

## **Instrumentation for State-Of-The-Art Aerosol Measurements in Smog Chambers**

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Aerosol smog chamber studies are performed to elucidate the chemical and physical processes that occur in the atmosphere leading to the formation of fine particulate matter. In order to obtain this goal, the number concentration, size distribution and chemical composition of secondary aerosol produced in an environmental chamber must be monitored as it evolves with time. An ideal instrument would be able to obtain both the chemical and physical properties of the aerosol at time scales comparable to the evolution of the aerosol in the chamber at infinite resolution. A road map on the available instrumentation and the desired measurements for an environmental chamber is laid out. Critical environmental control parameters are also discussed as are different techniques to ensure that the reactions and secondary aerosol formation in the environmental chamber can occur at time scales and size ranges that can be easily detected by current instrumentation. Also mentioned are some of the new techniques being implemented at Caltech to increase the accuracy and precision of measurements made in our chamber as well as improvements in the time and spatial resolution of our measurements.

There are two pathways for secondary organic aerosol (SOA) formation. The first is supersaturation of semi-volatile organics derived from gas phase oxidation of precursor hydrocarbons which lead to homogeneous nucleation; secondly, simple heterogeneous condensation which can occur on aerosol surfaces already present in the environment. Homogeneous nucleation and the resulting growth immediately following the nucleation can be extremely fast processes, often occurring on time scales much less than 1 minute. In order to monitor the early evolution of a homogeneous, nucleation aerosol, the aerosol instrumentation would have to be much faster than any aerosol measurement devices currently available. Moreover, homogeneous nucleation generates molecular clusters and extremely fine aerosol particles, below the size range typically obtained by available aerosol instrumentation. The difficulties created by nucleation events can, however, be avoided. By providing a sufficiently large surface area in the form of a nonvolatile, inorganic aerosol, homogeneous nucleation can be suppressed as semi-volatile organic compounds partition onto those surfaces. This process occurs as semi-volatile organics achieve a large enough saturation to form an initial organic layer around the inorganic salt. Subsequent growth depresses the supersaturation below the level that would lead to homogeneous nucleation. The growth of the seed particles is slower than that of the nuclei so it can be followed with available instrumentation. Moreover, the smallest particles are then determined by the seed particles, so all particles can be measured. This process is quick; typical times for full growth range from 30 minutes to 12 hours for conditions in the Caltech environmental chamber.

Choosing the best instrument for the measurement of the physical and chemical processes occurring the chamber involves looking at the time scales and spatial distributions of the aerosol inside of the chamber. Instrumentation used currently for particle size distribution measurements includes the stepping mode differential mobility particle sizer (DMPS), the scanning electrical mobility spectrometer (SEMS), the aerosol mass spectrometer (AMS), the optical particle counter (OPC), and the micro-orifice uniform deposit impactor (MOUDI). Of these instruments, the SEMS system provides us the best picture of the physical processes occurring in the chamber because of its fast response and good size resolution in the submicron range that dominates the aerosol dynamics. The SEMS can provide size and number distributions on time scales of less than 1 minute over 3 decades of size with reasonable resolution. While the OPC can also obtain data at this high rate, the extinction coefficient and scattering properties of each individual aerosol must be known for high accuracy. Moreover, the

OPC can only size particles larger than about 0.1  $\mu\text{m}$  (some extend down to 0.08  $\mu\text{m}$ ). Recently developed AMS instruments, which have seen limited use in chamber studies to date, enable chemical analysis of the aerosol, but the time resolution of these instruments is longer than the time scale for growth occurring in the chamber. Moreover, most versions of the AMS can only measure relatively large particles. Lower bounds on AMS measurements range from 0.04 to 0.3  $\mu\text{m}$  aerodynamic diameter. The stepping mode DMA requires several minutes to measure a size distribution, too large to follow the fast aerosol dynamics encountered in chamber studies. MOUDI sampling times required to collect sufficient material for measurement are even larger. Hence, the SEMS provides the best real-time measurements of aerosol physical properties for smog chamber experiments.

