Summary of 2nd Aerodyne AMS Users Meeting (Nov. 5 – 7, 2001)

Summary by Dr. Frank Drewnick, SUNY Albany

Organized by Manjula Canagaratna, Jose-Luis Jimenez, John Jayne, and Doug Worsnop

AMS Upgrades

Available Upgrades:

16 mm Quadrupole
- More Ion Transmission, especially for large m/z (>100 u)
- Not much Benefits proven for low Masses
- Adds ca. 30 lbs
- Price: ca. 52 000 $ (Without Electronics Box: ca. 42 000 $)

Conical Heater with Thermocouple
- Reduces Particle Bounce
- 'nicer' Single Particle Histogram
- Direct Temperature Measurement
- Price: ca. 2500 $

New Aerodynamic Lens and adjustable Inlet
- Better Transmission for small Particles, 50% cut-point shiftet down to ca. 30-40 nm (according to *Fluent* Calculations, no Measurements available yet)
- Adjustable Inlet simplifies Beam Alignment (NO collection of Spots anymore!)
- Allows Beam Profile Measurements
- Price: ca. 2000 $

Conversion Dynode Multiplier
- eliminates the Mass Dependence of the Multiplier Gain
- Reduces Ion Collection Efficiency (needs further Investigation)
- Price: ca. 4000 $

Differentially QMS and Ionizer Chamber
- improves Water-Vapor Background significantly → Possible to measure Particle Water content
- Improvement of Ammonium Measurement (at mass 16)
- Adds another Pump to the System
- Price: ca. 5000 $ (Upgrade for small QMS)

Hybrid Turbo/Drag Pump at the Inlet (Alcatel Pump)

- Reduces Gas Load at the Skimmer Chamber (enhanced Turbo Pump Lifetime)
- Adds ca. 50 W to the Power Load
- Price: ca. 5000 – 6000 $

Channel Skimmer/Apertures
- Reduces Gas Load in Ionizer Chamber, lower Background
- Better S/N for the AirBeam
- Price: free !

Future Upgrades:

High-Throughput Inlet
- more Pumping at first Chamber with Varian V301 Turbo Pump
- better S/N due to more Inlet Flow
- V301 replaces 2 V70 Pumps
- New Lens design necessary
- Not yet tested

Light Scattering Probe
- Sizing and Counting of all Particles that hit the Heater
- Calculation of the non-volatilazed Particle Mass
- Not yet tested

Beam Width Probe
- Wire on Micrometer-Translation Stage
- Information about Beam Width (Particle Shape ?)
- Tested, available soon, if requested

Ionizer Redesign
- Improvement of Ionization Efficiency
- IE not anymore dependent on Position of Particle Impact on Heater
- Not yet tested

High Temperature Heater (1500 deg. C ?)
- Detection of low-volatility Species (NaCl ?)
- Issues with Organics ?
- Not yet tested

Re-Evaluation of Pressure Gauges
- Elimination of the Ionization Gauge (not useful, many problems, can be replaced with QMS)
- Replacement of Inlet Gauges with Baratron (more reliable, more accurate)
- Not yet implemented

Reduction of the Cabling

- Replacement of all Turbo Pump Cables with one common Cable
- Replacement of the Signal and Controller Cables with a view Cables
- Not yet implemented

Re-design of the Rack-mount Boxes
- available soon

ToF Mass Spectrometer with EI Ionization
- Full Mass Spectrum for single Particle
- Signal Processing and Data Handling Issues due to the large Amount of Data produced by the ToF MS
- Not yet tested/planned

New Software Features

AMS USERS Lists:

After shut-down of the old AMS Mail-List by Microsoft ☹, Manjula has set up 2 new lists that are dedicated to different topics:

AMS-USERS : General AMS Stuff, of Interest for every AMS User
AMS-IGOR: Discussion related to the IGOR Analysis Software

YOU NEED TO JOIN THESE LISTS IF YOU WANT TO WRITE TO THEM!!
You can subscribe to these lists by following the directions in the Aerodyne HomePage at: **http://www.aerodyne.com/mailinglists.html**

Technical Support issues (AMS software or hardware) can be dealt w/ by sending e-mails to ams-support@aerodyne.com . E-mails sent to this address will automatically be connected to Aerodyne Personnel (John, Manjula, Doug) and Jose Jimenez

Data Acquisition Software:

Latest Software Version : 3.7.8 (available soon!)

