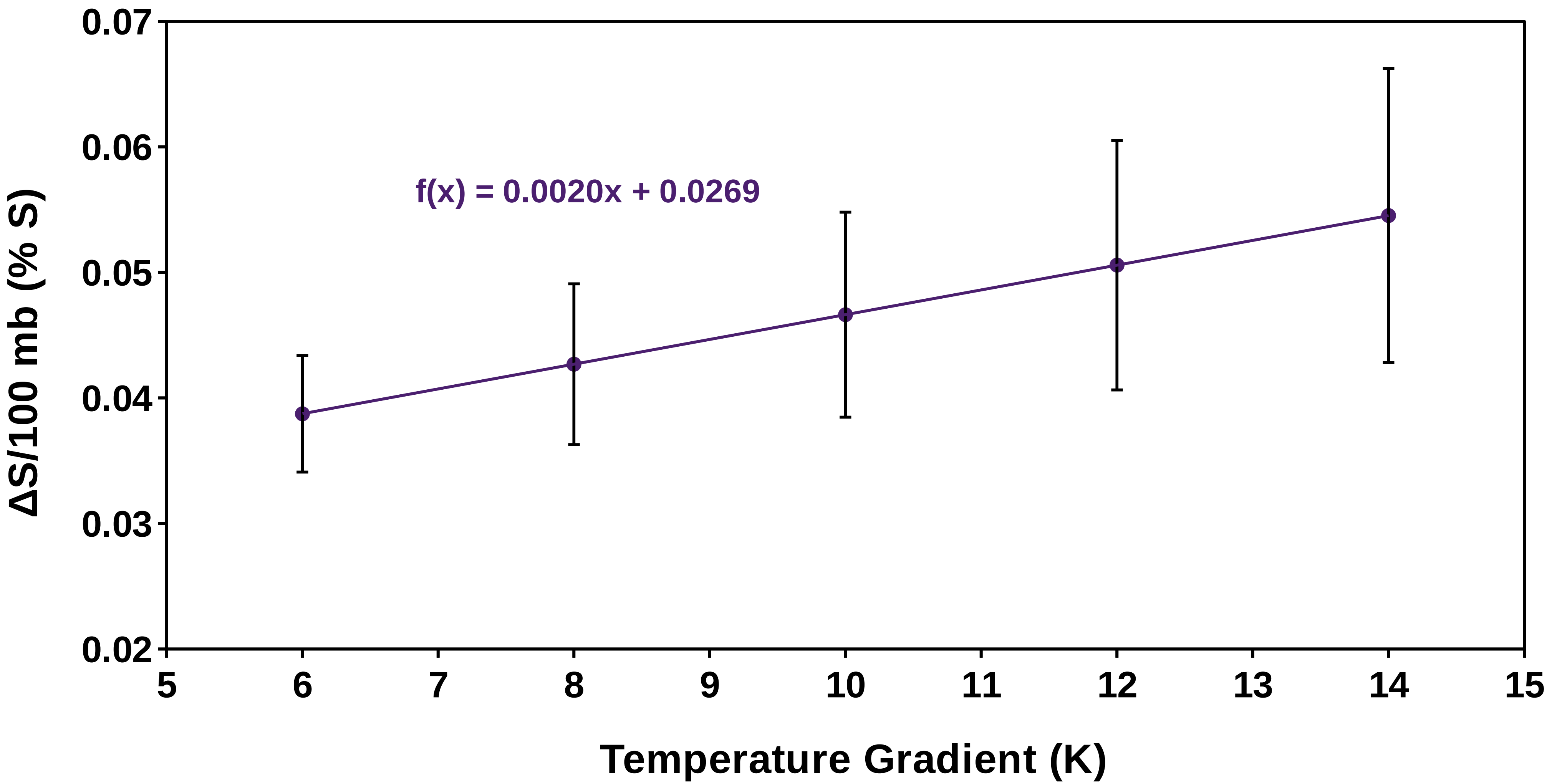
Calibration	Uncertainty
Pressure	Negligible
Sample Flow	4.3 %
Sheath Flow	2.5 %
Supersaturation (single point)	0.1 – 0.3 %
Supersaturation (calibration line)	
980 mb	2.3 %
840 mb	3.1 %
700 mb	4.4 %

