

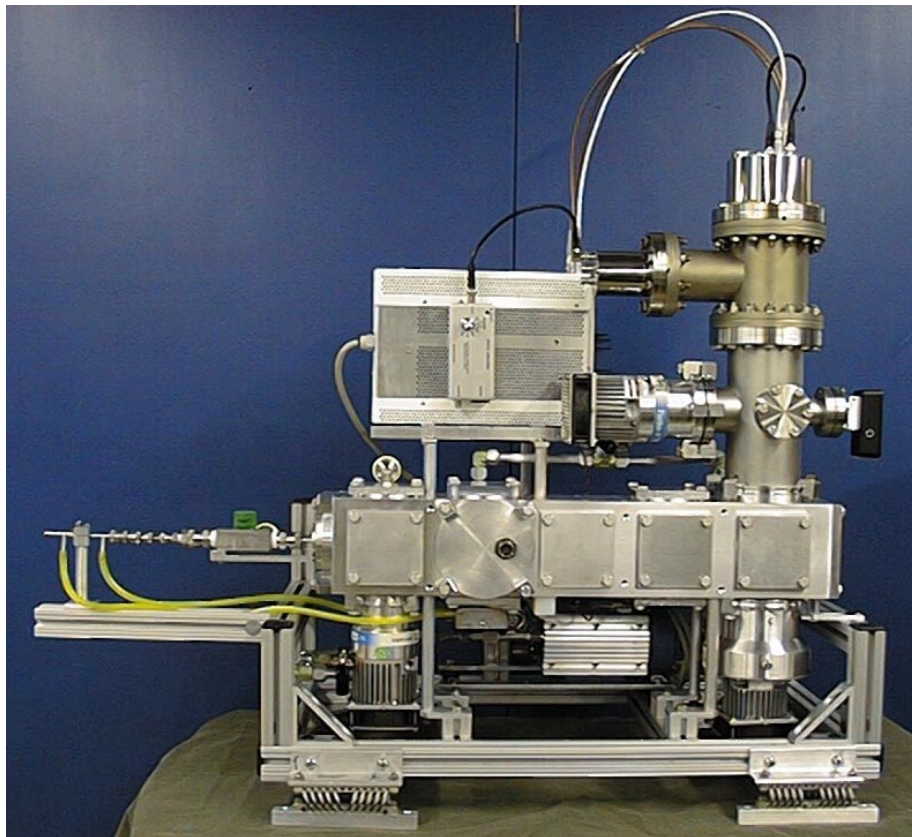
# Aerosol Mass Spectrometer

## Operator Manual

Version 3.2

Aerodyne Research, Inc.  
45 Manning Road  
Billerica, Ma 01821-3976  
978-663-9500

Revised: September 2002



# Table of Contents

## AMS Manual Part 1: General Operating Procedures

<b>Theory</b>	<b>1</b>
<b>Initial Procedures</b>	<b>7</b>
Pump Down	7
Instrument Performance	9
Venting	10
Signal Summary	10
<b>Calibrations</b>	<b>13</b>
Electron Multiplier	13
Ionization Efficiency	16
Size	20
Resolution	21
Lens Position	25
Collection Efficiency	26
Tuning QMS	28
Servo Travel	29
<b>Sampling</b>	<b>30</b>
MS	30
TOF	30
Field	31
<b>Troubleshooting/Diagnostics</b>	<b>34</b>
Leak Test	34
Small Signals	34
Quadrupole Mass Spectrometer	35
Pumps	36
Flow rate	36
Chopper	36
Airbeam	36
Baseline	37
<b>Hardware</b>	<b>38</b>
Multiplier Replacement	39
Pump Replacement	39
Orifice Cleaning	39
Filament Replacement	40
Chopper Replacement	41
<b>Appendix 1.1: Scheduling</b>	<b>43</b>
<b>Appendix 1.2: Technical Information</b>	<b>44</b>
<b>Appendix 1.3: Issues/Upgrades</b>	<b>50</b>

<b>Appendix 1.4: Publications/Online Resources</b>	<b>54</b>
<b>Appendix 1.5: Basics of Mass Spectrometry</b>	<b>56</b>

## **AMS Manual Part 2: AMS Software**

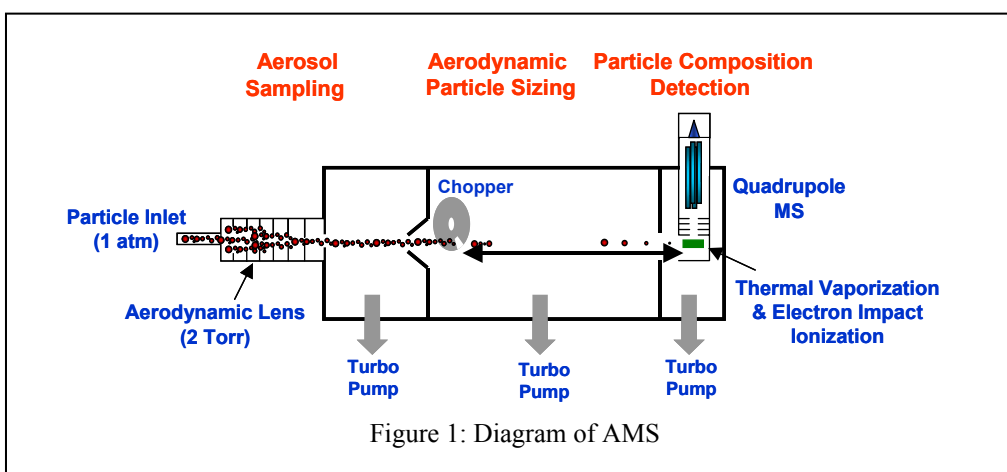
<b>Overview of AMS Screens</b>	<b>60</b>
The Main Menu	60
The TOF Mode	61
The Single Particle Window	66
The m/z Setting Window	67
The MS Mode	69
<b>User Control of AMS Operating Parameters</b>	<b>72</b>
The AMS Parameter Menu	72
The Default Menu	79
<b>AMS Software Shortcuts and Keystrokes</b>	<b>81</b>
The Help Window	81
<b>Diagnostics and Tools</b>	<b>84</b>
Check Airbeam	84
Raw Signal	85
Particle Calculator	85
<b>Description of Saved Data Files</b>	<b>85</b>
MS Data Files	85
TOF Data Files	86
<b>Appendix 2.1. Information Saved in Info and Par Waves</b>	<b>89</b>

# AMS MANUAL PART 1

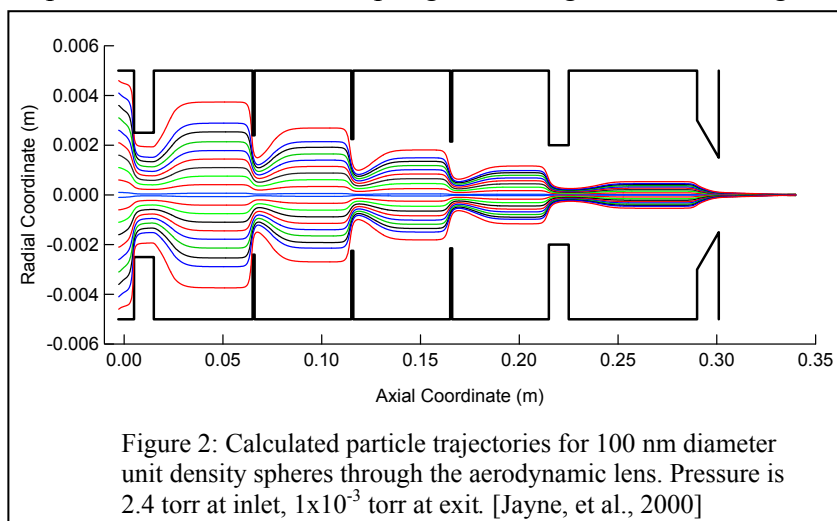
## Theory of the Aerosol Mass Spectrometer

The Aerosol Mass Spectrometer (AMS) quantitatively measures the size and chemical composition of volatile/semi-volatile submicron aerosols. The AMS is designed to provide quantitative composition information on ensembles of particles, with limited single particle information. The present instrument combines standard vacuum and mass spectrometric techniques with recently developed aerosol sampling techniques.

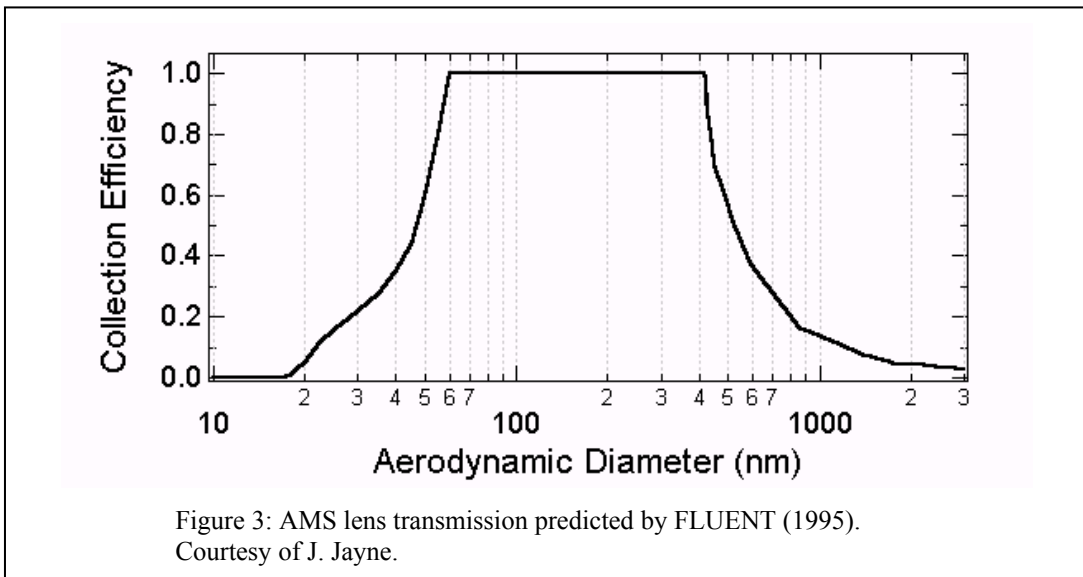
## Instrument Description



Aerosols enter the instrument through a sampling inlet that restricts the flow with a  $100\mu\text{m}$  (or similar diameter) critical orifice and then through the lens following the design of Liu et al. [1995], which focuses the aerosols into a tight beam of approximately one millimeter using 6 apertures while removing most of the atmospheric gas. As the aerosols exit the lens, they are accelerated in a supersonic expansion caused by the difference in pressure between the sampling and sizing chambers that gives different



velocities to aerosols of different sizes. The FLUENT [1995] calculation below shows particle trajectories for spherical 100 nm aerosols of unit density. Similar model results show that this lens system allows 100 percent transmission efficiency for particles between 60 and 600 nm in diameter and partial transmission down to 20 nm and up to 2000 nm. The loss of particles at the small end of the size range is a result of less efficient focusing in the aerodynamic lens, causing the particles to have a wide angular dispersion, similar to air molecules, as they exit the lens and consequently they do not follow the straight path across the sizing chamber (usually 45 cm, may be smaller for flight instruments) that allows them to pass into the particle detection chamber. The particles greater than 600 nm suffer from impaction losses, so that only those particles that are already close to the centerline pass through the lens. [Jayne, et al., 2000]



After passing through the lens, the aerosols enter the particle sizing chamber. A rotating chopper wheel with two radial slits located 180° apart intercepts the focused particle beam. The chopper can be placed in any of three positions relative to the particle beam: completely blocking the beam so that no particles pass through (beam closed), not blocking the beam so that all the particles pass through (beam open), and partially blocking the beam so particles pass through the radial slits only (beam chopped).