Additional physical issues for environmental chamber studies of SOA include control of temperature and relative humidity, wall effects, and homogeneity or heterogeneity of chemical and physical aerosol properties during measurement of SOA. The vapor pressures of semi-volatile compounds that contribute to aerosol formation are strong functions of temperature, so the temperature of the chamber must be well characterized. Moreover, the temperature at the point of measurement can bias the results, particularly when instrumentation is located outside of the chamber. Another important control parameter is the relative humidity. Variations in relative humidity strongly influence particle size and may perturb the partitioning of reaction products between the gas and aerosol phases. The chamber volume should be large to achieve a small surface area to volume ratio in order to minimize particle wall loss and wall effects. The chamber should not be so large that poor mixing or thermal stratification leads to a heterogeneous reaction environment, however.

Optimization of the SEMS enables even more powerful analysis of the physical processes occurring in the chamber. Caltech has fully automated the SEMS system to acquire data and process size and number distributions in real time. A computer is used to control the flows and the voltage of the system, making any necessary adjustments 100 times a second. A proportional-integral-differential (PID) controller maintains the flow rates of the instrument to within  $\pm 0.2\%$ . Fast inversions allow for the data to be deconvoluted, stored and displayed in graphical form in times of less than 1 second allowing the experimenter to follow the evolution of the aerosol in real-time. Minimization of the lengths of tubing reduces the fluid-mechanical smearing time of the measurements. Full size distributions are obtained over a size range extending from 28 to 800 nm are obtained each minute.

Caltech has further modified the SEMS system to increase both the range of measurement of the SEMS as well as the time of the scan. The size range for the SEMS instrument has been limited at the low end by resolution and on the high end by the breakdown voltage of air at high voltages. However, by increasing or decreasing the flow rate of the DMA, smaller and larger diameter particles can be measured respectively. Caltech has developed a scanning flow system that can increase the dynamic range of the measurement. While the technique has the drawback of a more complex deconvolution of the data involving back-calculating the trajectories of the particles to determine the system transfer function, size distributions over greater dynamic ranges can be achieved. A limitation to the temporal resolution of the instrument has been the delay times between classification and detection of particles in the DMA. A majority of the delay time is currently caused in the system by delays in the measuring time of the CNC. Caltech has developed a fast CNC that reduces the delay time of measurement of the CNC by two orders of magnitude allowing for size distributions to be achieved in less than two seconds.

While SEMS can provide us with adequate physical characterization of the aerosol on the time scales of heterogeneous condensation, it is unable to provide us with chemical

composition of the aerosol. Ideally, chemical compositions should be determined sufficiently rapidly to identify any changes in composition during the evolution of the aerosol, but none of the available techniques are capable of such time resolution. At present, we use denude/filter apparatus to separate the gas-phase and aerosol-phase. Derivatization coupled with GC-MS analysis facilitates identification and quantification of the chemical composition of the aerosol. Given the low reactant concentrations in environmental chamber studies, we can only collect bulk samples, i.e., with no size classification, one sample per hour for off-line analysis.

The tandem differential mobility analyzer (TDMA) can be used for faster inference of changes in the chemical or physical properties of the aerosol. The technique uses a DMA to select particles of a given size. Those particles are then subjected to an environmental perturbation that may cause them to change size, e.g., humidification to induce growth of hygroscopic particles. One can deduce the hygroscopicity or other properties of the aerosol, and determine whether all particles have similar properties or whether particles with different compositions have been produced.

Through control of the temperature and humidity of the environmental chamber, the use of the SEMS the TDMA, and denuder/filter sampling for chemical analysis of gases and particles, the physical growth of particles and the chemical composition of the aerosol can be obtained. This instrumentation enables investigation of the physical and chemical transformations occurring in the environmental smog chamber.