

PMTACS – NY AMS METADATA REPORT For Whiteface Mountain Summer Campaign 2002

Frank Drewnick

Atmospheric Sciences Research Center, University at Albany

11/28/2002

Instrument Description

The Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc.) is a compact on-line measuring quadrupole mass spectrometer, based on thermal evaporation of aerosol particles.

The particles are focused by an aerodynamic lens while they are accelerated into a differentially pumped vacuum chamber. The inlet flow is 0.1 l/min. Particles in a diameter range from 40 nm to 600 nm are transmitted through the lens with 100 % efficiency. The particle beam passes a skimmer and a chopper before it crosses a flight chamber (0.39 m) and impacts onto a heated surface (500 °C). Volatile and semi volatile particle components are evaporated on the heater. The vapor is ionized by electron impact ionization and analyzed by a quadrupole mass spectrometer. Ions are detected with a multiplier. A more detailed description of the instrument is given in Jayne et al. (2000).

The instrument can be operated in two different modes: In the *mass spectrum mode* (MS mode) the chopper is moved completely out of the particle beam and the mass spectrum is scanned over a range of 1 to 300 amu with a frequency of 3 Hz. In this mode a quantitative measurement of the bulk mass concentrations of the volatile and semi volatile aerosol species is performed. For background measurement the particle beam is blocked by the chopper.

In the second mode, the *Time-of-Flight mode* (ToF mode), the particle beam is chopped by the chopper (2% duty cycle) and the time resolved MS signal is recorded for selected masses that are typical for some aerosol species. During the acceleration in the aerodynamic lens the particles reach a final velocity depending on their aerodynamic size: Larger particles are slower, smaller particles are faster. Using a particle velocity calibration (performed with laboratory particles of known sizes) the flight times, measured in the ToF mode can be converted into sizes, yielding to particle size distributions for the species that belong to the selected masses.

Field Operation

During the PMTACS-NY summer intensive at Whiteface Mountain in summer 2002 the AMS was operated at the measurement site at the 'Lodge Level' ASRC field station on Whiteface Mountain from July 9th until August 7th. The measurement site was located about 10 m above the ASRC field station and a small parking lot, only used by the field



staff. It was surrounded by dense forest. The closest public road was a small local road about 500 m to the east of the station.

The AMS was housed in an air-conditioned shelter together with other aerosol sizing and counting instruments. The sampling inlet was mounted on a tower at a height of 5 m above ground level, attached to the shelter. Ambient air was sampled via a PM_{2.5} cyclone at 10 l/min and through 14.1 mm ID copper tubing. The tube diameter was chosen to minimize losses by impaction and gravitational settling for the given flow rate. The overall transport losses were calculated using simple formulas for diffusion, gravitational settling and impaction losses (Hinds (1999)) for the given inlet geometry. For 25 nm particles the losses are about 2.5 %, dominated by diffusion; at 2.5 µm the impaction and settling dominated losses are about 3 %. The minimum of losses is about 0.2 % for 330 nm particles.

At the entrance of the AMS inlet, a sample flow of 0.1 l/min is isokinetically extracted from the 10 l/min transport flow and introduced into the AMS inlet. The transport losses within the first few centimeters of the AMS inlet are larger than in the copper tube, especially for the small particles, due to the very low flow rate

In the field the AMS was operated to periodically switch (i.e. 20s cycle) between the ToF mode (size information for pre-selected masses) and the MS mode (complete mass spectrum for bulk aerosol). In the ToF mode the size distribution information was measured for mass 15, 16 amu (ammonium), 30 and 46 amu (nitrate), 32 amu (air, oxygen), 48, 64 amu (sulfate) and 43, 44, 55, 57 amu (organics). In MS mode the mass spectrum was scanned from 1 to 300 amu at a 3 Hz rate. After 5 seconds of analyzing the particle vapor the particle beam was blocked for another 5 seconds by moving the chopper wheel completely into the beam to measure the background signal. Every 10 minutes the mass spectrum and size distribution averages were saved to disc.

The multiplier signal and gain, the inlet flow rate, and the efficiency of ionization and transmission of the ions through the QMS are necessary to calculate particle mass concentration. The inlet flow meter was calibrated in the field at the beginning of the campaign, ionization and transmission efficiency calibrations were performed several times in the field. The calibration procedure involves producing ammonium nitrate particles of 350 nm mobility diameter and introducing them into the AMS. The average number of ions per particle reaching the multiplier entrance is determined from the multiplier signal, using the freshly calibrated multiplier gain. The ionization and transmission efficiency is the ratio of ions per particle as determined in this calibration procedure and molecules per particle, calculated from particle diameter, particle density and molecular weight. The multiplier gain was calibrated using single ions, produced from the background gas in the ionizer region at reduced electron current.



Data Processing

Since the ionization and transmission efficiency didn't change significantly over the time of deployment, an average value was used for the whole campaign.