Preliminary Software Manual for sofware versions upto 3.6.6. is AMSSoftwareManual_v1.0.pdf

It can be found at:
ftp://ftp.aerodyne.com/AMS/AMSManuals/

Multiplier Calibration

- Select Mass for Calibration in F6 Window (selected mass should have low enough background to avoid coincidences, but high enough for good sampling statistics)
- Calibrate Multiplier (Button on Main Menu)
- Multiplier Calibration Routine selects a Calibration Voltage at the beginning of the Plateau of the Gain Curve (stable Calibration on Plateau, Voltage as low as possible)
- If desired, choose other Calibration Voltage by clicking in top Window
- NEW: Do measurements at Calibration Voltage, don't set Multiplier Voltage to match Gain of 2e6 (introduces additional error)

Quadrupole Mass (m/z) and Mass Resolution Calibration

- NEW: AMU and Resolution Calibration Window (**Press Calibrate MS button in Main MS window**) for multi-point Calibration of AMU Calibration
- Display of Mass Spec Intervals in two windows. Select nominal Mass for Calibration above Windows, click in Window on Peak to select Peak.
- Program will automatically determine # bits that need to be output to achieve the maximum signal at chosen mass
- Repeat for as many Peaks in Mass Spec as desired
- Press 'Calibrate' Button to do AMU calibration
- Optimize Resolution for intensive signal and minimized leaking of signal in neighbouring masses by changing Resolution Settings in lower part of Window
- Repeat Mass m/z Calibration if necessary

Summary Window (NEW_ Access by Shift-S from MS or TOF windows)

- Provides quick Overview over Instrument Performance: Inlet Flow, AB-values, AB modulation Ratio, Background Signals, Total Nitrate, Sulfate, Ammonium, Organics
- Future upgrade: Button for online Delta-Analysis

F6 Window

- Many columns of the Table disappear (NEW)
- Only necessary Information and Values that could need a change by the User are kept in the Table: Nominal m/z, Offset, SP Threshold, # of Points of sliding Windows, # of DC Markers, Species, Group Member, m/z set (amu), m/z set (bits), QMS Resolution Setting
- Ammonium uses only second DC Marker. (Otherwise you have NH3 gas inteference in signal)

- Necessary Group Members: “I” for Multiplier Calibration, “B” for AirBeam, Chopper Position Calibration (Name has to be “AIR” !)
- IE Calibration Buttons disappear from F6 Window

Parameter Menu

- Menu contains to many Information, much of it is never changed
- Division of Parameter Menu in two Parts (NEW):
- Instrument Settings: Main Setting Changes (like Eddy Correlation Mode, Airplane Mode), Board Settings, Software Control Settings, Hardware Settings
- Operation Settings (less Entries, re-arranged): Settings that have to be changed for/at Operation of the Instrument

History Window

- Tells about Changes in Parameter Menu
- Displays Warnings if Inconsistencies or strange Settings are detected
- To much Information, will be reduced

Data Saving

- Also in HDF format possible now (select in Parameter Menu)
- Changes in Single Particle Saving: Time Scaling after SP event stepwise increased to include more Information with less Data amount

Mass Spec Window

- Only Nitrate, Sulfate, Organics, Ammonium mass loadings (in Nitrate-equivalent masses) displayed, not all Masses, selected in TOF Mode (this feature can be changed in Parameter Menu for Lab Experiments)

NH_4NO_3 Mass Calibration Procedure

- Select Masses for Calibration (Nitrate: m30, 46, AB: 28/32, Ammonium: 15, 16, 17, 18); Species Group for Nitrate has to be ‘NO3’
- Set SP Threshold for all selected Masses
- Set Integration Region 2 in TOF Window properly: Should be close around single Charge-Peak in Histogram Window
- Start Alternate Mode to save MS and TOF Data
- Check in SP (INSERT) Window that average SP shape represents the single Particles well, if not: change Number of TimeSteps to calculate IPP in Parameter Menu
- Press ‘Shift M’ in TOF Window to open Calibration Window
- Select AMS for Particle Counting in Parameter Menu
- Insert Species, Mass Fraction, Particle Diameter, Density, Shape Factor in Table
- Actual Values are displayed
- Press ‘Calibrate Now’ Button

- Calculates New Ionization Efficiency; NEW: Calculates IPP for every Particle first, averages all IPPs for Calibration (old: first Averaging of all Particle Signals, then calculation of IPPs)
- Display of Calibration Results in 'Shift M' Window, writes a TOF and MS.ITX file on Disk (non-auto-save directory)

Data Processing Software:

The Unified Analysis Toolkit is now available from James Allan !