When the chopper wheel is in the beam chopped position, the particle beam is blocked most of the time and allows particles through only when the slits allow it, usually between 1 and 3.5 percent of the time depending on the width of the slits. This allows for particle sizing of up to 25 selected masses and is called time-of-flight (TOF) mode. A pair of photo diodes detects the position of the chopper slits, defining the start of each cycle. As the particles travel on a straight path through the sizing chamber, they spread out according to their size as a result of the supersonic expansion through the final aperture of the lens, with the smaller particles traveling faster than the larger particles. When the particles reach the detection chamber, the time to travel across the sizing chamber is determined, and from this the particle velocity and aerodynamic diameter are calculated.

Particles are detected as the particle beam reaches a resistively heated surface and the volatile and semi-volatile portions of the aerosols are vaporized and then immediately ionized by electron impact in a custom-built closed source electron impact ionizer/heater assembly. A standard quadrupole mass spectrometer detects the positive ion fragments generated by the electron impact ionization. Quick bursts of ions (tens of microseconds in length compared to the 3-4 milliseconds required to traverse the particle sizing chamber) classify single particle events of sufficient size. For a pure  $\text{NH}_4\text{NO}_3$  particle, only a particle containing approximately  $5 \times 10^7$  molecules (approximately  $7 \times 10^{-15}$  g) or 200 nm will rise above the background levels to be counted as a single particle. [Jayne et al., 2000]

When the chopper wheel is in the chopped position, the mass spectrometer is set to measure only one mass fragment at a time so that the complete size distribution for that fragment can be measured. The size distribution for up to 25 masses can be monitored in this way with a cycle of 3.3 masses per second, so that all the masses (assuming 25 masses have been selected) can be measured in less than eight seconds. Often, the masses selected for TOF mode are those with the largest concentration as determined from the mass spectrum.

A complete mass spectrum (0-300 amu) can be measured by moving the entire chopper wheel in and out of the particle beam to measure both the background of the chamber (beam closed) and the total signal (beam open). This is called mass spectrum (MS) mode. The difference of these two signals gives the particulate signal at each mass with the exception of some of the predominant air species ( $\text{N}_2$ ,  $\text{O}_2$ , Argon, and  $\text{CO}_2$ ). However, no size data can be collected in this mode because all particles are passed through and there is no timing information to determine sizes. The MS mode is especially useful for getting an idea of the overall composition of the total aerosol mass and noting the individual chemical species with the largest concentration.

Although the AMS can characterize the volatile and semi-volatile components of particles, it does not detect the non-volatile components of particles (e.g., crustal oxides and elemental carbon).

### ***Quantification***

(This section is taken from J. Jimenez et al., Ambient Aerosol Sampling Using the Aerodyne Aerosol Mass Spectrometer, *J. Geophys. Res.*, 2002, in press.)

The signals measured with the AMS can be converted into mass concentrations ( $C$ , in  $\mu\text{g}/\text{m}^3$ ) of aerosol chemical species in the following way (adapted from Bley [Bley, 1988]). The molecular flux  $M_i$  (molecules / s) of species  $s$  entering the AMS detection region per unit time is calculated from the signal at a single  $m/z$  as:

$$M_s = \frac{I_{sf}}{X_{sf} IE_s} \quad (1)$$

where  $I_{sf}$  is the number of ions detected per unit time at the  $f^{\text{th}}$  fragment ( $m/z$ ) of species  $s$ ;  $X_{sf}$  is the fraction of the ions formed from species  $s$  that are detected at its  $f^{\text{th}}$  fragment;  $IE_s$  is the ionization and detection efficiency (ions detected / molecule vaporized) for species  $s$ .  $IE_s$  is calculated by sampling a known mass flux of monodisperse particles (generated with a collision atomizer, diffusion dryer, and electrostatic classifier, TSI, St. Paul, Minnesota) and counting them with the AMS and/or with a Condensation Particle Counter (CPC, TSI 3010/3022/3025, St. Paul, Minnesota). If the gain or detection efficiency of the detector (electron multiplier) and/or the transmission efficiency of the quadrupole are a function of the  $m/z$  in the range of interest, these dependences need to be accounted for before using equation (1) by:

$$I_{sf}^{\text{corrected}} = \frac{I_{sf}^{\text{measured}}}{T_{m/z} G_{m/z}} \quad (2)$$

where  $T_{m/z}$  and  $G_{m/z}$  are the relative quadrupole transmission and the relative response (gain and detection efficiency) of the electron multiplier detector.

The mass concentration of species  $s$  in the aerosol can then be calculated as:

$$C_s = \frac{M_s MW_s}{Q N_{AV}} = \frac{I_{sf}^{\text{corr}}}{Q N_{AV} X_{sf}} \frac{MW_s}{IE_s} \quad (3)$$

where  $MW_s$  is the molecular weight of species  $s$ , and  $Q$  is the air volume sampling rate into the AMS. This procedure assumes that only one species contributes to the signal at that particular  $m/z$ , an assumption that can be tested with the procedures described above. For laboratory experiments with known species,  $MW_s$  is known, while  $IE_s$ , and  $X_{sf}$  can be measured with the calibration procedure described above. For unknown species the values for  $IE_s$ ,  $MW_s$ , and  $X_{sf}$  need to be estimated from the available data.  $X_{sf}$  can be estimated from all the detected fragments that have the same time and size evolution and are thus likely to originate from the same species (or group of species). If nothing is known about the molecule,  $IE_s/MW_s$  is assumed to be equal to  $IE_{NO_3}/MW_{NO_3}$ , with  $IE_{NO_3}$  being measured during routine calibration of the AMS. If the chemical nature of the molecule (or group of molecules) is known, e.g. a hydrocarbon, or an oxygenated organic, or an inorganic salt, e.g. by the methods described by McLafferty and Turecek [McLafferty and Turecek, 1996],  $IE_{NO_3}$  is multiplied by a relative response factor obtained for that type of molecules ( $R_t$ ).

$$\frac{IE_s}{MW_s} = R_t \frac{IE_{NO_3}}{MW_{NO_3}} \quad (4)$$

To illustrate the appropriateness and limitations of that assumption, the data for electron impact ionization cross-sections ( $\sigma$ ) with 70 eV electrons is shown in Figure 4 vs. the number of electrons in the molecule [Flaim and Ownby, 1971; Irikura, 2000; NIST, 2000; Summers, 1969]. The ionization efficiency of a molecule is directly proportional to  $\sigma$ , since  $\sigma$  merely captures the efficiency of ionization on a per-molecule basis. The number of electrons in a molecule is highly correlated with the molecular weight of the molecule, especially for the volatile and semi-volatile molecules present in aerosols. This is due to the fact that the ratio of the atomic number to the atomic weight is very similar for most

of the atoms involved: 0.99 for H; 0.50 for C, N, O, S, and Ca; 0.49 for K and Mg; and 0.48 for Na and Cl. The larger value of the atomic ratio for H is neutralized in typical aerosol molecules by the larger contribution of larger atoms to the number of electrons and the molecular mass. For example, saturated hydrocarbons will have an electron to molecular weight ratio of  $\sim 0.57$ , aromatic hydrocarbons  $\sim 0.54$ , and ammonium nitrate and ammonium sulfate have ratios of 0.52 and 0.54 respectively. Thus, if nothing is known about the molecule present in the aerosol, it can be assumed that its electron-to-molecular weight ratio is about 0.52 with an uncertainty of about 8%. In summary, since  $IE_s$  is directly proportional to EICS and  $N_e$  (where  $N_e$  is the number of electrons in the molecule) is approximately proportional to  $MW_s$ ,  $IE_s/MW_s$  will be proportional to  $\sigma/N_e$ .

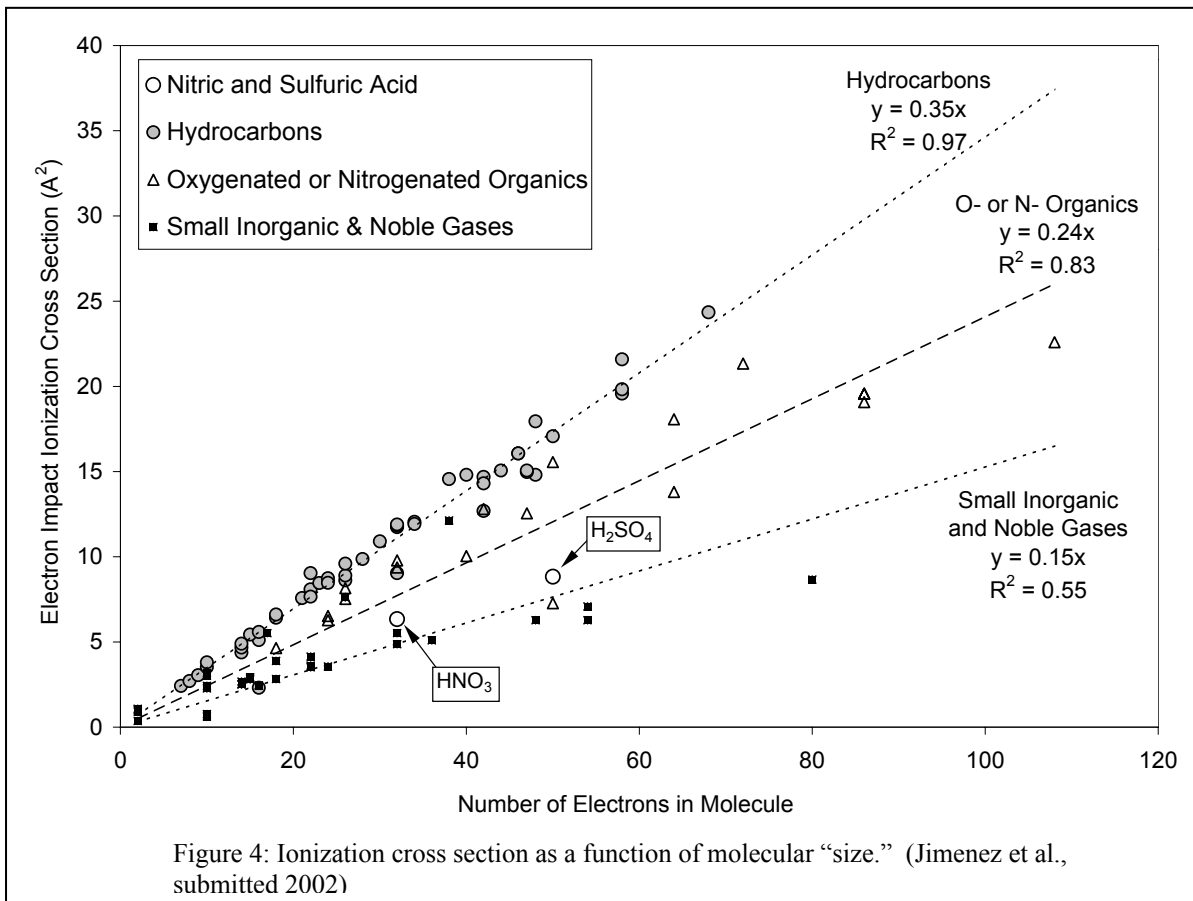


Figure 4 shows that for small molecules of a given type,  $\sigma/N_e$  is approximately constant. From the data and regressions in the figure  $R_t$  is estimated at 0.57 for hydrocarbons, 0.83 for oxygenated hydrocarbons, and 1.12 for sulfuric acid. Experimental verification of this relative calibration procedure with individual aerosol molecules is undergoing in our laboratory and will be the subject of a future publication.