Supersaturation Pressure Dependence



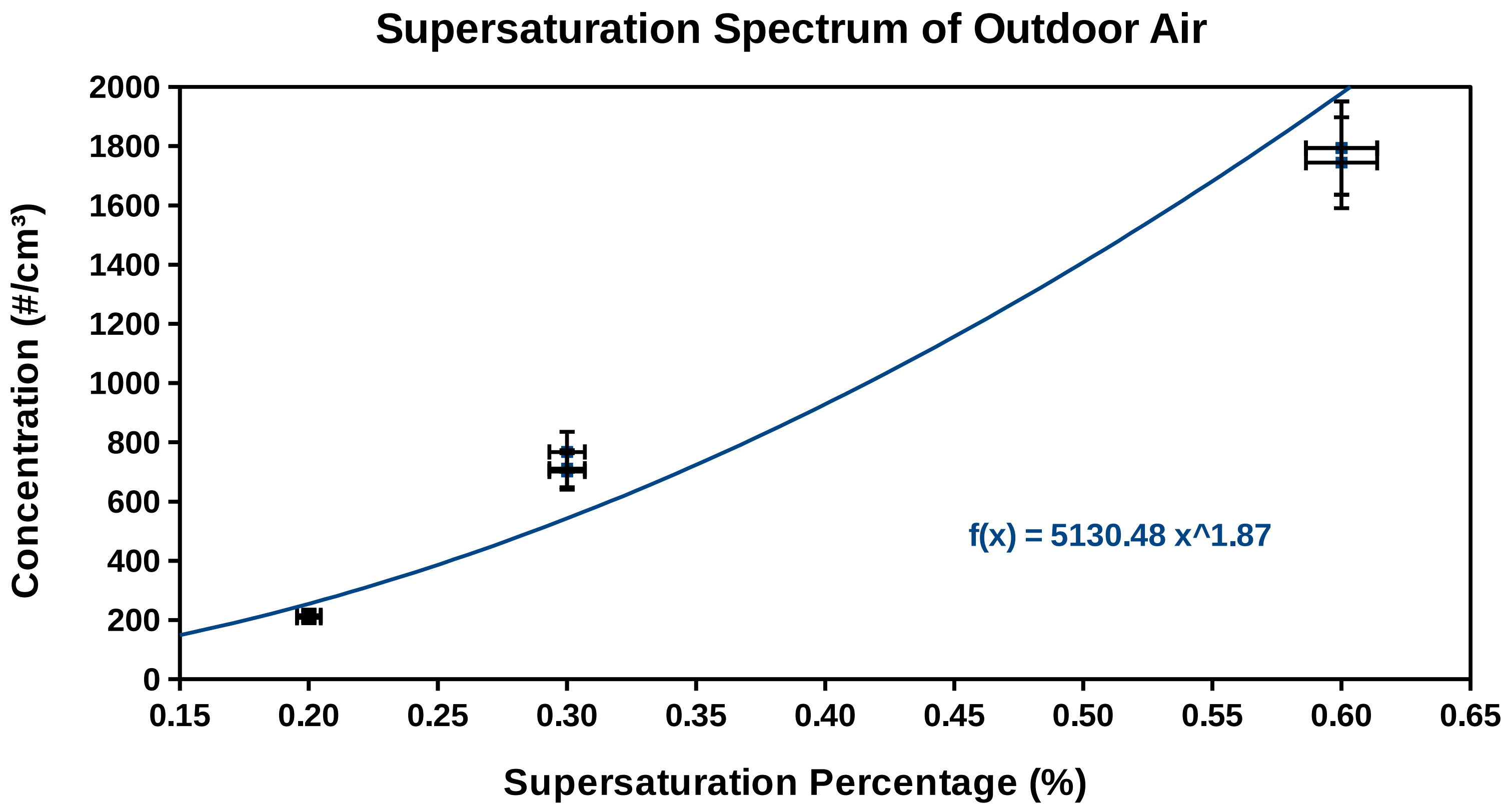
- Observed average pressure dependence of 0.047 % supersaturation per 100 mb
  - Rose et al. (2008) found a pressure dependence of 0.037 % supersaturation per 100 mb at a temperature gradient of 5 K while this research found 0.039% per 100 mb at a temperature gradient of 6 K
- Slope of calibration lines increases 5.6 % per 100 mb decrease in pressure meaning pressure dependence is not constant
- Single supersaturation offset leads to a corresponding error in supersaturation percent between 1-5%

Supersaturation Pressure Dependence with ΔT



- The supersaturation pressure dependence increases 0.002 % supersaturation per K
- Pressure dependence ranges from 0.039 % per 100 mb at a ΔT of 6 K to 0.055 % per 100 mb at a ΔT of 14 K
- Within 10 % of previous research (Rose et al., 2008)

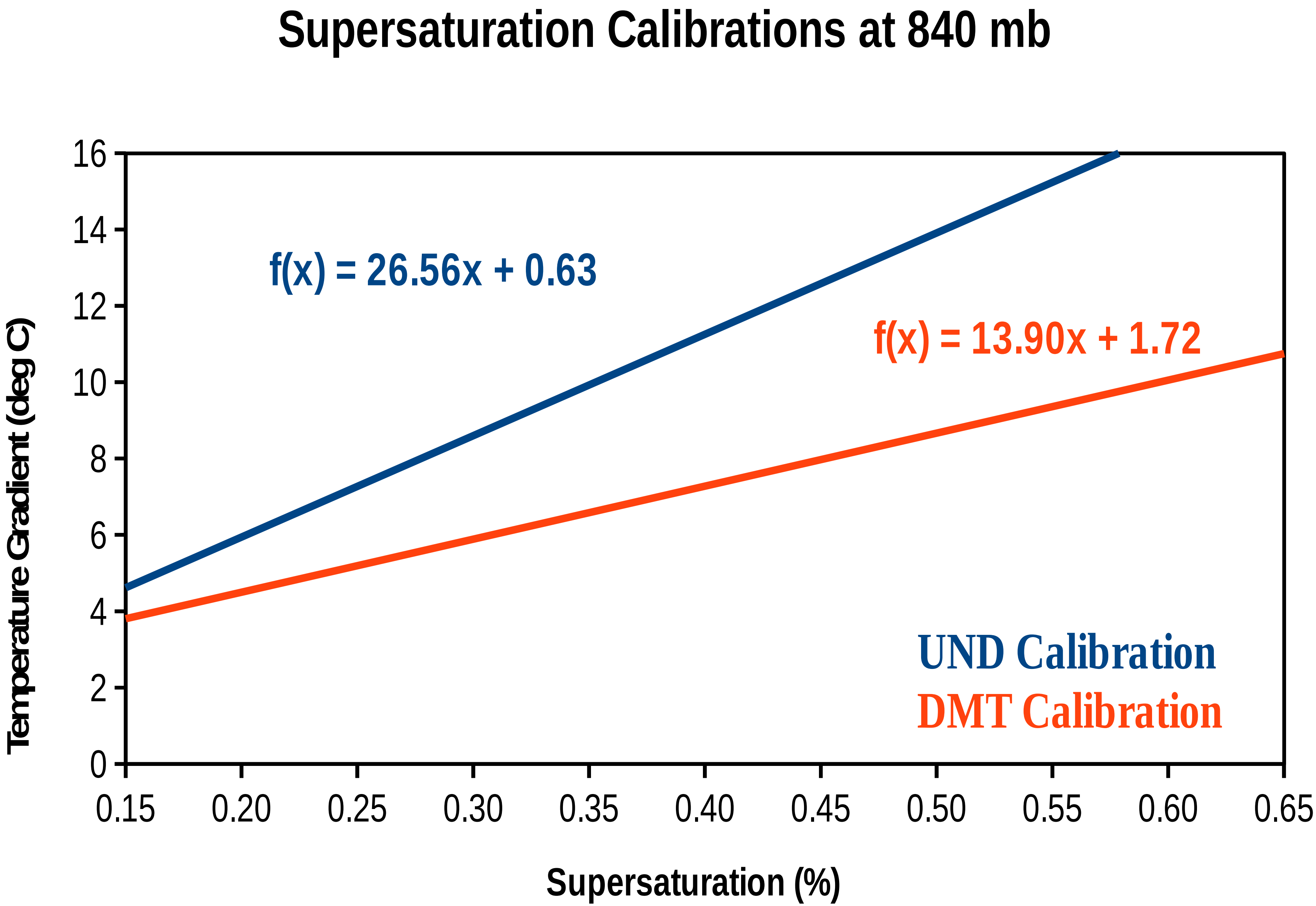
Uncertainty Effects on Concentration Measurements



