A Novel Technique to Measure Ultrafine Particle Size Distributions for Environmental Science Applications

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BACKGROUND

Importance of Ultrafine Aerosol Particles

- Definition: aerosol particles with diameters <100 nm in diameter
- Correlated with increased human mortality and morbidity
- Can include organic matter such as polycyclic aromatic hydrocarbons
- Larger ultrafine particles can be cloud condensation nuclei
- Serve as nuclei for growth to climate-relevant sizes
- Used for a variety of engineering "nanotechnology" applications

Measurement Issues

- Highly variable in time and space
- Highly diffusive
- Difficult to detect with optical methods
- Electric mobility spectrometers (SMPS) very expensive (>75 k$)

A New Approach: Sizing by Nucleation (Kelvin) Diameter

- Use existing condensation particle counter (CPC) design (counting only; no sizing)
- Vary the operating conditions of the CPC to vary the size nucleated (Kelvin diameter)
- Use inversion technique to recover size distribution

Potential Advantages of the New Technique

- Lower cost (= more units deployed)
- Simpler operation
- Better counting statistics (= faster time response)

Expected Limitations of the New Technique

- Size range more limited than SMPS
- More sensitive to ambient temperature and flow changes (temperature and flow stability critical)
- Working fluid is expensive and perfluorinated (potentially ozone depleting)

This project was focused on developing and evaluating this technique, called the *scanning condensation particle sizer (SCoPS)*

DESCRIPTION, OPERATION, AND CALIBRATION

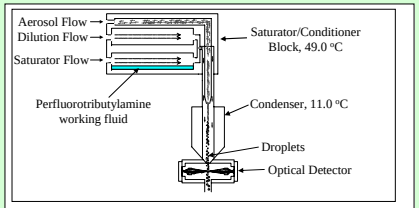

Figure 1. Schematic diagram of the SCoPS. Three flows--aerosol, dilution, and saturator--are brought to identical temperatures of 49.0°C. The dilution and saturator flows are mixed, then used to sheath the aerosol flow prior to the condenser, which is chilled to 11.0°C. The vapor concentration is controlled by varying the ratio of saturator to dilution flows; total flow is constant.

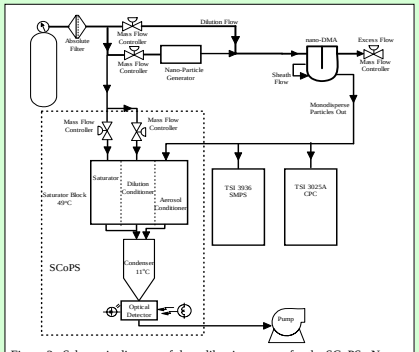

Figure 2. Schematic diagram of the calibration system for the SCoPS. Nano-particles of oleic acid are generated in an ion-assisted nucleation source, size-selected by a nano-DMA, and provided to the SCoPS, a TSI nano-SMPS, and a TSI 3025A CPC.

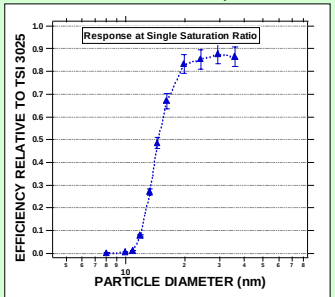

Figure 3. Detection efficiency of the SCoPS relative to a TSI 3025 CPC at a single setting of saturation/dilution flow ratio as a function of the diameter of the calibration aerosol particles.

Operation of a Typical CPC

- Surround aerosol flow with vapor-laden flow
- Cool the combined aerosol/vapor flow
- Supersaturation is achieved
- Particles larger than the critical (Kelvin) diameter nucleate and grow to droplets
- Detect and count the droplets optically

Operation of SCoPS

- Same as CPC, but
- *Vary the vapor mixing ratio* in the flow that is combined with the aerosol flow
- This varies the critical (Kelvin) diameter
- Count the number of particles nucleated under each vapor condition
- Use inversion to calculate size distribution

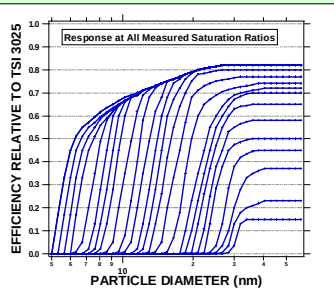

Figure 4. Measured counting efficiency of the SCoPS relative to a commercial TSI CPC for different conditions of vapor and dilution flow as a function of particle diameter.

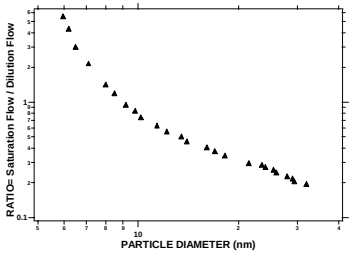

Figure 5. Ratio of saturator flow to dilution flow needed to achieve nucleation efficiency of 50% for particles of given diameter. (Half-height diameter of curves in Fig. 4.)

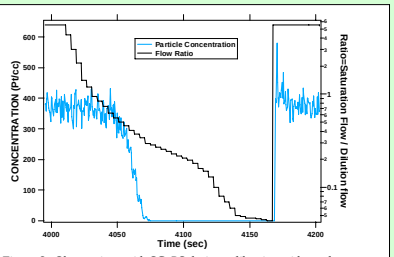

Figure 6. Observations with SCoPS during calibration with nearly monodisperse particles. Saturation/dilution flow ratio is stepped (right axis); particle concentration (left axis, blue) falls as response curves (Fig. 4) shift to larger particle diameters. Cycle begins to repeat (right-hand portion of graph--note response time to a large step function in flow ratio.