See Appendix 4 for more AMS publications describing the operation and measurements performed by various groups in the AMS community.

## References

- Bley, W.G., Quantitative Measurements with Quadrupole Mass Spectrometers: Important Specifications for Reliable Measurements, *Vacuum*, 38 (2), 103-109, 1988.
- Flaim, T.A., and P.D. Ownby, Observations on Bayard-Alpert Ion Gauge Sensitivities to Various Gases, *Journal of Vacuum Science and Technology*, 8 (5), 861, 1971.
- FLUENT, 1995: Version 4.47, Fluent, Inc., Lebanon, New Hampshire.
- Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, D.W. Worsnop, 2000: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles. *Aerosol Sci and Tech.*, **33**, 49-70.
- Liu, P. P.J. Ziemann, D.B. Kittelson, P.H. McMurry, 1995: Generating Particle Beams of Controlled Dimensions and Divergence: I. Theory of Particle Motion in Aerodynamic Lenses and Nozzle Expansions. *Aerosol Science and Technology.*, **22**, 293-313 .
- Liu, P. P.J. Ziemann, D.B. Kittelson, P.H. McMurry, 1995: Generating Particle Beams of Controlled Dimensions and Divergence: II. Experimental Evaluation of Particle Motion in Aerodynamic Lenses and Nozzle Expansions. *Aerosol Science and Technology.*, **22**, 314-324.
- McLafferty, F.W., and F. Turecek, *Interpretation of Mass Spectra*, University Science Books, Mill Valley, California, 1996.
- NIST, *NIST Electron Impact Ionization Cross Section Database*, <http://physics.nist.gov/PhysRefData/Ionization/Xsection.html>, 2000.
- Summers, R.L., NASA Technical Note TND 5285, Ionization Gauge Sensitivities as Reported in the Literature, Lewis Research Center, National Aeronautics and Space Administration, 1969.

## Initial Procedures

The AMS can operate continuously with minimal supervision, but the instrument must be set up first to operate correctly. This section contains step-by-step instructions for these activities.

### *Set-up*

This is a complete set of steps to begin using the AMS when it is newly set up in a laboratory or field location. These do not have to be performed every time the AMS is used, although some of these calibrations are completed on a regular basis (See Appendix 1 for suggested calibration intervals).

- Connect all hardware (install inlet and quadrupole and connect pump, multiplier, and RF cables)
- Pump down the chamber
  - If chamber does not pump down fully, go to leak checking procedure in the *Troubleshooting/Diagnostics* section.
  - Make sure everything is working by checking instrument performance
    - If signal is low, perform electron multiplier (EM) calibration to increase the signal to a measurable level; do not spend a lot of time on this, as it will be repeated later.
- Vent the chamber (in case of emergency, turn all pressure sensitive elements off first – leave on only the main power supply unit; see this section)
- Check servo motion (automated procedure on main menu; see *Calibration* section)
- Check lens alignment (see manual procedure in *Calibration* section)
- Tune quadrupole mass spectrometer (automated procedure in main menu; see *Calibration* section)
- Multiplier calibration (automated or manual procedure; see *Calibration* section)
  - Repeat quadrupole tuning
- Check Faraday signal (manual procedure; see *Calibration* section)
- Check peak shape and resolution (see *Calibration* section)
  - Repeat quadrupole tuning if resolution changed
- Mass calibration with  $\text{NH}_4\text{NO}_3$  aerosols (automated or manual procedure; see *Calibration* section)
- Size calibration with PSL aerosols and/or  $\text{NH}_4\text{NO}_3$  aerosols (manual procedure; see *Calibration* section)
- Check true instrument background with filter (manual procedure; see *Troubleshooting/Diagnostics* section)

### *Pump Down Chamber*

From atmospheric pressure to vacuum.

- Close inlet valve and all turbo pump bleed valves before starting pumps

- Start up the forepump to begin evacuating the chamber
- Pump down with this pump to <5 torr on TC1 or on the Baratron pressure gauge for the newer AMS design (should take only a few minutes)
- Turn on the electronics and turbo pump switches on the AMS Power Supply unit (Note: the turbo pump switch also turns on the pump fans)
- Turn on turbo pumps 1, 2, and 3 (more will overload the system-see note below).
  - The total current on the AMS Power Supply unit will rise to ~10 A, and then decrease to ~4.5 A as the turbo pumps reach full speed.
  - Wait until the first 3 pumps spin up to 100% speed (check speed and current on AMS Electronics unit display).
  - Turn on the remaining turbo pumps and again wait until they spin up to full speed and the total current returns to ~4.5 A.
  - All pumps should now be at 100% speed and TC1 and TC2 should read  $10^{-3}$  torr (indicating that the pressure is below detection) or \_\_\_\_ on the Baratron pressure gauge.
    - If there are pumping problems (i.e., the pressure is higher than indicated above or the turbo pumps do not reach 100%-indicating a leak), check bleed valves on the turbo pumps and double check tightness of fittings. [If leak persists, check all fittings and flanges with He to locate leak (see leak detection procedure in the *Troubleshooting/Diagnostics* section).]
- Turn on Balzers power supply to warm up; this takes about 10-15 minutes, a green light appears on the RF supply when unit is ready.
- If your instrument contains an ion gauge in the detection chamber, turn on Ion Gauge (press *Emis* on SenTorr unit) when all the pumps have spun up to full speed (should be  $<10^{-5}$  torr)
- Electronics front panel
  - Turn on preamp, chopper, and heater power
    - If heater light is off, check speed of pumps 5 and/or 6 – electron multiplier and heater power are interlocked to 100% on these pumps
- Ionizer filament: When pressure falls to  $\sim 10^{-6}$  torr (all the pumps are at 100% speed) and the Balzers control unit is fully warmed up, turn on the filament with the Balzers control unit (low settings initially,  $\sim 0.5$  mA) to degas. If pressure remains steady, quickly increase filament current.
  - Press the *emis* button in the ion source group on the Balzers control unit front panel to view the filament settings (the emission current and filament protection). The emission current should read “OFF” initially; press the button beneath the emission current display and the display will begin flashing, indicating that it is selected. On the right side of the control display are up and down arrows; press the up arrows to increase the emission current to 0.5mA, then press the *filam* button in the operation group to turn the filament on (this button turns the filament on or off only). If there is no significant increase in pressure (or there is an increase in pressure, which subsequently decreases), continue to increase the emission current in steps to 2.0mA (this is the maximum value of the control unit, but the software will allow 2.5mA).

[The Balzers control unit should be used initially because the AMS software will turn on the filament at the default setting of 2.5 mA, which may increase the pressure enough (due to surface outgassing) to turn the filament off. If the filament goes off at the reduced setting, increase the protection (also in the *emiss* settings) or decrease the initial emission current and wait longer for the pressure to stabilize and/or decrease before increasing the emission current (the pressure may spike and then decrease with each increase in emission current).]

- Switch to the AMS software to increase the emission current to the default setting of 2.5 mA (run the AMS program, select *Mass Spectrum* mode, select the control voltages, *shift-B*, and select the default setting for “Em. Current”). (*Note: the AMS software always overrides the Balzers, so control will switch automatically to the AMS software. If you need to restart with the Balzers control unit again, press “CTRL” and then “CONFIG.” The control is at the leftmost position and will be set to “ASCII” for computer control. Press the button beneath this label and then use the up/down arrows to change to CS 422.*)
- If at all possible, pump the system overnight before turning on the electron multiplier power and resuming data collection. This should lower the background and help preserve the electron multiplier.

*NOTE: The Power Supply unit only delivers a current of 10 A (or 15 A in the newer systems) for the turbo pump controllers. This is enough for running all pumps, but is insufficient to start all of them at the same time. The pumps require approximately 0.5 A without the gas load, but the pumps at the front require more than the maximum of 2.5 A with a gas load and therefore usually run at less than 100%. **It is important to keep track of pump speeds and pump currents as a function of time since drastic changes in “typical” values for these parameters can be indicative of a failing pump.***

### ***Check instrument performance***

After pumping down the system, it is usually a good idea to make sure that everything is working correctly before beginning measurements.

- Run program (*double-click on AMS executable file on desktop*)
  - Choose *Mass Spectrum* mode
    - In the *Parameter Menu*, choose the *Multiplier & Chopper* tab: check EM voltage
      - If a fresh pump-down, note electron multiplier (EM) voltage setting and lower about 500 V in order to protect multiplier (lower voltage reduces EM gain)
- Signal should be 2-10 MHz for water (*m/z* 18)
  - Water should be  $<10^{-7}$  torr (see upper left display scale after resizing window)
    - [*Note: pressure scale is approximate*]
- If the water signal is in the above range, increase EM voltage to initial setting
- If the water signal is low:
  - ✓ Check EM connections
  - ✓ Check front panel: Preamp on (Should be set to  $10^{-6}$  A/V)  
Chopper on (set to manual control)

Multiplier on (set to computer control)

Heater on (set to computer control)

- ✓ Check multiplier volts: ~2 kV for new multiplier (as above)
- ✓ Check heater bias: 4-6 volts below Ion Ref (e.g. 38 V or 74 V)
- ✓ Check Ionizer settings: compare with previous settings
- ✓ Check conversion dynode (if applicable): 6 kV

*NOTE: Background water ( $m/z$  18) signal should be 5-10 times larger than  $N_2$  ( $m/z$  28) signal; which is ~4 times larger than  $O_2$  ( $m/z$  32) signal (if air peaks are larger than water signal with the inlet valve closed, then there is a leak – see **Troubleshooting/Diagnostics** section)*

- Open inlet valve – air signal should increase to about same size as water  
Toggle chopper (*shift T*) so that both the open and closed signal are measured and record airbeam signal (the airbeam is the signal at either  $N_2$  or  $O_2$  and should remain approximately constant)  
 **$N_2$  ( $m/z$  28) difference signal should be 0.75 to 2MHz**
- Low airbeam signal likely indicates low EM gain (need to calibrate EM)
- High airbeam signal likely indicates poor vacuum after pump down

### ***Venting the Chamber***

From vacuum to atmospheric pressure.