- 2.3 percent uncertainty from the supersaturation calibration and 4.3 percent uncertainty in sample flow
- Based on the supersaturation spectrum with the ambient calibration and the uncertainties found, concentrations will be within 8.8 percent of the measured value
- Assuming the same supersaturation to concentration relationship, measured values will be within 10.4 percent at 840 mb and within 13.0 percent at 700 mb

Comparison of Calibration Methodologies

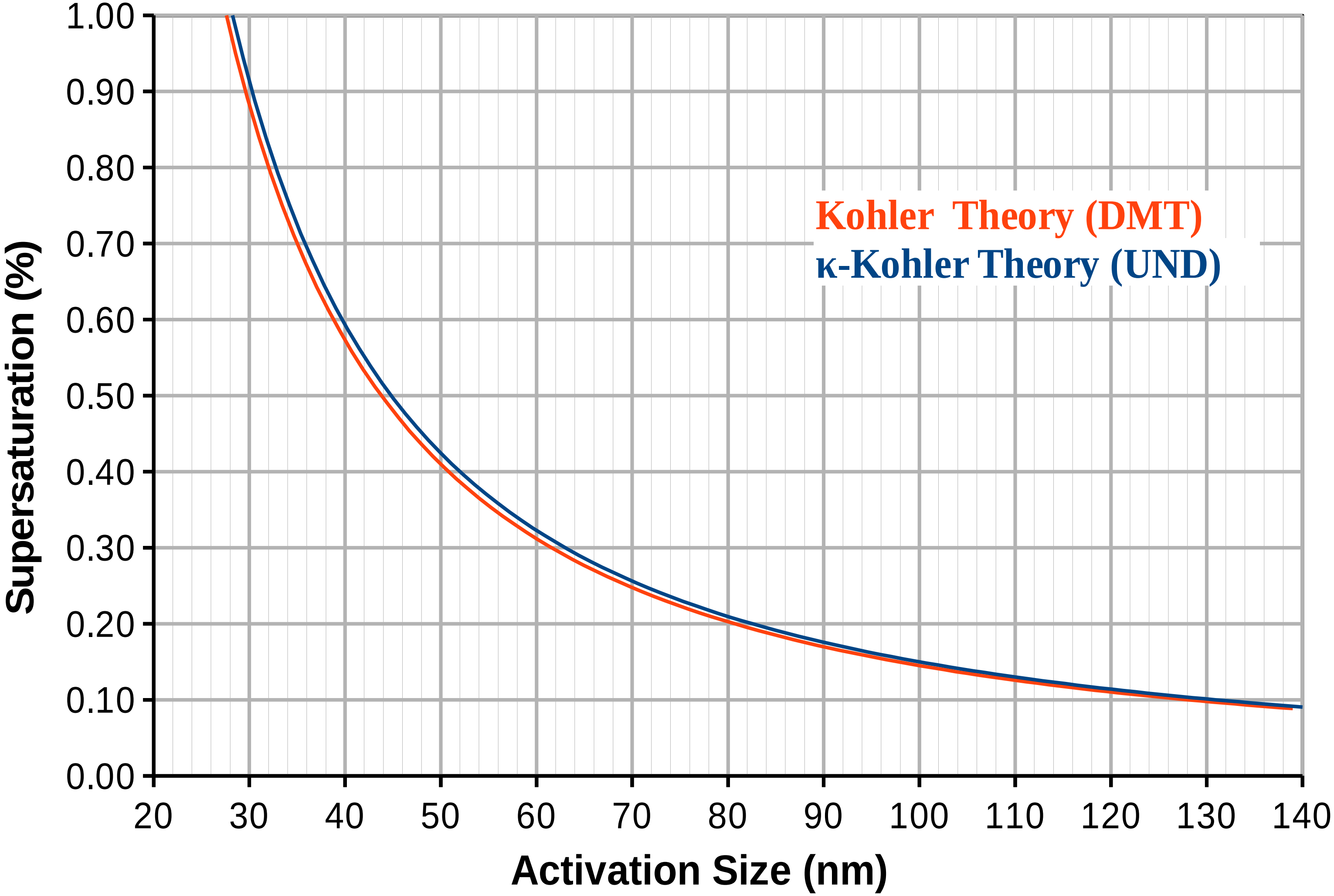
- DMT performed a calibration on SN 062 June 2015
- UND calibrations were done approximately one year later
- Performance checks confirmed that all major leaks developed during shipping were fixed before UND calibrations begun



