

Description of the University of Colorado Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) in the DC8 for DC3 and SEAC4RS

The Aerodyne Aerosol Mass Spectrometer (AMS) measures the size-dependent and chemically speciated mass concentration of non-refractory species (sulfate, nitrate, ammonium, chloride, organic) in particles with sizes between 50 nm and $\sim 1 \mu\text{m}$. Total mass measurements can be performed with up to subsecond time resolution and approximate chemically speciated mass concentrations are reported in real time [DeCarlo et al., *Anal. Chem.* 2006; Canagaratna et al., *Mass Spec. Rev.* 2007]. Subsequent detailed analysis of the full, high resolution mass spectrum allows a more accurate determination of the inorganic species and further analysis of the organic fraction to determine its O/C and H/C [Aiken et al., *ES&T* 2008], as well as performing factor analysis [Ulbrich et al., *ACP* 2009, *AMT* 2012].

The AMS is based on the principle of impacting a tightly focused submicron aerosol beam on an inverted-cone, porous tungsten vaporizer at 600°C under high vacuum, ionizing the resulting gas plume with a 70 eV electron beam and extracting those ions in a pulsed manner into a time-of-flight mass spectrometer. Separating the desorption and ionization steps suppresses matrix effects, and 70 eV ionization is a universal detection approach for any molecules that can be desorbed into the gas-phase, with similar sensitivity for all species within a factor of 2. Since species-dependent sensitivities can be calibrated and are reproducible, quantitative mass

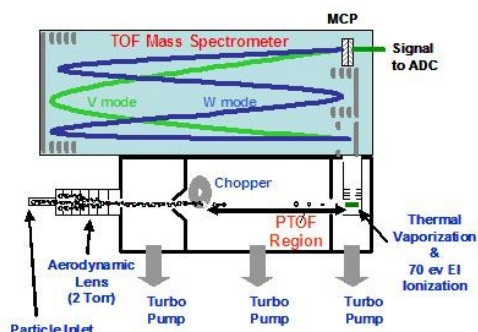


Figure 1: High resolution AMS Schematic

concentrations can be retrieved [Jimenez et al., *JGR* 2003]. This detection approach is limited to “non-refractory” aerosol species, which includes most submicron salts (sulfates, ammonium, nitrates) and organic species, and excludes dust, sea salt and black carbon. Less refractory metals such as lead and zinc can be detected [Salcedo et al., *ACP* 2010], while refractory metals cannot. The aerosol inlet (critical orifice plus aerosol lens) limits transmission to particles of roughly $1 \mu\text{m}$ vacuum aerodynamic diameter (d_{va}), so the mass response of the AMS response is generally referred to as $\text{PM}_{1.0}$. Finally, the lack of focusing performance of the aerosol lens and the detection limits of the technique limit quantitative detection to particles $d_{va} > 50 \text{ nm}$.

Absolute mass concentrations are derived by calibrating the AMS ionization efficiency with different sizes of ammonium nitrate aerosol, and using species-specific relative ionization efficiencies determined in the laboratory. The main limitation of the AMS quantification approach is due to a - mostly phase dependent - particle bounce on the AMS vaporizer, which is quantified by the AMS collection efficiency (CE). However there is a reproducible variation of CE with aerosol composition, which has been characterized in many field campaigns as part of a large AMS community effort. An algorithm based on these studies is used as part of the quantification procedure and generally results in accuracies of 30-35% for the different species [Middlebrook et al., *AS&T* 2012].

A chopper wheel intercepting the particle beam inside the vacuum chamber allows to select between the two main modes of operation, total submicron mass (“MS mode”) and size resolved mass (“Particle time-of-flight or PToF mode”). In MS

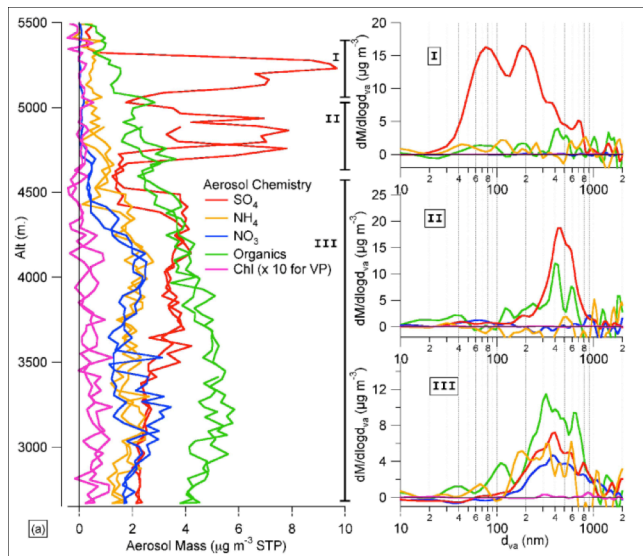


Figure 2: Vertical profiles (left) of the main chemical species found in the aerosol as recorded by the HR-ToF-AMS on Research Flight 12 as part of the MILAGRO campaign. (Right) Aerosol mass size distribution by species for three selected heights during the same flight.

expected to improve sensitivity during flights considerably, by a factor of 2x to 4x, especially during the early hours of the flights.

The AMS can also operate at higher time resolutions (1 s or faster) at the expense of not recording size-dependent data. Time acquisition intervals of 1 s were used during the ARCTAS campaign to considerably improve the spatial resolution of the data, which was very useful in e.g. the biomass burning plumes. However, given the reduction in S/N, the usefulness of this mode in very clean conditions is limited, although the improved sensitivity provided by the cryopump might make its use during SEAC4RS more relevant.

The AMS installed on the DC-8 uses a High Resolution Time-of-Flight Mass Spectrometer (HR-ToF) with a resolution of about ($m/\Delta m$) of 2500. Thanks to this high mass resolution it is possible to separate and identify most ions below m/z 200 with high accuracy. This in turn makes it possible to assign these ions to the proper species without most of the assumptions needed when recording unit mass resolution spectra (as an example, the ammonium signal can be separated clearly from water). It also allows for a much more comprehensive analysis of the organic fraction, so that H/C and O/C ratios can be measured directly, without relying on proxies.

For further information about the AMS and its data products, we recommend the following FAQ page: http://cires.colorado.edu/jimenez-group/wiki/index.php/FAQ_for_AMS_Data_Users
Please contact pedro.campuzanojost-1@colorado.edu or jose.jimenez@colorado.edu

mode, the chopper wheel is moved so it blocks and unblocks the beam to take aerosol signal and background traces, typically every few seconds for aircraft deployments. In PToF mode, the wheel chops the aerosol beam at ~ 150 Hz rate (4% duty cycle), and the arrival of the ions on the detector relative to the chopper position can be translated into a particle time-of-flight and hence, a vacuum aerodynamic diameter (d_{va}). The relationship between d_{va} and other diameter definitions are discussed in DeCarlo et al. [AS&T 2004]. For aircraft studies, this mode is operated at 10 s intervals. With 10 s time resolution, ultimate detection limits in MS Mode for sulfate, nitrate and ammonium are about 10 ng/m^3 , and 60 ng/m^3 for organics. In practice, detection limits in typical aircraft studies are about 10x higher due to the short pump down of the instrument. The addition of a new cryopump to the AMS for SEAC4RS is