- Close all lines into the system.
- Turn off the filament emission current, heater power, multiplier power, and Balzers power (also the preamp and chopper power, although these are not affected by high pressure).
- Turn off all turbo pumps and ion gauge and wait for pumps to wind down (audible decrease in pitch). It is best to wait a little longer after pump speed reaches zero and the pumps wind down (15-20 minutes) for the heater and filament to cool off.
- Turn or close off the roughing pump when turbo pump speeds are at 0% and pressure approaches 1 torr.
- Slowly leak air into turbo pumps (starting with pump underneath detection chamber) until sensors read ambient pressure.

### ***Check Signal Summary Values***

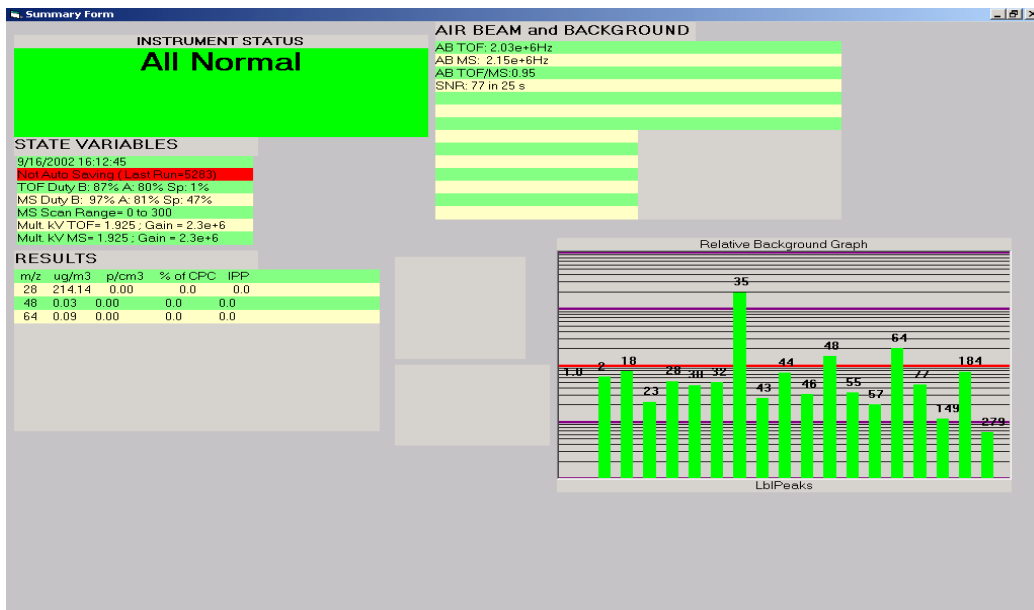
This is a quick and easy way to determine the overall instrument performance. It displays the background signal for some representative masses and checks that the MS and TOF modes are in sync. This should be done frequently when measuring in the field (every day or every other day) and before every new experiment in the laboratory.

- Quit (press *q*) and choose *Check Airbeam*

- Immediately quit (press *q*), choose *Time of Flight* mode, reset (press *F5*), quit (press *q*), choose *Check Airbeam* again [this is a software issue, eventually, automatic reset will be fixed in the code]
- Note signals:
  - ✓ Airbeam TOF/MS (should be ~ 1)
  - ✓ Water background (see below)
  - ✓ Backgrounds at 30, 46, 48, 55, etc. (see below)
- If TOF/MS airbeam signals differ by more than 10%:
  - Check the Mass Calibration Offset for airbeam m/z in F6 window- Typically this should be around -0.6 amu. If the offset is set properly but the maximum of the AB peak is not properly aligned with the quad setting for the AB mass in the TOF mode, then go to MS mode, and do an automatic mass calibration.
  - Check chopper duty cycle in the *Multiplier & Chopper* tab
  - Also check servo positions to ensure the chopped position in the middle of the “top-hat” (See *Servo Travel* in the *Calibration* section)

Typical background values:

- 18: 2-10 MHz
- 30: 1-5 kHz
- 46: 0.1-2 kHz
- 48: 0.1-2 kHz
- 43,55,57: 1-20 kHz



*Note: The relative background graph shows the ratio between the current background values for some of the background peaks and a typical reference background for an AMS instrument (The current reference used comes from the CalTech Aircraft AMS).*

## Calibrations

There is an extensive set of calibrations, listed below, that ensures that the AMS is operating at peak performance. The electron multiplier and mass calibrations need to be performed on a regular basis (every few days for regular ground or lab measurements), but most of the others should be completed at the beginning or end of a field study or new setup or when diagnosing instrument problems (see Appendix 1 for a suggested schedule). For most of these calibrations, it is a good idea to save a picture of the screen (press alt + PrntScrn) in a PowerPoint file for later reference in addition to noting the calibration values.

- Multiplier
- Mass
- Size
- Quadrupole mass and resolution
- Lens Position
- Collection Efficiency
- Tuning QMS
- Servo
- Line Transmission

### *Electron Multiplier Calibration*

The purpose of the electron multiplier calibration is to determine the gain of the multiplier and track, and compensate for, its decrease over time. The gain is calculated by comparing the observed area of a single ion (in contrast to the burst of ions produced by a particle) with the expected area of the single ion. The area of the single ion is measured in bitsteps (basically, the voltage multiplied by time – a 10  $\mu$ s time step).

Inside the multiplier 1 ion<sup>+</sup> produces 1 e<sup>-</sup>, which is increased by the value of the gain. This produces the current (or charge) measured at the output of the multiplier. So

$$V = I \cdot R = q \cdot R / t$$
$$V \cdot t \text{ (bitsteps)} = q \cdot R = G \cdot q / e^- \cdot R$$

where R is the preamp resistance (1e6  $\Omega$ ), I is the current, q is the charge, q/e<sup>-</sup> is the charge per electron (1.6e-19 C), t is the time, and G is the gain of the multiplier.

Since q/e<sup>-</sup> and R are not changing over time, the area of the single ion (V\*t) depends only on the gain of the multiplier.

The multiplier gain is described by the gain curve – the gain of the multiplier vs. the multiplier voltage. For low voltages the multiplier gain increases proportionally to the voltage. The gain increase levels off for higher voltages, resulting in a “plateau.” In this region of the gain curve, higher voltages do not increase the gain further. The edge of this plateau is the best setting for the multiplier – the highest gain at the lowest voltage setting is used, giving the best possible signal while extending the lifetime of the multiplier.

The gain curve is described by the following equation:

$$\text{Gain} = \text{scaling factor} * 10^{(C_1 + C_2 * U_{\text{mult}} + C_3 * U_{\text{mult}}^2)}$$

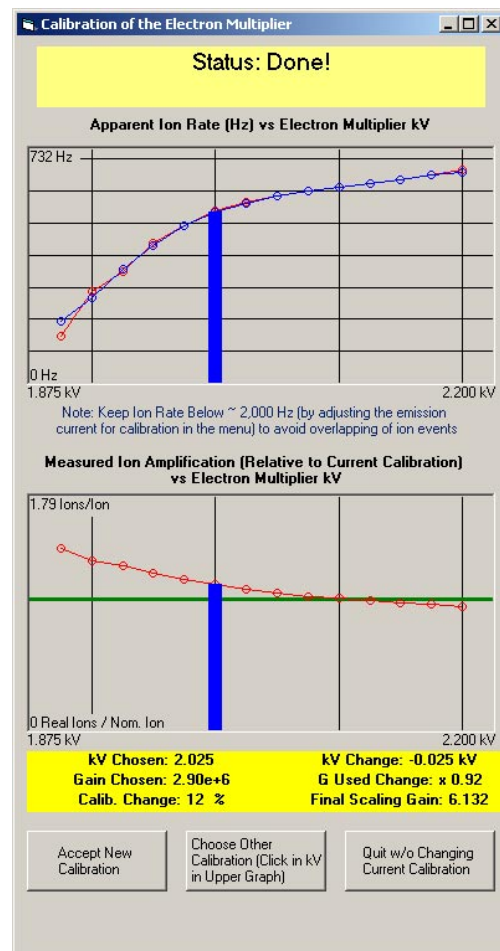
where  $U_{\text{mult}}$  is the voltage of the multiplier in kV and  $C_1$ ,  $C_2$ , and  $C_3$  are constant coefficients. The coefficients are determined when a new multiplier is first installed by determining the multiplier signal of single ion events for different multiplier voltages and fitting the results to the curve described by this equation. This equation is stored in the software and used for all subsequent multiplier gain calculations. This procedure is similar to performing the multiplier gain calibration and will be described in more detail later in this section. Except for the first calibration of a new multiplier, the automated calibration procedure can be used to calculate the gain. Typically when the multiplier ages, the decay in gain can be captured purely by changing the value of the scaling factor in the Gain equation. The multiplier calibration process involved determining the proper scaling factor necessary to represent the actual gain of the multiplier as it decays.

The automated multiplier gain calibration procedure in the AMS software (version 3.4.3 and higher) determines the correct multiplier voltage and gain by measuring single ion pulses and plotting multiplier gain vs. voltage.

- In *Mass Spectrum* mode, toggle the chopper (*shift T*) and record the airbeam signal (usually  $N_2$ ,  $m/z$  28) for reference.
- Set the chopper to beam closed or close the inlet so that only background ions are used for the calibration.
- The mass used for the multiplier calibration is chosen in the TOF  $m/z$  selection window (press *F6* from the TOF screen) by the first mass to have “I” in the “Group Member” column on the far right of the screen. The mass chosen for this calibration should be one with a low background level (e.g.,  $m/z$  42 or 46), although any mass will work. If possible, make a completely separate entry for the single ion mass in the TOF  $m/z$  selection window, since the threshold and sliding window (number of points for averaging; this equals two instead of four because a single ion pulse is smaller than a particle pulse) will be different for the single ion then for regular operation and the automatic change in sliding window from 4 to 2 may not be included in every version of the code.
- After choosing the single ion mass, return to the TOF window and set the threshold. This can be done automatically by clicking on the Set Thresholds button on the lower left of the TOF window. Keep the ion current between 200 and 1000 Hz so that there are enough for good statistics, but not so many that the ions are double-counted. Increase or decrease the emission current to stay in this range. When a reasonable number of ions are present, go to the *Multiplier & Chopper* tab and change the emission current used for the automatic procedure. Set the emission current back to the default value.
- Move the blue marker bars in the TOF window to the edges of the screen in the *Averaging & Saving* tab.
- Quit (press “*q*”) to main menu
- Choose *Calibrate Electron Multiplier* from the main menu and wait while the single particle thresholds are set automatically (screen message “Setting SP Thresholds”).