- UND calibrations are 42-45 % lower than DMT calibrations

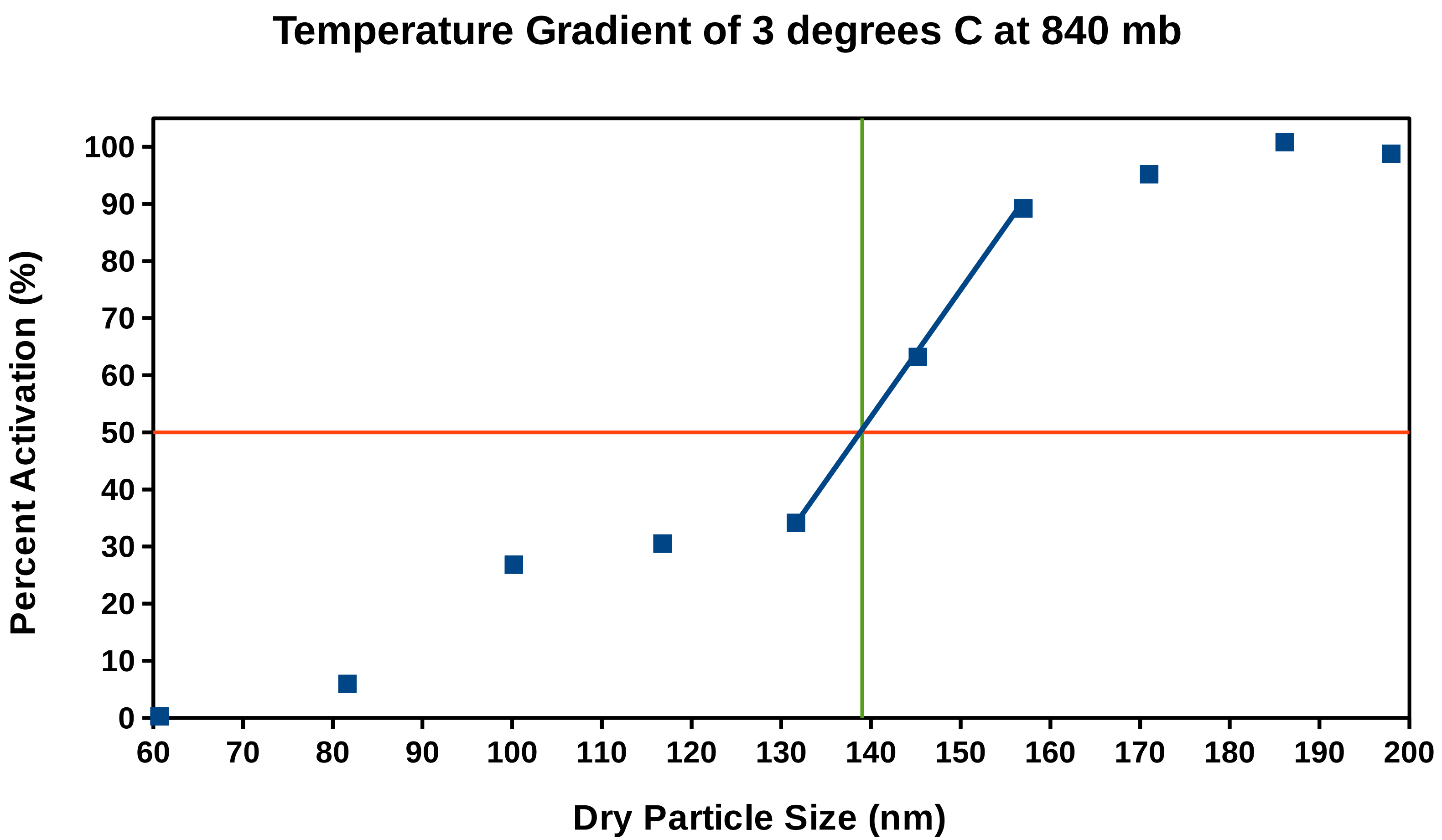
Possible Differences in Calibration Methodology

- The assumptions made in Köhler theory calculations can dramatically alter calculated supersaturation
- Multiply charged particles can get through the Electrostatic Classifier and influence the activation curves
- Fitting methods other than a sigmoidal fit lead to large error in calculating activation size
- Calibration points used can significantly affect the slope of the calibration line



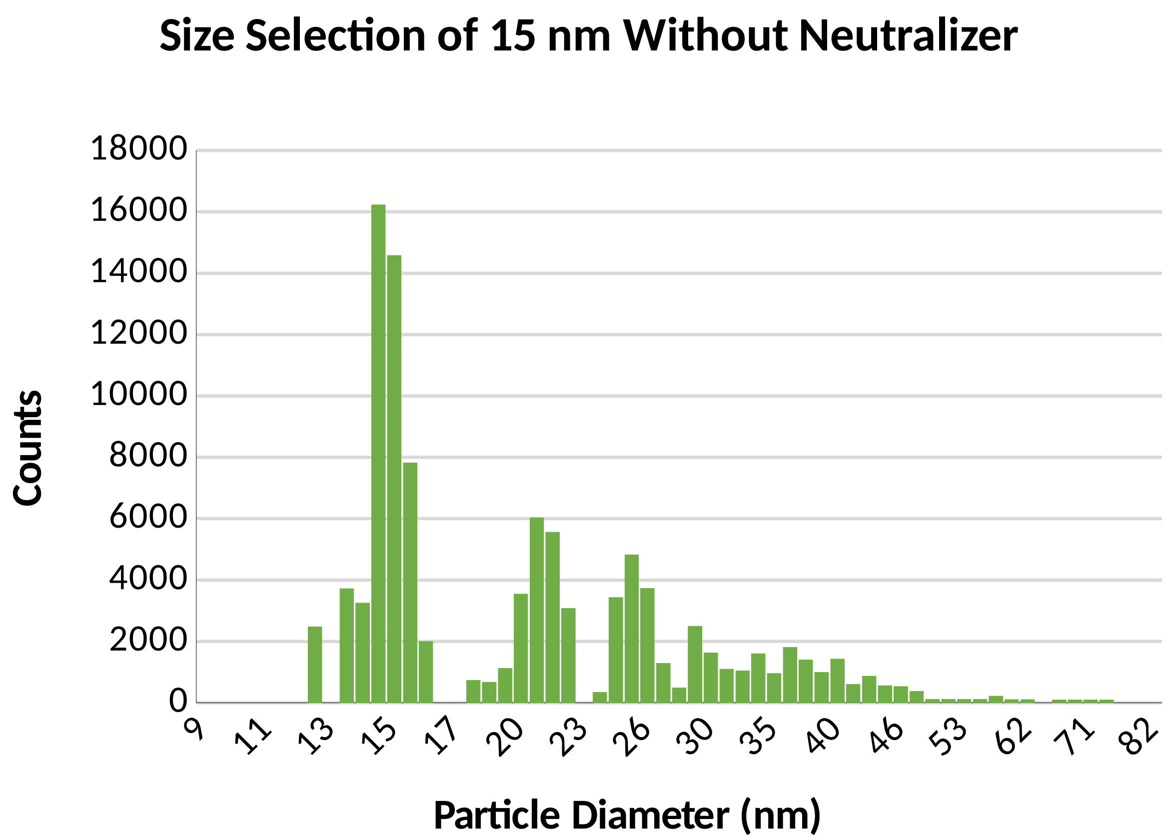
- The calculated supersaturation using the DMT variation of Köhler theory is on average 3.3 % lower than when using κ-Köhler theory