Evaluation of SCoPS

- Aerosol with ±10% diameter dispersion provided to SCoPS and CPC
- Ratio of saturator to dilution flow stepped from high to low (right-hand axis) (4-sec steps)
- Concentration (left-hand axis) falls when response curve (Fig. 4) shifts to diameters larger than the calibration aerosol
- Concentration time response to changes in flow ratio is ~1sec
- Lag time to changes in flow ratio is ~2 sec
- Concentration X after each step i is recorded:

$$X_i = \int N(D_p) K_i(D_p) dD_p ,$$

where N is the particle size distribution function, and $K_i(D_p)$ the response function of the SCoPS at flow ratio i to particle size D_p (Fig. 4).

- Given $K_i(D_p)$ and X_i measured with known uncertainty, what is $N(D_p)$?
- Use nonlinear inversion method (Twomey-Markowski) to determine the particle size distribution that can produce the observed response for all i's (not unique).

PERFORMANCE: COMPARISON WITH SMPS

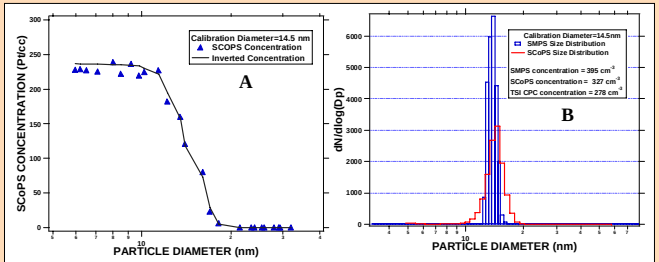

Figure. 7. A) Particle concentrations measured by the SCoPS (symbols) for each step in saturation ratio (Fig. 6) as a function of the threshold Kelvin diameter associated with that saturation ratio (Fig. 5) for a calibration aerosol with a peak diameter of 14.5 nm and a dispersion of ±10%. The curve is the calculated response of the SCoPS instrument to the recovered size distribution shown in red in (B). B) Particle number size distribution measured by the SMPS (blue bars) and by the SCoPS (red bars). The area under the curve is the total particle concentration. The resolution of the SCoPS is poorer than the SMPS, but the peak diameter and integrated particle number are more accurate for this case. The SCoPS scan time was set to match that of the SMPS (~120 s), but could be reduced by a factor of 3 with little performance loss. The SMPS accuracy is limited by the poor counting statistics of the instrument, which measures only the charged fraction of the calibration aerosol (<5% of the total).

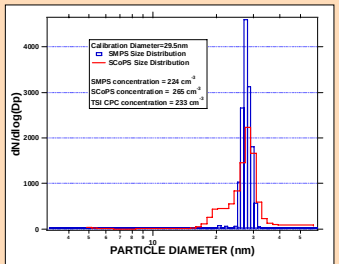

Figure. 8. Particle number size distribution measured by the SMPS (blue bars) and by the SCoPS (red bars) for a calibration aerosol with a peak diameter of 29.5 nm and a dispersion of ±10%. The area under the curve is the total particle concentration. The resolution and accuracy of the SCoPS is poorer than the SMPS for this size, which is near the upper limit of sizing capability for the SCoPS under the flow and temperature conditions studied.

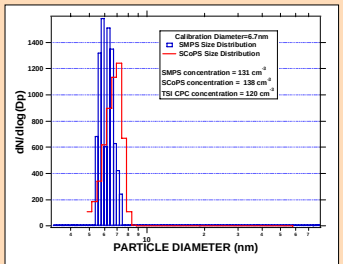

Figure. 9. Particle number size distribution measured by the SMPS (blue bars) and by the SCoPS (red bars) for a calibration aerosol with a peak diameter of 6.7 nm and a dispersion of at least ±10%. The area under the curve is the total particle concentration. The resolution of the SCoPS is similar to the SMPS for this size, and the sizing accuracy is slightly better. This size is near the lower limit of sizing capability for both the SMPS and SCoPS under the flow and temperature conditions studied.

CONCLUSIONS

Performance of the SCoPS Technique

- The proof-of-concept was successfully demonstrated
- The diameter of nucleation (Kelvin diameter) can be controlled over a range from 5 to 30 nm with the current configuration (flows, temperatures, fluid properties)
- The time response of the system is ~1 second to changes in flows, meaning that scans of particle size distributions over this range can be accomplished in ~30 s with good counting statistics
- The inversion method can successfully recover the diameter and concentration of nearly monodisperse calibration particles as well as polydisperse aerosols
- An unexplained shift in performance occurred near the end of the project, necessitating a complete recalibration of the response functions. Flow controller calibration change?
- The size resolution and size range is less than that of the competing SMPS technology
- Detection efficiencies for particles <10 nm were reduced by diffusional losses. All efficiencies <100% (?)

Needs for Further Development

- Extend diameter range by testing different flows, temperatures, and fluids
- Increase sample flowrate to reduce time lag and sample smearing
- Reduce particle losses to diffusion by changing sample flow geometry and flowrate
- Improve and automate software, improve system packaging
- Improve accuracy and robustness of response curves
- Shorten stepping time and/or develop true scanning mode algorithm for size distribution inversion

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