- After the voltage is finished scanning (the multiplier voltage is scanned +/- 175 V around the initial setting), note values:
  - *kV chosen (kV)* – new multiplier voltage value
  - *kV change (kV)* – difference between initial and new voltage setting
  - *Gain chosen (usually around 3e6)* – new gain, determined by the multiplier voltage and the scaling factor
  - *G used change* – fractional gain change
  - *Calib. change (%)* – represents the degree to which the multiplier gain has decreased (or increased) since the last calibration (ratio of the ion pulse area to the green line in the lower panel)
  - *Final Scaling Gain* (new multiplier: 100, old multiplier: 0.01) – gain scaling factor, decreases over lifetime of multiplier (i.e., measures “age” of multiplier)
- Display curves
  - The upper panel shows the background count rate for the mass chosen for calibration (the count rate should be ~0.2-1 kHz).
  - If the rate is high or low, adjust the emission current down or up via “emission current for calibration” in the *Mass Calibration* tab in the parameter menu.
- For proper multiplier gain calibration the filament is set to the low emission current value that is set in the multiplier tab of the menu and the multiplier voltage at which the calibration is to be performed is selected. This selection is made so that calibrations are not performed in regions of the gain curve where small fluctuation in voltage result in large changes in gain. In order to identify the appropriate voltage, a series of single ion measurements are performed as a function of multiplier voltage and the voltage at which the single ion count rate begins to plateau is selected.
  - Upper curve: the ion count rate should not increase with multiplier voltage after the gain is large enough so that all ions pulse above the electronic threshold



- Once the curve ‘plateaus,’ the increase in signal with gain is maximized and a further increase in voltage will not increase the signal but will shorten the lifetime of the multiplier.

The blue bar attempts to choose the optimal multiplier voltage at which to measure the gain based on the plateau: this can be changed by selecting the “Choose Other Calibration” button at the bottom of the screen and then clicking at the optimal multiplier voltage/gain point on the upper curve. The results of the gain calibration at that voltage are displayed in the yellow section of the window. NOTE: if the top curve does not plateau nicely, then the calibration should be done at a voltage that results in a calibrated gain of 3E6.

- Lower curve: shows the single pulse area normalized to the multiplier gain curve [the gain curve is set by the gain parameters (coefficients) in the *Multiplier & Chopper* tab of the parameter menu]. After the gain is properly calibrated at a given voltage, then the value of the lower curve at that voltage should be equal to 1 real Ion/Nom Ion.
- Select *Accept New Calibration*
- Depending on the ‘plateau’ shape, **repeat the procedure**  
Note: the blue bar should not be close to the right hand axis
- Quit (press “q”) and return to *Mass Spectrum* mode
- Toggle chopper (*shift T*) and note airbeam signal
- AB signal should change according to “Calib. Change” measured above (e.g., for a change of -60%, the airbeam count rate should be 2.5 times higher than before setting new gain  
*[NOTE: if procedure is repeated, then multiple % changes are compounded]*

There is also a manual procedure for checking the multiplier gain as described below. This is essentially what the automated procedure does.

- Choose the mass for multiplier calibration (e.g.,  $m/z$  42 or 46) in the  $m/z$  selection window (press *F6* from TOF window). Make sure that the sliding window is set to 2 instead of 4.
- Set the chopper to beam closed or close the inlet so that only background ions are used for the calibration.
- Turn off the filament.
- Set threshold manually for selected  $m/z$  (right click on threshold and use *u* and *d* to raise and lower the threshold).
- Turn filament on low setting ( $\sim 0.1$  mA) and check the number of ions; there should be 200-1000 ions/second – if too few ions are present, turn up the emission current or lower the threshold; if too many ions are present, lower the emission current.
- Go to the average single particle signal screen (press *insert* when in TOF mode).
- If the multiplier voltage and scaling factor are set correctly, the Ions/Particle should be 1 (you are not looking at particles, only ions, so actually have ions/ion = 1).

- If Ions/Particle  $\neq 1$ , modify the multiplier voltage and/or scaling factor until it does (the scaling factor marks the age of the multiplier; it should be  $\sim 100$  for a new multiplier and  $\sim 0.01$  for a multiplier at the end of its lifetime).
- Check that both TOF and MS mode have same new multiplier voltage setting.

**For a new multiplier**, select the mass for multiplier calibration and set the threshold as described above, then follow the steps below.

- Set the multiplier voltage to a low value ( $\sim 1500$  V) and go to the single ion window (press *insert* when in TOF mode). Ions/particles should be  $\sim 1$ ; if it is not, go to the *Multiplier & Chopper* tab and change the scaling factor ( $\sim 100$  for a new multiplier) until the ions/particle in the single ion window  $\sim 1$ .
- Increase the voltage by 500 V and repeat this process several times.
- Fit the gain vs. multiplier voltage values to the gain equation
 
$$\text{Gain} = \text{scaling factor} * 10^{(C_1 + C_2 * U_{\text{mult}} + C_3 * U_{\text{mult}}^2)}$$
 where  $U_{\text{mult}}$  is the voltage of the multiplier in kV and  $C_1$ ,  $C_2$ , and  $C_3$  are constant coefficients.

At low multiplier voltages the measurements are very noisy because the only weakly amplified single ion signals are not much more intensive than the electronic noise. Therefore gain data from very low multiplier voltages have to be skipped and only the data measured at higher multiplier voltages should be taken.

### ***Ionization Efficiency Calibration***

The ionization efficiency calibration, also called the mass or nitrate calibration, determines the ionization efficiency of ammonium nitrate. Ionization efficiency can be defined as the ratio of the number of ions made to the total number of available parent molecules for that ion species (e.g., if the ionization efficiency is  $1e-6$ , then 1 molecule in 1 million molecules is ionized). For any given parent molecule, the total number of ions produced is determined by a sum of ion intensities of all its fragment ions. If a precise fragmentation fraction for a given fragment ion is known, then the total number of ions from the parent molecule can also be expressed as the product of that fragment ion intensity and the inverse of the fragmentation ratio. The quantification of the AMS is based on the linearity of the ionization efficiency. Basically, larger molecules have larger ionization efficiencies than smaller molecules and the increase in ionization efficiency is linear with increasing molecule size. [McLafferty and Turecek, 1993] Therefore, if the ionization efficiency of one molecule can be determined, the ionization efficiency for all other species can be related to the measured ionization efficiency of the initial species. This topic is discussed in more detail in the quantification theory section at the beginning of this manual.

Ammonium nitrate is used as the primary mass calibration species because the ionization efficiency, density, and shape are well known and ammonium nitrate does not leave much residue to interfere with subsequent measurements. Ammonium nitrate vaporizes with close to 100% efficiency, so the ionization efficiency of  $\text{NO}_3^+$  can be quantitatively

measured and it is well-focused by the aerodynamic lens so that all the particles can be detected.

The fundamental assumption as described above is:

$$\frac{MW_i}{IE_i} = \frac{MW_{NO_3}}{IE_{NO_3}} \times f_i$$

where  $MW_i$  and  $IE_i$  are the molecular weight and ionization efficiency of a given species,  $MW_{NO_3}$  and  $IE_{NO_3}$  are the molecular weight and the ionization efficiency calculated for ammonium nitrate and  $f_i$  is the calibration factor representing the relationship of the ionization cross section of the species to that of ammonium nitrate.

The ionization efficiency for nitrate ( $IE_{NO_3}$ ) is calculated by determining the number of ions produced per particle of a select size as shown in the equation below.

$$\frac{IonsPerParticle}{\frac{\pi}{6} \times d^3 (nm) \times \rho (1.72 g / cm^3) \times (1e - 7 cm / nm)^3 \times SF (0.8) \times f_{NO_3} (0.775)} \times \frac{MW_{NO_3} (62 g / mole)}{N_{AV} (6.02e23 molec / mole)}$$

where ions per particle is determined from the calibration (usually several hundred),  $d$  is the mobility diameter of the calibration particles (typically 350 nm),  $\rho$  is the density of ammonium nitrate,  $SF$  is the shape factor ( $<1$  for non-spherical particles),  $f_{NO_3}$  is the fraction of  $NO_3$  in  $NH_4NO_3$  ( $MW_{NO_3} / (MW_{NO_3} + MW_{NH_4})$ ) and  $N_{AV}$  is Avogadro's number.

So to get the aerosol mass loading (i.e., mass/volume) for a particular ion from the mass spectrum, the following calculation must be performed.

$$\frac{ions / sec(Hz)}{Flow(cm^3 / s) \times N_{AV}(6e23molec / mole)} \times \frac{MW_i}{IE_i} \times 1e6cm^3 / m^3 \times 1e6\mu g / g = \mu g / m^3$$

Or, using the substitution above:

$$\frac{ions / sec(Hz)}{Flow(cm^3 / s) \times N_{AV}(6e23molec / mole)} \times \frac{MW_{NO_3}(62 g / mole)}{IE_{NO_3}(\sim 1e6)} \times 1e6cm^3 / m^3 \times 1e6\mu g / g = \mu g / m^3$$

If calculating the mass from TOF mode, the duty cycle of the chopper must also be taken into account.

### Mass Calibration Procedure

- Set up a DMA with 300 or 350 nm  $NH_4NO_3$  particles ( $\sim 0.1M$   $NH_4NO_3$  solution).
  - Optimum number density is  $\sim 300/cm^3$  (too many results in the AMS counting two particles as one particle – double counting).

- If there are too many particles, increase the size of the DMA-selected particles or dilute the  $\text{NH}_4\text{NO}_3$  solution  
*[NOTE: use  $(350 \text{ nm}/X \text{ nm})^3$  if the size is changed, since all mass calibrations reported as 350 nm].*

There is an automated routine to calculate the mass calibration, but it is often helpful to look first at the shape of the single ion and the pulse height distribution to make sure everything is set correctly.

***Need screen pictures here.***

- Go to the TOF screen and press **F6** to go to the TOF masses list, and then type **N** in the process window on center right and click **process**
  - Check the offset of  $m/z$  28 and 44 because they have strong mass peaks. The middle of the peak should cross the middle vertical green line. Change the offset by changing the values in the Offset column (it should be  $\sim -0.6$ ).
  - Change the offset for  $m/z$  30 and 46 to match the offset for  $m/z$  28 and 44  
*[NOTE: in the TOF mass list window, the offset is typically 0.1 amu greater than the 0.5 amu offset of the bars in the mass spec window because of the slow scan in TOF (appropriate for fixed mass in TOF) compared to the fast scan (1 amu / millisecond) in the MS mode.]*
  - Make sure only 30 and 46 are highlighted and press **enter** to return to the TOF window
  - Reset the thresholds by clicking on the “SP Auto Threshold” button near the bottom of the parameter column (to set thresholds manually, right click on this tab and use the **u** and **d** keys to move the threshold up and down).
  - Press **F5** to reset the averaging
- Particle pulses and integrated signals should be clearly visible for 300 or 350nm DMA particles.
  - If not, click on lowest integrated TOF window and press **F2** to normalize full scale.
  - If there are still no particles, check the DMA connections and make sure that the atomizer is actually making particles.
- Set the blue lines for selecting only  $q=1$  from DMA right around the particles (typically  $\sim 4500$  and  $\sim 5000 \mu\text{s}$  for TOF(1) and TOF(2) in the **Averaging & Saving** tab).
- Note number of particles detected in TOF screen (should be  $>200$  for good statistics).
- Press the **insert** key to view the single particle screen. ***Need screen picture!!***
  - Press **F2** to normalize the signal.
  - Up to 3 traces appear on the single particle graph on the left side:
    - red: small particles (if thresholds are set correctly, this should be small or nonexistent)
    - purple: particles between the blue cursors
    - yellow: multiply charged particles, this trace should be larger
  - Ions per particle (IPP) is the bold number in the center of the window and reflects the purple trace only.