June 2015 DMT Supersaturation Calibration

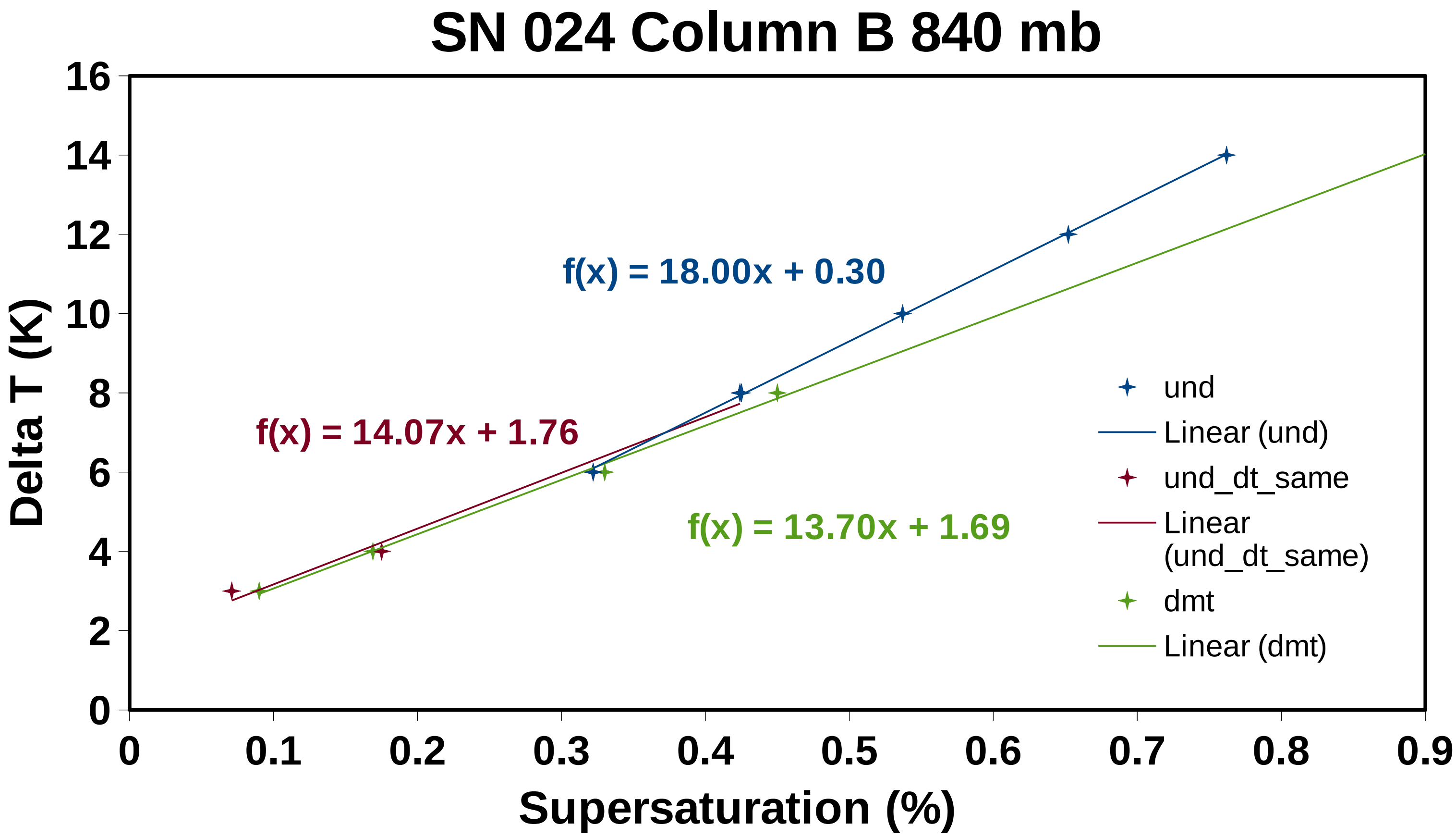


- Plateau around 30 % indicates that 30 % of particles are multiply charged
  - Research indicates plateau heights greater than 10% have a significant influence on calculated supersaturation (Rose et al., 2008)
- Concentrations of multiply charged particles are not constant over the size range making corrections difficult
  - Knowledge of the size distribution is necessary to correct the data
- A sigmoidal fit is necessary to determine the activation size, not linear interpolation (Rose et al., 2008)
  - Linear interpolation disregards the ends of the activation curve

Importance of Neutralization



- SMPS scan of DMA selecting 15 nm particles without a neutralizer installed.
- Each peak corresponds to a distinct charge state. 15 nm is +1, 21 nm is +2, 26 nm is +3, and so on.
- 5 distinct peaks representing 5 charge states. This indicates the charge distribution of generated particles is much wider than previously thought.
- 51.6 % of all particles in this scan are not within 2.5 nm of 15 nm.
- Electrostatic Classifier manual notes that aerosols can accumulate inside the neutralizer. If it is not older than Kr-85 half-life of 10.7 years, then accumulation is a possible reason the neutralizer may lose effectiveness (thin layer can block alpha radiation).