Some Features (more in the upcoming manual):

- Toolkit Panel is divided in 5 Tabs for better overview
- Load Data Panel: Selection of Data Path, Run Numbers to load, also Keywords possible like 'all', 'new'
- Corrections Panel: AB Correction (selection of 'reference' interval by typing in run Numbers or Selection in Graph), Error Calculation, Recalculation of Stick Spectrum for changed AMU calibration, Recalculation of Diameters with new Velocity Calibration Parameters
- MS Panel: Display of single and averaged Mass Spectra, Display of Time Series of single Masses, Species, Sum of Masses/Species, Ratios of Masses/Species, Batch Calculation of Mass Concentration Time series for single Masses, Species, Differences, Ratios and Products of them
- TOF Panel: Trace Averaging, Display of Image Plots for single Masses, Species or Combinations, for whole Time or Time Interval, Normalization of Size Distribution to Mass Spectra possible
- Misc Panel: Remap of Time Series for Comparison with other Data sets, Graph Controls, Change of Date/Time Format

MS of Organic Species

Results of Lab Experiments:

- Pretty good Agreement of AMS Mass Spectra with NIST Database Mass Spectra for PAHs
- For some Species: Shift of Fragments towards lower Masses observed
- Most Compounds (22 of 26) are 'first Hit' in MS Database in automatic Search
- Thermal decomposition of oxygenated Species to CO_2 and H_2O increases with increasing Number of OH-groups
- Higher Mass Compounds (M>200 amu) don't show linear IE/Mass dependency, Ionization Efficiency increases super-linear with mass. Further investigation necessary

Delta Analysis:

- Assignment of Series of Organic Mass Signals to 'Groups' with equal 'Deltas' (equal deviation of Mass from (13 amu + n * 14 amu))
- Assignment of Delta Groups to Groups of Organics (see Doug's presentation)
- Different Sources show different Patterns of Delta Groups
- Delta Analysis Software available (Manjula)

Lab Experiments and Field Studies

For Details of Lab Experiments and Field Studies see the Presentations, posted on the AMS_Incoming ftp site at

ftp://ftp.aerodyne.com/AMSIncoming/AMSUsers/ALLUsers/AMS_UsersMtg_1101

Lab Experiments:

UMIST: Heater Temperature Experiments for Inorganics and Organics
SUNY: Heater Temperature Experiments fo Inorganics, Sulfate/Nitrate Mix Experiments
Boston College: Activation Experiments of Soot Particles with Sulfuric Acid
CALTECH: Size Distribution Resolution Experiments and Theory
CALTECH: Aerosol Formation from Photooxidation of CH_2I_2
NOAA: PALMS Data Analysis Software

Field Studies:

CALTECH: HOUSTON 2000
UMIST: SASUA 3 (Edinburgh, Nov 2000)
UMIST: ACE ASIA (South Eastern Asia, March/April 2001)
CALTECH: ACE ASIA (Airplane Measurements)
Aerodyne: CEPEX 2000/2001 Bus Chasing Experiments (New York City)
SUNY: PMTACS NY 2001 (New York City)
ALICE/Aerodyne: PROPHET2001
UMIST: PACIFIC 2001
MPI: Crete Study 2001

AMS Field and Lab Operation Issues

A lot of things can go wrong in the field – some can be recovered (a lot of work) later, some can't
→ We need to do quality assurance to make sure, we get the best data we can get !

- Optimize QMS Resolution: Low Resolution makes it difficult to interpret Data, high Resolution decreases Signal Intensity
- Check Servo Position: At wrong Servo Position, Signal can become unquantitative; Changes in Servo Calibration can indicate an upcoming Servo Failure.
- Particle Size Calibration should be done beyond 1 μm to avoid ambiguity in sizing of large Particles. We should think about producing a common PSL particle mixture with several particle sizes.
- Mass Concentrations and Size Distributions should be corrected for limited Lens Transmission or at least these Limits have to be mentioned
- Maximize Size Resolution: Chopper Duty Cycle should be as small as possible (2% or less); Maximum Size in ToF Mode should be set as low as possible (leave enough time above largest expected Particle sizes to get a good DC level); for small particles the uncertainty due to the chopper duty cycle dominates, for large particles the evaporation time broadening dominates
- Flowmeter Calibration: Check Flowmeter Calibration at least by closing the inlet valve and making sure that Flow reading is zero. For flowmeter calibration a Gilibrator is recommended, DryCal produces a pressure drop, that could affect the calibration
- Effect of ambient Pressure: Inlet Flow, AirBeam and Size Calibration can change by up to 7 % only due to normal meteorological ambient pressure changes, record ambient pressure and lens pressure
- Size Calibration: Always make size calibration with PSL particles, not only with DMA. A 15 % error in size calibration results in a 50 % error in mass calibration!! While doing mass calibration check displayed size of calibration particles to check for drifting DMA
- For Mass Calibration check carefully that the particles are dry. Water content completely confuses the calibration.
- Dryer in CPC sampling line: If the particles are not dry, the Butanol in the CPC can pick up water, which causes a decrease in condensation efficiency – doesn't count anymore reliably
- Dryer in AMS sampling line? E.g. Nafion Dryer, switch between dried / not dried particles; Water uptake increases D_{aero} for particles of low density and decreases D_{aero} for particles of high density
- Black conductive Tubing: Organics are emanating from this tubing, this is enhanced when organic vapors like Toluene are sampled. Particles seem to be covered by outgased organics. No large change in mass concentrations likely, but changes in aerodynamic behavior possible
- Particle Production in Lab: Use Nitrogen instead of clean air (esp. for organic particles); use glass or stainless steel tubing, no plastic
- Multiple charged Particles: The concentration of multiple charged particles in the DMA (multi-mode distribution of the 'monodisperse' aerosol) can be

significantly reduced by dilution of the solution concentration (→ you're at the tail of the polydispersed size distribution with q=1 particles, for the larger q=2,3 particles there are no ones in the distribution)