- If two masses are chosen, (i.e., 30 and 46), NO<sub>3</sub> IPP is double the value (double the IPP value on the screen to get the actual value).
- Note pulse height distribution in the right window.
  - It should be “Gaussian”
  - It may have two peaks, depending on how different 30 & 46 pulses are
  - It is critical that the threshold does not cut off the pulse height distribution on the left side (the small pulses)
- Press *insert* to return to TOF window
  - Check the percent mass counted for 30 and 46 at the bottom of the left column It should be 100±5% for both (this confirms threshold level from pulse height distribution in single particle window).

### **Automated Mass Calibration**

- In F6 window select m/z for calibration. Make sure that the species column for the selected m/z's are filled in appropriately. If a new IE calibration is to be performed w/ NO<sub>3</sub>, the first m/z selected must belong to the "NO<sub>3</sub>" species. If other species are to be calibrated for as well, m/z fragments that correspond to those species must also be selected. IF AN ACCURATE IE IS TO BE CALCULATED, ALL MAJOR M/Z FRAGMENTS FORMED FROM THE SPECIES OF INTEREST MUST BE SELECTED.
- In addition to the species being calibrated for, select m/z belonging to species "AIR" so that the airbeam signal can be monitored at time of calibration.
- Go into TOF acquisition mode, set thresholds for selected m/zs. Set the blue lines in the Single Particle graph so that they separate the q=2 particles output by the DMA from the singly charged particles of the desired size. The IE will be calculated for Region #2 which should contain the particles of interest.
- If a CPC is attached, compare the AMS count rate of the 350 nm NH<sub>4</sub>NO<sub>3</sub> particles with that of the CPC. Typically 90-100% of the particles should be counted. Also, look at the Average TOF traces and make sure that all of the AMS NO<sub>3</sub> mass at m/z 30 and 46 for the 350 nm particle is counted. Otherwise check the single particle threshold that has been set.
- Once the initial checks are complete, activate alternate MS/TOF mode and let system average for a few minutes. After averaging is completed, press “Shift M” to bring up the calibration window.
- Fill in correct information about the calibration particles being used in User Input Section. Typical inputs for NO<sub>3</sub> calibrations are 350 nm pure NH<sub>4</sub>NO<sub>3</sub> calibration particles. In this case, the density used in the ug/m<sup>3</sup> calculations is that of NH<sub>4</sub>NO<sub>3</sub>, but these calculations need to be corrected for the fact that m/z 30 and 46 detect only NO<sub>3</sub>(MW=62) in NH<sub>4</sub>NO<sub>3</sub>(MW=80). This is done with the Mass Fraction of Species entry which is 62/80=.775)

- If only NO<sub>3</sub> is being calibrated for, then the mass fractions for species 2,3,and 4 should be set to 0. If any other species are being calibrated (e.g. NH<sub>4</sub> from NH<sub>4</sub>NO<sub>3</sub> or SO<sub>4</sub> in a mixed NH<sub>4</sub>NO<sub>3</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particle) then the appropriate mass fractions and species designations should be entered in the User Inputs.
- Click the "calibrate now" button. This action automatically starts the AMS in alternate TOF/MS mode and displays performance parameters. A TOF and MS file with the most recent run number will be saved in the C:/AMS/AMSData/NonAutoSave/ directory .
- Note down the AB (both MS and TOF), IPP, TOF/MS μg, IE, and IE/AB.
- Save a screen picture.

### ***Size Calibration***

Air passing the aerodynamic lens is accelerated to a supersonic velocity in the last aperture of the lens. Particles in this air stream are accelerated in the final aperture depending on their size. Larger particles with higher inertia will experience less acceleration than smaller particles. The time-of-flight of the particles from the lens (actually measured from the chopper) to the heater is therefore a measure of the aerodynamic particle diameter. The velocity dependence of the particle diameter is described by the expression below adapted from the Jayne et al paper (*Aerosol Sci. Technol.* **33** (2000) 49-70):

$$v = \frac{v_l + (v_g - v_l)}{\left(1 + \frac{D_{aero}}{D^*}\right)^b}$$

where  $v$  is the particle velocity of particles with diameter  $D_{aero}$ ,  $v_g$  is the gas velocity (typically ~550 m/s),  $v_l$  is the velocity within the lens (typically ~8 m/s),  $D^*$  and  $b$  are fitted coefficients.

The size calibration determines how the aerosol aerodynamic diameter is calculated by the AMS software and should be performed whenever the AMS is moved or at the beginning and end of a field study, but should stay constant once it is determined. This calibration must also be performed when the sampling pressure is changed (e.g., a lab experiment performed at 400 torr will have a different velocity curve than one performed at ambient pressure). PSLs are the most reliable method of performing the size calibration, but NH<sub>4</sub>NO<sub>3</sub> can also be used if the performance of the DMA is first checked with PSLs.

- Set up the atomizer (or other aerosol-generating instrument) to make a polydisperse array of PSL particles (several sizes of PSLs should be used – at least five sizes – spanning the range of the AMS and extending past 1 μm) and dry them.

- Connect the output of the atomizer (the dried PSL particles) to both the AMS and a Scanning Mobility Particle Sizing (SMPS) system (this is basically a DMA and CPC connected together). Set the SMPS to scan its entire range once (~ five minutes) for each PSL size to ensure that the PSLs are the proper size (i.e., have been dried sufficiently) and to check the DMA so that sized  $\text{NH}_4\text{NO}_3$  particles can be used as well. Connecting to the SMPS is not an essential step, but it provides a good check on the sizing.
- Increase the heater power on the AMS to ~ 3 W to ensure complete vaporization of the PSL particles.
- Record the TOF signal at  $m/z$  28 (or  $m/z$  32) and  $m/z$  104 while the SMPS scans and save the AMS TOF file as a NonAutoSave file (press *F3*) at the end of the SMPS scan.
  - The size distribution for  $m/z$  28 gives an additional point to constrain the small sizes. Air molecules have a diameter of approximately 0.25 nm.
- Repeat for each PSL size
- Plot the output of the AMS file (hist104\_Rxxxx) against the time (thist\_Rxxxx) to determine the time (in ms) for the PSL signal (using the histogram eliminates issues of slow vaporization or particle bounce).
  - Translate this time to velocity using the following equation:  
Velocity = TOF chamber distance (~ 0.39 m) ÷ TOF time (s)
  - Calculate the aerodynamic diameter using the following equation:  
Aerodynamic Diameter = Stated PSL Diameter \* PSL Density (1.05)
  - Plot the aerodynamic diameter against the particle velocity and fit the resulting curve to the equation:
    - $V_{\text{particle}} = (v_1 + (v_g - v_1)) \div ((1 + (D_{\text{aero}} \div D^*))^b)$
    - Some suggested values for these variables are:  
 $v_1 = 8$  (velocity inside the lens)  
 $v_g = 549$  (gas velocity after the lens)  
 $D^* = 15.98$  (fitted coefficient)  
 $b = 0.4354$  (fitted coefficient)
- Enter these values into the *Parameter Menu* in the *Flow, Size & Mass Calib* tab.

See Jayne et al., 2000 (Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles) for more details.

### ***Quadrupole Mass (Peak Position ) and Resolution (Peak Shape) Calibration***

The shape and position of mass spectral peaks must be calibrated to ensure that the AMS is performing properly. The resolution of the QMS determines the peak shape and spacing between peaks. It is important to have the optimum resolution because signal can be artificially lost or gained if it is set incorrectly.



## Peak Shapes in Quadrupole Mass Spectra

The quadrupole mass spectrometer is a mass filter, which can be passed by ions of a mass range depending on the voltage settings of the mass spectrometer electrodes. This range, for which the mass filter is 'open', defines the resolution of the mass spectrum. To distinguish ions of different mass number, the mass resolution ( $m/\Delta m$ ) at the mass of the ion has to be at least the value of this mass in amu ( $m/\Delta m = 100$  for resolution of mass 99 and 100).

At high resolution the mass line is a peak of asymmetric shape: It has a sharp tail on the right side (on the high mass side) and a longer, less sharp tail on the left side (on the low mass side). Decreasing the mass resolution of the QMS makes the peak wider. It does not change the shape of the peak and the position of its right tail. The left, long tail walks away from the right tail and the maximum rises up. (the peak shape can be changed by changing the value of the field axis, which is typically set at 14). The ideal peak shape would be a "top hat" or a "flat top" shape so that the signal intensity for each amu can be determined by averaging over the flat section of the top hat. To maximize the ion transmission through the QMS the resolution setting should be as low as possible. With too low resolution the left tail of the peak ends in the peak of the next lower mass, which changes the intensity of this peak. The AMS should be operated with a 1 amu resolution throughout the entire mass scan range. So for optimization of ion transmission you have to set the resolution as low as possible (to maximize the transmission) and as high as necessary (to get correct ion signals of the different masses).

In the **MS Mode** of the AMS program the ion intensity at the single masses (also referred to as stick intensities in the mass spectrum) is measured as averaged ion signal, averaged over a window region (adjustable in parameter window) in the center of the peak. The averaging width should be as large as possible to maximize signal to noise ratio. On the other hand it should not be wider than the flat top part of the peak to maximize signal intensity. Typically a window width of 0.4 amu centered about 0.5 amu to the left of the right hand edge of the peak is ideal for obtaining peak signal intensity. In the MS window this averaged ion signal is displayed as a box with height equal to the averaged intensity and width equal to the averaging window. The resolution of the mass spectra may be as low that the left tail of the peaks reaches the next peak on the low-mass side and alters the right tail of this peak. For correct ion signal calculation it only may not reach the integration box of the next lower mass peak.

In the **TOF Mode**, the signal intensity at each selected  $m/z$  is determined at a single point on the peak. Therefore, it is important that the maximum of the flat top section of the peak be used to determine the signal for each  $m/z$ . Since the Quadrupole scan in the TOF mode is slower than the MS mode, the peak shape in the two modes differ slightly. Typically, if the peak resolution has been set properly for the MS Mode as described above, then maximum of the peak for the TOF Mode is offset by approximately 0.6 amu to the left of the right hand edge of the peak. The value of the offset is usually the same for all masses and can be set for each selected mass in the  $m/z$  window (F6 from TOF window). In order to determine the best value for the offset in the TOF Mode, it is useful to enter the  $m/z$  window and then select  $m/z$  28 ( $N_2^+$ ). The top right corner of the

window contains a mass spectrum in the region about the m/z 28. The calibration is set properly when the mass peak in the middle of this window is located between the two black sticks rising into the window from the bottom. The rightmost black stick denotes the selected mass and the right edge of the signal peak should line up with this stick. Since the TOF measurement for a particular m/z is only obtained at one point along the signal peak, the quadrupole should be set to the point that coincides with the maximum of the signal peak. This can be done by varying the offset (in column 2 of the table).