- When the same calibration points are used, the UND method finds supersaturations on average 8.2 percent lower than DMT
- The calibration points used by UND are not at the instrument's operating limits and relevant to expected usage
- Calibration points used affect the calibration line more than any other methodology difference
  - It is known that the calibration line slope changes near 0.1 % supersaturation (Roberts and Nenes, 2005; Rose et al., 2008)

Conclusions

- The uncertainty in the DMT CCN counter's concentration measurement using this calibration methodology is 8.8, 10.4, and 13.0 % for 980, 840, and 700 mb respectively
- The average supersaturation pressure dependence is 0.047 % supersaturation per 100 mb
  - The supersaturation pressure dependence changes with ΔT at a rate of 0.002 % supersaturation per K
- Comparisons between the calibrations done at UND and DMT show 42-45 % lower supersaturations for the same temperature gradient using the UND methodology
- Calibrations should be done under the environmental conditions the CCN counter will be operating under for the most accurate measurements

Summary

- Uncertainties will help in quantifying the magnitude of CCN variability
- Applying the uncertainties to aerosol parameterizations for more accurate modeling
  - Better understanding of aerosol indirect effect
- Improvements in the calibration methodology
  - Reduction of multiply-charged particles
  - Calibration points used

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Optical Particle Counter

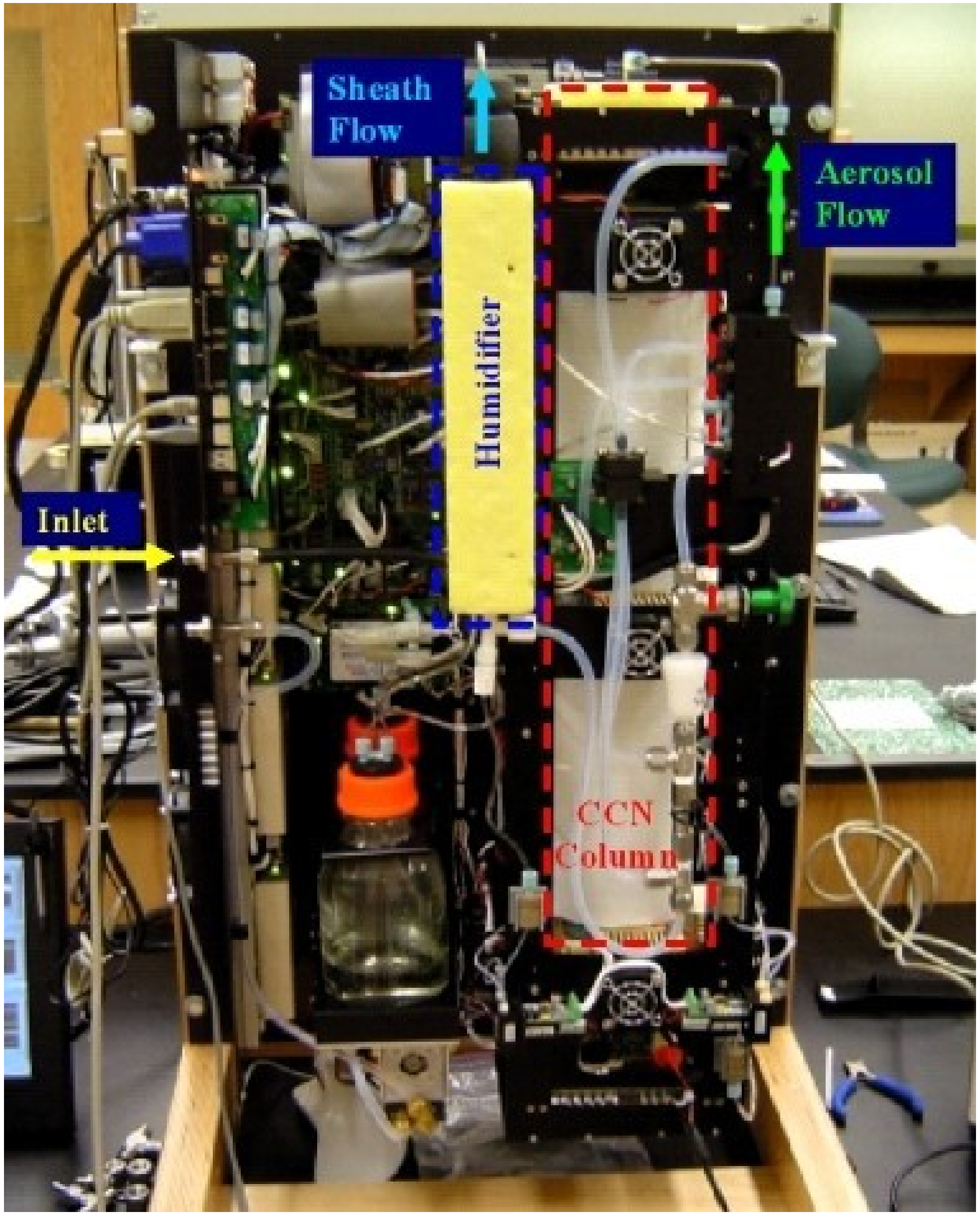
- Counts grown droplets at the bottom of the chamber
  - 1 Hz data
  - 660 nm laser
- Sizes droplets between 0.75 – 10 um in 20 size bins
  - First bin up to 0.75 um, second 0.75 -1.0 um, and 0.5 um bins thereafter
- Provides details on the growth of CCN and instrument performance