The mass concentration of a species is calculated from the multiplier signal, using the multiplier gain calibration and the ionization and transmission efficiency calibration together with the inlet flow meter reading.

For *nitrate* particles the mass concentration is simply the sum of the mass concentrations calculated for all fractions: 30 amu (NO) and 46 amu (NO₂). Losses due to incomplete focusing of internally mixed nitrate and sulfate particles were accounted for by multiplication of the nitrate mass concentrations with a factor of 1.48. This factor was determined from AMS – PILS comparison, see below, using the relative ionization efficiency of sulfate as determined in laboratory experiments.

Chloride typically is measured as Cl⁺ and HCl⁺, considering chloride's two isotopes this includes mass 35, 36, 37 and 38 amu. As a result of strong interferences with fractions of organic species, only mass 35 and 36 amu are used to calculate the chloride mass concentration. The chloride mass concentration is corrected, using the natural isotope ratio of ³⁵Cl and ³⁷Cl. Also the correction factor of 1.48 for incomplete focusing was applied to the chloride data, since it was assumed that chloride is internally mixed with sulfate/nitrate.

Ammonium has fractions at mass 15, 16 and 17 amu (NH, NH₂, NH₃). Due to interferences with O₂²⁺ (16 amu) and fractions of water (OH, 17 amu) the signals at these masses first were corrected for contributions by other species before the ammonium signal was derived. Since all of these signals are very noisy, the resulting ammonium signal is noisy, too. This ammonium signal was multiplied by a correction factor for the relative ionization efficiency of ammonium (0.222, determined in laboratory experiments) and for the correction factor for incomplete focusing of the particles (1.48, internal mixture with sulfate/nitrate assumed).

Sulfate fractions (and their isotopes) are located at mass 16, 17, 18, 32, 48, 64, 65, 80, 81, 82 and 98 amu. Interferences with organic fractions and water fractions require, that many of these signals have to be corrected for organics and water or have to be calculated using fragmentation patterns, determined in laboratory experiments. The sulfate signal is corrected for its relative ionization efficiency by a factor of 0.85. In addition sulfate particles exhibited a systematic loss of signal that thought to be related to incomplete focusing of the sulfate particles in the aerodynamic lens. This loss in sulfate signal is accounted for by multiplying all sulfate mass concentrations with an empirical factor of 1.48. This factor was determined once by comparison of the AMS sulfate mass concentration with the sulfate mass concentration measured by another instrument (PILS) during the beginning of the campaign.

Lab experiments by Aerodyne Research Inc. indicate that the ionization efficiency of organic molecules is larger than for inorganic molecules of equal molecular weight. This is accounted for by multiplication of all organics signals by a factor of 0.7. The *total organics* signal is calculated adding up all masses of the mass spectrum larger than 11 amu besides the masses that belong to extremely large fractions of other species or air. Masses that also belong to minor fractions of other species are corrected for these species before being added to the organics signal. According to the size distribution



measurements it is assumed that the organic aerosol mass is also internally mixed with sulfate and nitrate particles. Due to this mixture also the organics mass concentrations are corrected by the factor of 1.48 that accounts for incomplete focusing of the particles in the aerodynamic lens.

Mass concentration calculations as well as all the corrections to the mass spectrum were performed using the AMS Analysis Toolkit V1.20 Deluxe, written for IGOR PRO by James Allen, UMIST Manchester.

The *size distribution data*, measured at the different masses were averaged for sulfate, nitrate, ammonium and total organics. The size bins of the raw data are determined by the time steps of the time resolved data acquisition. To obtain more useful size bins, that reflect the size resolution of the instrument, the raw data were re-binned, using 20 size bins per decade, equally spaced in the $\log D_p$ space.

The size distribution raw data were transformed into mass concentration units ($\mu\text{g}/\text{m}^3$) and corrected to match the mass concentrations, measured by the MS mode. They are calculated as $dM/d \log D_p$ data.

Data Quality

All valid data that were not qualified in any way were flagged with 'V0'.

Valid 10 min data that were below the detection limit were flagged with 'V1'. The detection limit was calculated for the MS mode using the noise of the background signal. For the size distributions the detection limit was calculated for every bin separately using the noise of the signal at large flight times (corresponding to large particle sizes above 2.5 μm , i.e. above the cut-off of the inlet cyclone) and the number of bins of the raw size distribution, accumulated in the re-binned size distribution bins. Accordingly every bin of every size distribution data set has its own flag.

Valid 10-min data, where the actual sampling and averaging time is below 7.5 min, but not below 5 min were flagged with 'V2'.

Values missing, because the instrument was not sampling were flagged with 'M1'.

Values invalidated, because the sampling and averaging time was below 5 min were flagged with 'M2'.

No other flags were used.

Reference

Jayne, J.T., Leard, D.C., Zhang, X., Davidovits, P., Smith, K.A., Kolb, C.E., Worsnop, D.R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles. *Aerosol Science and Technology* **33** (2000) 49-70