### **Peak Shape Calibration**

The peak shape is a function of the quadrupole resolution which is described as a linear function of amu as follows:

$$\text{Actual Resolution} = \text{ResolutionSetting} * (1 + \text{Slope} * \text{amu})$$

The Resolution Setting and Slope values are menu parameters that can be changed during calibration. The Quadrupole resolution can be calibrated by a two point calibration at 2 different amus. It is recommended to use a low mass like m/z 28 for one calibration point and a high mass like m/z 149 (which is typically present as a background peak) to perform this calibration. If a manual calibration is being performed, start the program in on MS mode, focus the display onto the mass being used, and vary the ResolutionSetting and Slope values in the menu until both peaks have the ideal “Flat top” peak shape described above.

In newer versions of the AMS software, an automatic resolution calibration can be performed by clicking the “Calibrate MS” button on the top right hand corner of the MS window. This opens up a calibration window with two graphs that display sections of the mass spectrum for the masses that will be used for the calibration.

- As mentioned above, typically one graph should focus on a low mass like 28 amu (always present due to N<sub>2</sub> airbeam) while the other should focus on a high mass like 149 amu (Pthalic ester contaminant that is always present as a background peak). Other masses can be selected from the drop down menus on top of the graphs. The left hand axes labels for both graphs are signal intensity in units of bits. The text box at the top right hand corner of each graph displays the signal intensity for the selected peak obtained by integrating over the 0.4 amu window (shown as a rectangular box).
- Vary the actual Resolution setting for mass 1 and mass 2 so that the peak shapes look appropriate (as described a few paragraphs ago) and the calculated average signal intensity at each mass is maximized.
- Changes in the actual resolution settings will automatically be used to determine the slope and intercept for the resolution calibration. These values are displayed in the “fit results” section.

*NOTE: In this formulation, the ‘Resolution Setting’ value is reverse proportional to the resolution of the mass spectrum*

## Peak Position Calibration

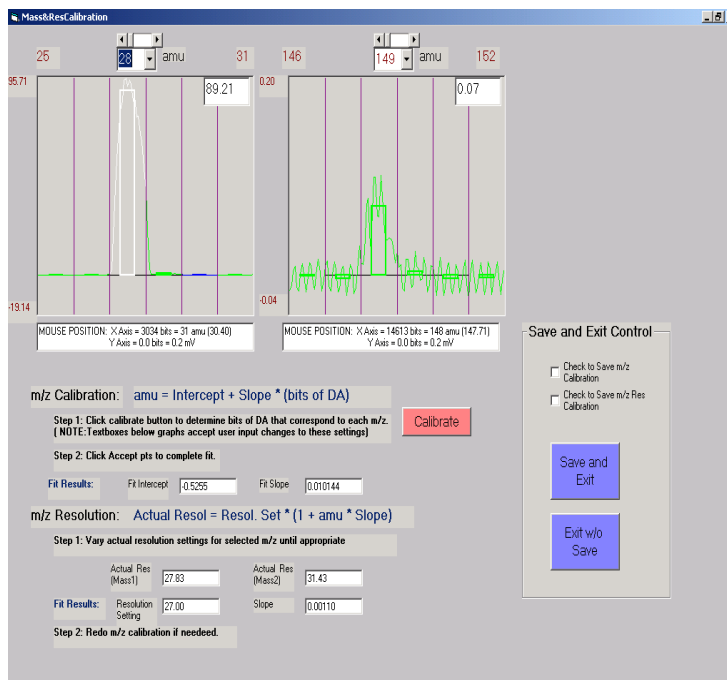
Once the peak shape has been set, the peak position can also be calibrated. The quadrupole mass (amu) positions can be described by a linear equation which relates the amu that is scanned to the bits output by the computer to the data acquisition board (the output bits are converted to an output voltage to the quadrupole using 16 bit resolution such that 10V = 32768 bits).

$$\text{Amu} = \text{slope} * \text{bits DA board} + \text{Offset}$$

The parameters for this linear relationship (which are found in the “mass spectrometer menu” tab) are determined by a two point calibration at two different  $m/z$ 's. Typically the mass calibration needs to be corrected if the rectangular boxes which denote the averaging widths for the amus of interest do not line up with the maximum intensity sections of the peaks.

If a manual calibration is being performed, these menu parameters have to be manually changed so that the 0.4 amu averaging window is centered on the “flat top” part of each  $m/z$  being used for the calibration. In newer AMS software versions, automatic quadrupole mass calibration can be performed as follows:

- Press the “Calibrate MS” button in the upper right corner of the MS screen, the following window appears.
- Press the “Calibrate” button and if the new positions are acceptable, then click the “accept” button. Otherwise, the values in the textbox that shows the “DA bits for  $m/z$ ” can be changed to modify the suggested position of the boxes before clicking the “accept” button.
- Results of a linear fit to the 2 point calibration are displayed in the text boxes in the “fit results” section.
- Before exiting, select the “Check to Save  $m/z$  Calibration” button or the fitted slope and intercept will not be saved.



## NOTES:

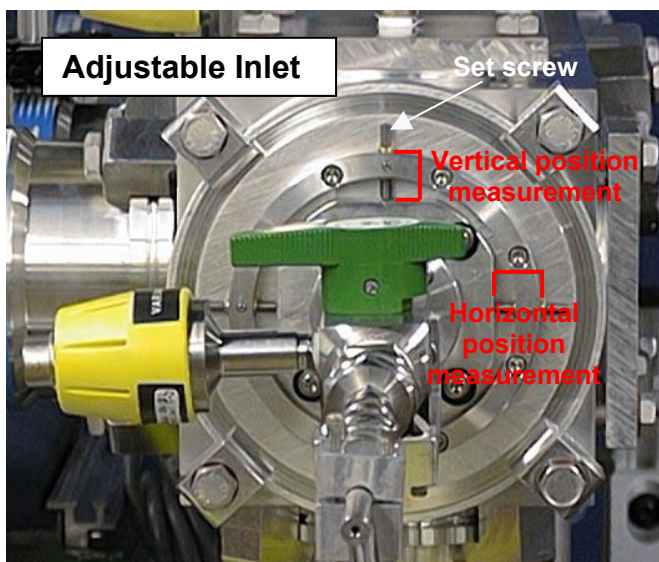
- Often it is only the offset in the  $m/z$  calibration that changes as a function of time. In this case, the offset in the mass scale can be moved by pressing the 'y' and 'Y' key while viewing MS peaks and their signal average boxes in the normal MS window.
- Changes in resolution and  $m/z$  calibration can affect each other so it is often necessary to reiterate the calibrations until no large changes are observed.

## Lens Position Calibration

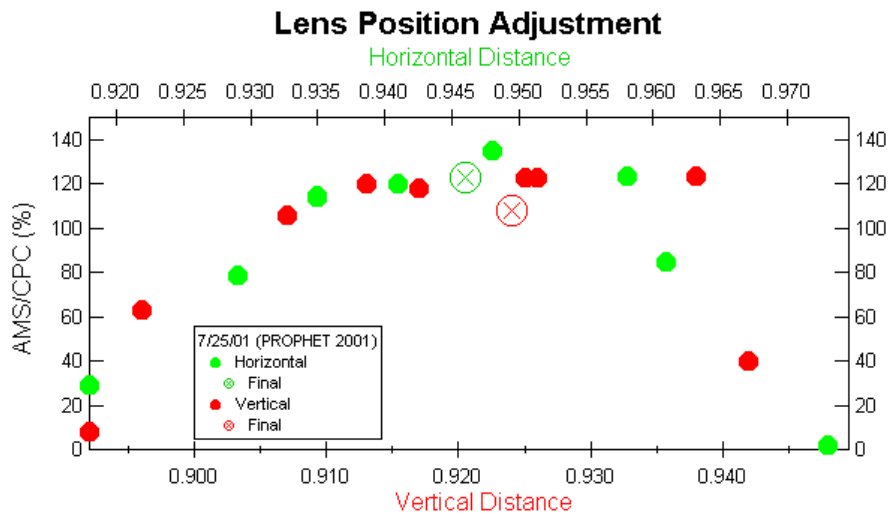
The aerodynamic lens forms an air beam, which expands with supersonic velocity into the vacuum. Aerosol particles in this beam are focused in the middle of the beam to form a very thin low-divergence beam of particles. The particle beam passes the skimmer, the chopper and finally hits the heater at the ionizer assembly of the QMS.

The lens position is critically important to getting the strongest possible signal. This calibration should not be performed frequently since it will change how the aerosols travel to the heater/ionizer assembly and could therefore affect the ionization efficiency (the ionization efficiency must therefore be calibrated after the lens position has been changed). Normally, the lens position should be adjusted after moving the instrument and then locked in place and not moved again.

- First, set up a DMA to produce 300-400 nm particles and connect a CPC to the AMS. Make sure that the output of the DMA is constant by watching the number reported to the CPC and AMS before beginning the lens position calibration.
- Loosen the screws holding the lens plate so that the lens plate floats on its o-ring and loosen the ultratorr fitting holding the lens in place.
- Set the AMS to detect  $m/z$  30 and 46 in TOF mode (press **F6** in TOF mode to get to the  $m/z$  selection window).
- Note down the IPP and AMS/CPC percentage at the initial position.
- Then loosen the set screws holding the lens in place and move the lens either horizontally or vertically.
- Measure the lens position carefully from the outside of the lens plate to the lens, ~0.9 inches (the lens position is easily changed when all the screws are loosened, so be careful not to change the position while measuring). Always measure from the same place, usually right next to the set screw (see red bars on diagram).
- Again note down the IPP and AMS/CPC percentage at this position.



- Continue moving the lens either horizontally or vertically and noting the IPP and AMS/CPC percentage until the performance of the AMS in that direction has been fully mapped.
- Move to what appears to be the best position (highest IPP and AMS/CPC= ~100%) and then continue mapping in the other direction.
- Again, find the best position and double check the AMS performance (see plot below).
- Tighten the screws holding the lens plate and the ultratorr fitting and then recheck the IPP and AMS/CPC since tightening the lens plate can alter the lens position.



### Collection Efficiency

The signal received by the multiplier does not always perfectly reflect the amount of material entering the system. Therefore, it is important to characterize what is actually being measured by determining the collection efficiency of the instrument. There are two different types of collection efficiency important to the AMS.

The **particle collection efficiency** is a measure of the transmission of particles through the lens and body of the AMS. It is simply the ratio, translated to a percentage, of the number of particles measured by the AMS to the number of particles measured by a CPC. This value is determined by the lens transmission, shape of the beam, and aerosol chemical characteristics. For  $\text{NH}_4\text{NO}_3$ , the collection efficiency approaches 100%. However, for  $(\text{NH}_4)_2\text{SO}_4$ , the collection efficiency is closer to 15% in the laboratory. This means that only 15% of the particles measured by a CPC are reaching the heater. This is a significant issue, since  $(\text{NH}_4)_2\text{SO}_4$  often constitutes a major portion of the aerosol mass. However, field studies indicate that the collection efficiency for  $(\text{NH}_4)_2\text{SO}_4$  is much better for ambient than for laboratory particles. Several hypothesis have been proposed to explain this phenomena, including that the  $(\text{NH}_4)_2\text{SO}_4$  particles may be bouncing out of the heater or that they may be defocused coming out of the lens because of their shape or other properties. Ambient particles may include other species

than  $(\text{NH}_4)_2\text{SO}_4$  that may cause the particles to focus better. When comparing the number of particles detected by the CPC and the AMS it is important to avoid biasing either measurement by having different sampling conditions.