Temperature Control

- Three temperature control zones: top, middle, and bottom of the chamber
  - Difference between top and bottom temperatures – ΔT
- Ability to regulate the temperature up and down rapidly with quick response time
  - 30 seconds is required for temperature readings to stabilize but actual supersaturation in the chamber takes longer to develop ~2+ minutes
- OPC temperature is maintained 2 degrees C above T3 to prevent fogging on the OPC
  - To protect the laser diode, OPC temperature cannot exceed 55 degrees C
  - No loss of concentration when TOPC-T3 < 5 degrees C, but 20% loss when TOPC-T3 >7

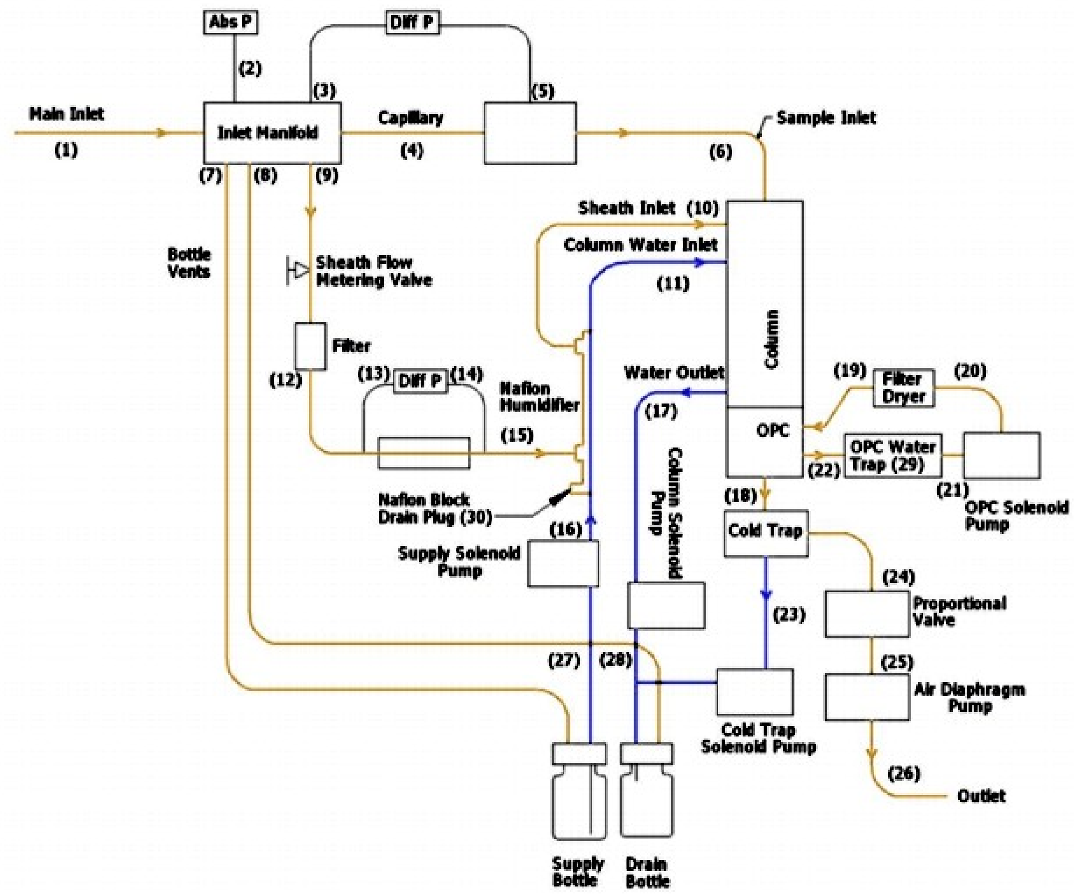
Flow Measurements

- Flow pulled into the CCN counter at 0.500 Lpm
  - Flow is split for a sheath air flow of 0.455 Lpm and a sample air flow of 0.045 Lpm
- 10:1 sample to sheath flow ratio keeps the sample confined to the center of the growth chamber where the supersaturation is constant
- Differential pressure transducers measure the sample and sheath flows
- Absolute pressure is sampled from the same manifold flow measurements are taken