- A check list for daily or frequent checks is recommended. This check list should contain name of operator, date, time of check, all important details of the check, performance of the instrument; The format should make it easy to keep track of the evolution of values (columns next to each other better than on different pages)
- For Frequency and further information on AMS Calibration procedures see ftp site

AMS Data Presentation Remarks

- The way of presenting the size distribution data as image plot could be confusing to people. Presenting in a scheme that makes clear how to extract the size distribution for a certain time and how to get the mass concentration time series is recommended.
- The IGOR Rainbow color scale should be inversed to get blue for low and red for high concentrations
- The total AMS mass should not be called 'Total Mass'. This will lead to confusion with 'total mass' of other instruments. A different name is recommended like: 'Non-refractory Mass', other suggestions: 'Measured Mass', 'Evaporated Mass', 'Desorbed Mass'
- The lens transmission function should be incorporated in size distribution presentations, either by correcting for it or by adding it to the plots (light grey)
- The broadening of the size distribution due to the chopper duty cycle and evaporation duration should be mentioned or corrected for
- The median is the most robust number for representation of the size distribution
- To minimize confusion a common AMS Color Scheme is recommended:

Species	Color for color Plots	Line pattern for b/w Plots
'Total'	black	Black, solid, thick
Sulfate/Sulphate	red	Black, dashes, thin
Nitrate	blue	Black, dots, thin
Organics	green	Black, solid, thin
Ammonium	Orange (British mustard)	Black, dots, thick
Chloride	pink	Black, dashes, thick
Water	Light blue	Grey, solid, thick
Air	grey	Grey, solid, thin

Presentation of Data to Databases:

- Time series of Sulfate, Nitrate, Ammonium, Organics, 'Total Mass' in $\mu g/m^3$ (vectors), flags for data below detection limit (vectors)
- Time series of mass spectra in relative intensity, hertz or 'NO_3 equivalent mass/m^3' (matrix)
- Mass spec detection limits in 'NO_3 equivalent mass/m^3' (vector)
- Don't discard negative numbers, add error bars to data
- Size distribution size/time matrix for Sulfate, Nitrate, Ammonium and relevant Organics in $\mu g/m^3$, scaled to MS data. Ca. 15-20 size bins per decade represents the size resolution well
- Size distribution detection limits (vectors)
- Time series of Size indicators (vectors), median seems to be the most robust number
- Report size distribution limits, lens transmission function

AMS Unified Manual

- A manual based on drafts by Alice Delia and Frank Drewnick will be compiled by Hacene Boudries . An outline for the Manual was decided and will be available at ftp://ftp.aerodyne.com/AMSIncoming/AMSUsers/ALLUsers/AMS_UsersMtg_1101

AMS INCOMING ftp site

- The AMS Incoming Site will be set up so that it can be password protected. Separate passwords will be given to different groups/institutions.

Miscellaneous, Open Questions, Future Work

- Ammonium Nitrate is not completely satisfactory for mass concentration calibration. We should stay open for another calibration aerosol
- What are the correct factors to calculate the sulfate and organics mass concentrations? More lab/field work needs to be done to really understand this issue! Default values: Nitrate: 1, Sulfate: 2.5, Organics: 0.7, Ammonium: 10 * m15
- What is the right heater temperature?
- What are the benefits/disadvantages of high heater temperature operation?
- Masses to monitor in TOF mode in the field: Minimum: AirBeam, Sulfate (48, 64), Nitrate (30, 46), Ammonium/Water (15, 16, 17, 18), Organics (43, 55, 57); AND: all masses that show good signal to noise ratio in the MS
- HDF format is/will be implemented in data acquisition software and data analysis software. Delta-Analysis will be implemented soon
- Should we look for a 'standard compound' for MS comparisons?

- Should we try to get some sort of 'User Group Paper' together, which shows PIE CHARTS for the 'AMS aerosol composition' around the world?

The Figures of Merrit for the AMS:

Signal at mass 18
AirBeam Signal (mass 28 or 32)
Ratio of AirBeam to AirBeam background
Background at mass 55, 57 and 149
Ionization Efficiency
Ionization Efficiency / AirBeam ratio
Electronic Noise