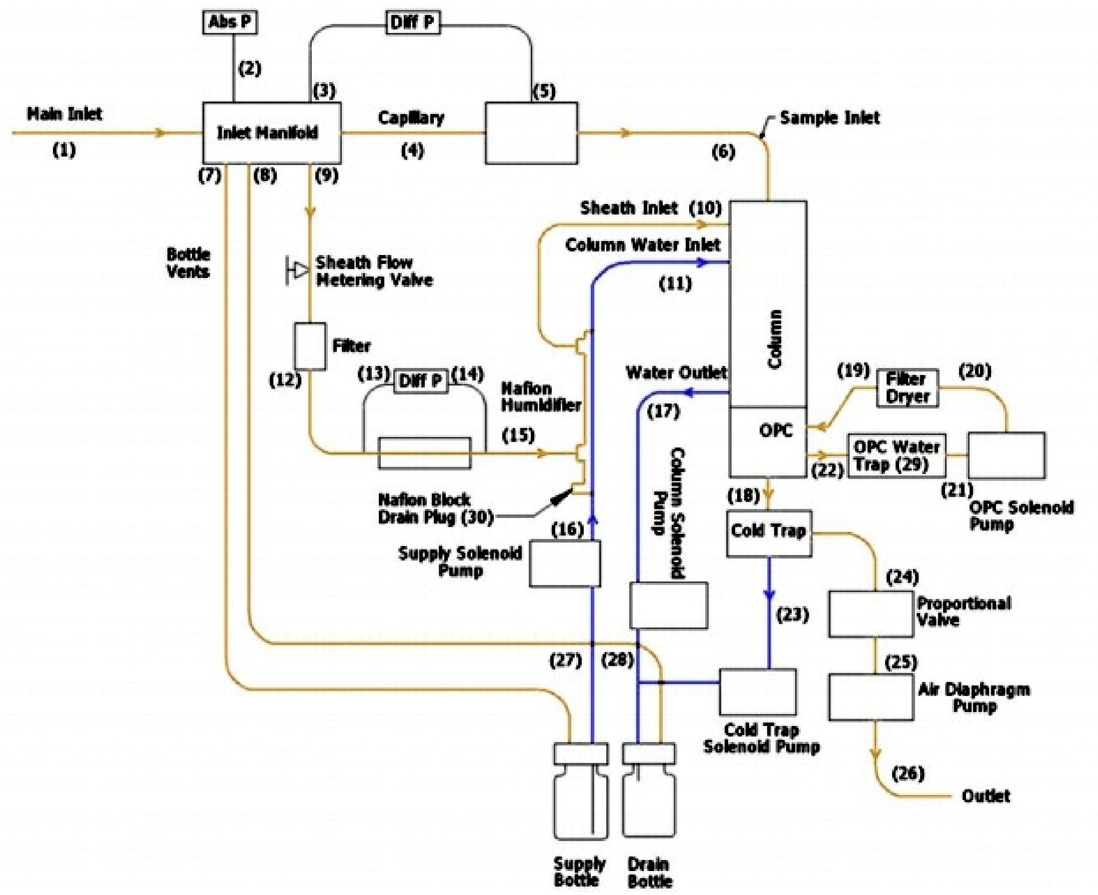
Sheath Air System

- Sheath air valve is used to adjust the flow ratio
- Sheath air is passed through an inline filter removing all particles
- Sheath air is humidified in a Nafion humidifier
  - In order to maintain supersaturation in the chamber the sheath air needs to be humidified
- Introduced along the wall of the chamber and has a laminar flow down the chamber

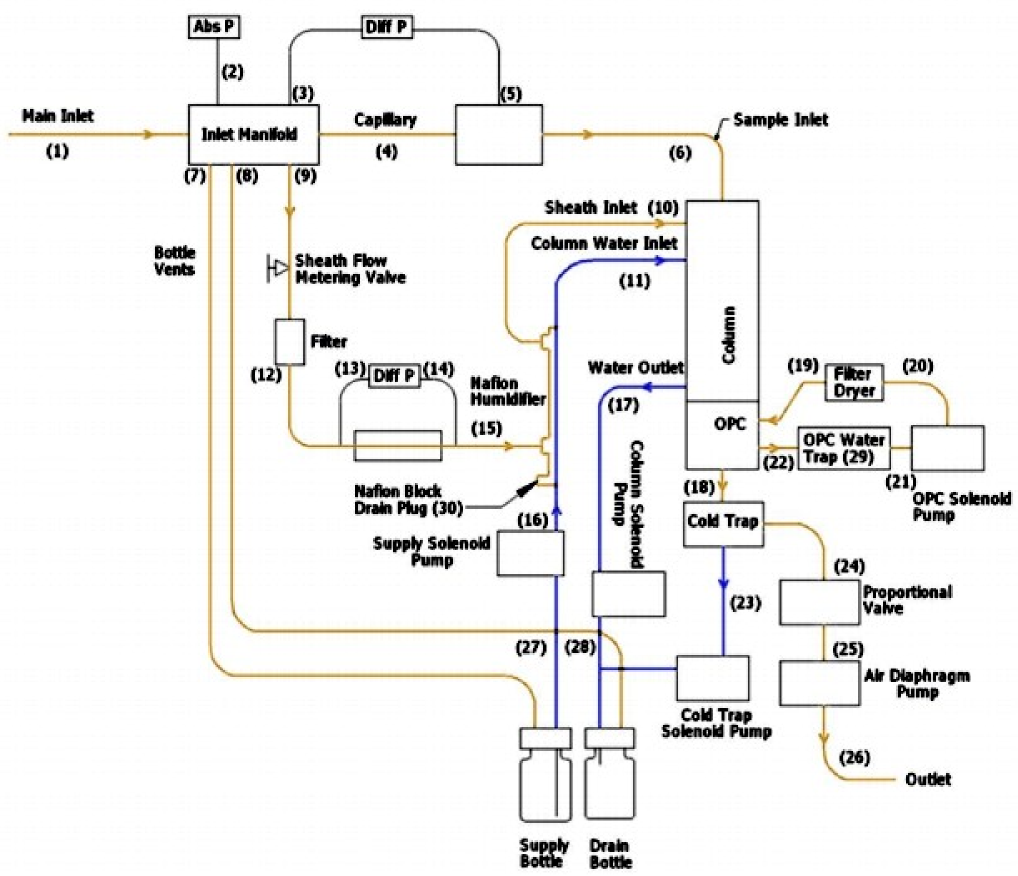


Sample Flow System

- Sample air is introduced at the top of the chamber in the center
- CCN that activate will grow into droplets of a detectable size
- Optical particle counter at the bottom of the chamber counts grown droplets as they exit the chamber
- Sample flow determines the volume in which the grown droplets reside



Water Flow System



- Water pumps exist throughout the system to maintain a continuous flow of water to and from the droplet growth chamber and other instrument parts
- Pumps pull water from the supply bottle to the nafion block and droplet growth chamber
- Pumps pull water away from the OPC and from the chiller block
  - As water deposits in the system after the chamber it is necessary to remove it to maintain proper flow
- Water pulled away from these areas is pumped to the drain bottle in a fully enclosed system