The **ion collection efficiency** is a measure of the number of ions that are actually measured by the electron multiplier out of the total number of ions produced. This is determined by taking the ratio of the electron multiplier signal to the faraday cup signal for nitrogen ( $\text{N}_2 = m/z 28$ ). Both signals should be measured with the AMS software to ensure the same values are being measured.

*Measuring the electron multiplier signal:* The  $\text{N}_2$  signal (in mV or Hz) can be determined directly from the AMS MS screen (beam open signal only). Note the gain and multiplier voltage.

*Measuring the Faraday collector signal:* The amplifier setting (A/V) and signal voltage are needed to determine the Faraday collector signal. The raw Faraday signal will be the negative of the multiplier signal because the signal going through the multiplier has been transformed into electrons and the Faraday signal is still positive ions. Record the change in voltage of the  $\text{N}_2$  signal (mV) and the setting on the amplifier ( $1\text{e-}9$  or  $1\text{e-}10$  A/V).

- Connect the amplifier to the Faraday cup (middle connection, which is normally connected to V7) and then connect the output of the amplifier to the AMS signal input.
- Switch the signal leads or set the AMS screen to show negative values since the Faraday cup detects positive ions, not electrons.
- Let the signal average for several minutes.
- Read the peak of the  $\text{N}_2$  signal in V (should be  $\sim 0.002$  V with  $1\text{e-}9$  A/V amplifier setting). The S/N ratio in the Faraday cup measurements is low, so these measurements have to be done carefully. This is best done by saving the datafile (*F3*) and then reading the file into IGOR. Make sure that the zeros for the Faraday Cup signal have been set properly and that the mass calibration of the raw average MS is fine. If the mass calibration has shifted, redetermine the proper signal intensity for the peaks.

The voltage reading can be converted to Hz as follows:

$$\frac{\text{Amp}(A/V) \times \text{N}_2 \text{Signal}(V)}{1.6\text{e-}19\text{C/ion}} \Rightarrow \frac{(1\text{e-}10\text{A/V}) \times (0.06V)}{1.6\text{e-}19\text{C/ion}} = 3.75\text{e}7\text{Hz}$$

So, by taking the ratio of the electron multiplier current to the Faraday cup current, the nominal ion collection efficiency is determined. For example, if the electron multiplier Measured  $4.87\text{E}6$  Hz for the Faraday signal above, then the collection efficiency is :

$$\frac{EM}{FC} = \frac{4.87\text{e}6\text{Hz}}{3.75\text{e}7\text{Hz}} = 0.13 = 13\%$$

## ***Tuning the Quadrupole Mass Spectrometer***

After significant change in the instrument configuration, especially when the instrument has been exposed to atmosphere (e.g., replacing the multiplier), the MS should be retuned to ensure optimal performance. However, tuning the MS should not be performed regularly since it will change the instrument configuration and will require ionization efficiency calibrations before and after the tuning procedure. Essentially, tuning the MS means changing the MS voltages (see Appendix 5: Basics of Mass Spectrometry for a description of the voltages involved) to optimize the ion formation at the heater, the ion extraction into the quadrupole mass spectrometer and the ion deflection behind the mass filter into the multiplier to get the largest signal possible. These values can be seen and changed manually in the Balzers control unit after pressing the *V1...V6* and *V7* buttons below the display or in the AMS software (*shift-B* from the MS window). There is an automated procedure for this in the AMS software.

The parameters and typical values are as follows (these are approximate values and will change from instrument to instrument):

Ion Reference (V1)	90 V
Cathode (V2)	70 eV
Focus (V3)	11 V
Field Axis (V4)	13.75 V
Extraction (V5)	130 V
Deflection Inner (V6)	15 V (~250 V with the new module on Caltech AMS)
Deflection Outer (V7)	30 V (~60 V with the new module on Caltech AMS)
Emission Current	2.5 mA (0.25 mA with new module)
Heater Bias	-5.0 V

The ion reference, cathode, and emission current are not changed during the automatic tuning procedure. The cathode voltage defines the energy of the electrons impacting on the vapor molecules and the emission current is set as high as possible to increase the electron density. The cathode setting can be changed to produce a softer or harder ionization for specific species, but for normal sampling it should not be changed. The ion reference is the nominal potential on which the ions are formed and is the reference potential for all other potentials. Changing the ion reference will completely change how the quadrupole mass analyzer operates, so this should not be changed except as a last resort. See Appendix 5 for more information on the mass spectrometer voltages.

To optimize the voltages, the program changes the values for one voltage at reasonable intervals and measures the signal at the mass set for ionizer tuning. That voltage is set to the value of maximum ion transmission. The rest of the voltages are optimized in the same way.

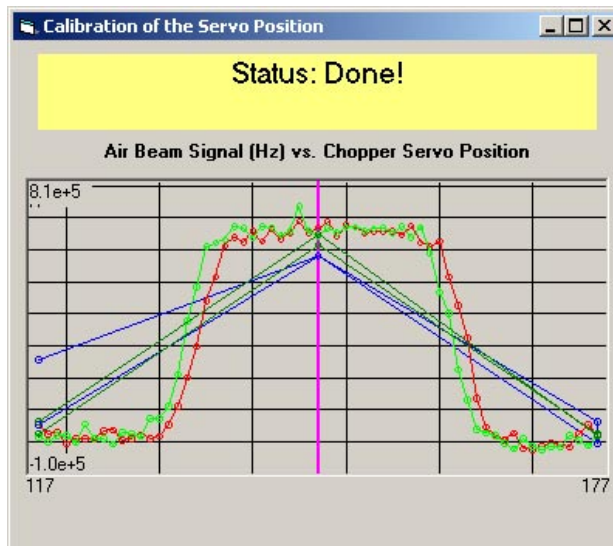
- Open the inlet.
- In *Mass Spectrum* mode, toggle the chopper (*shift T*) and note airbeam signal (in Hz)

- Toggle chopper (*shift T*) again when the chopper is open to keep the chopper open (so that the tuning will be performed on the largest signal)
- Quit to the parameter menu (*enter*), go to the *Mass Spectrometer* tab, make sure that “m/z for ionizer tuning” is set to 28 (N<sub>2</sub>)
- Quit to the main menu (press *q*) and choose “*Tune Balzers Mass Spec*”
  - Note % improvement when procedure is finished. If signal is much lower (<50%), check that the outer deflection voltage is non-zero and positive. If this voltage is zero or negative, reset to half of inner deflection voltage value and repeat procedure.
  - If % improvement is acceptable, note change in voltages and select “OK” to accept changes
- Quit (press *q*), choose *Mass Spectrum* mode, toggle chopper (*shift T*), and note airbeam signal.

### ***Servo Travel Calibration***

This calibration should be performed after transport and or manipulation of the chopper flange; it does not need to be performed at any other time unless there is a significant difference between the sizes of the MS and TOF airbeam.

- Quit (press *q*) to main menu and choose *Servo Adjust*
- Let it run and note shape of signal as servo walks the chopper across the beam in both forwards (red trace) and backwards (green trace) directions
  - There should be a “top hat”
  - If the “top hat” is positioned evenly over the initial servo positions (i.e., the set chopped position is in the middle of the “top hat” and the completely open and closed positions are beyond the edges of the “top hat,” then the servo is adjusted correctly
- If the “top hat” is not positioned evenly, calculate center of top hat and note center number
  - Quit (press *q*) and choose the *Multiplier & Chopper* tab
  - Set the three positions based on the center of the “top hat”: center – 30, center, center + 30  
Typical values: 10, 38, 65 (screen shows values 110 greater than these)



- Note: 1<sup>st</sup> position must be made positive to turn off single stepping even if there is no change of chopper position (this will eventually be automated in the code)*
- Quit (press *q*) and return to *Mass Spectrum* mode



- Toggle chopper position (*shift T*) and note airbeam signal (this should not change if servo was set correctly)

## Sampling

The process of setting the AMS for sampling depends on the type of information desired. Only the basic sampling will be described here.

### *Mass Spectrum Mode*

As described earlier, the MS mode is used to determine the complete chemical composition of all volatile and semi-volatile constituents of the aerosols. Examination of the full mass spectrum will also indicate the mass fragments with the largest mass, which are often the most interesting and useful for time of flight measurements.

After checking that the AMS is operating correctly (EM gain, mass calibration, size calibration, etc.), make sure the AMS is scanning 0-300 amu and the mass offset is correct. Note down the important values on the checklist sheet (*see Jose's list or make new one*). Set the display update appropriately – if want to watch display closely, set update time for one second, if don't want to watch the display often, set update time for 3-5 seconds or pause the display update (press *p*) to save computer memory.

### *Time of Flight Mode*

The TOF mode is used to obtain size information on the most important or most interesting mass fragments.

To set the TOF masses:

- Go to the TOF screen and press *insert* to go to the TOF m/z selection screen
- Highlight the desired masses by clicking on the number at the beginning of the row (the number box will turn red and the rest of the row will turn green).
- If a mass is not present, make one by changing the values for one of the masses not being used.  
*NOTE: on this screen, the values are changed by clicking on the box and then using the "backspace" key to delete the values before entering new values.*
- Make sure that all the masses selected have the sliding window of 4, and that the molecular weight of the parent ion is the same as the mass selected for "organic" and 98 for SO<sub>4</sub>, 62 for NO<sub>3</sub>, and 18 for NH<sub>4</sub>. If the same set of masses are always measured it is often easier to designate a letter in the "Group Member" column so that all the masses do not need to be individually selected every time.
- After the masses have been selected, return to the TOF screen by pressing *insert* again
- Set the thresholds by clicking on the "SP Threshold Auto" tag on the left side of the screen-this may take a few minutes if many masses are selected.

After the MS and TOF modes have been set, set the autosave interval in the *Averaging & Saving* tab. For typical ground ambient sampling this is often 5-20 minutes.

Return to the main menu and select *Alternate MS-TOF* to begin sampling.

### **Field Measurements**

To get all the information you need for adequate data analysis the program has to be set up in a particular way for normal field measurements. First, perform all of the calibrations and checks to ensure that the AMS is working correctly (see the *Calibrations* section). Then select the masses that will be monitored in TOF mode. Some masses should always be measured, especially to determine the inorganic species, and the mass spectrum should be studied to determine which masses are dominant and therefore likely to be of interest. At a minimum, most of the following masses should be observed in TOF mode for regular ambient sampling.

Mass	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Organic	H <sub>2</sub> O	Air	Comment
15			X	X		X	Can have organic interference
16			X		X	X	Best for NH <sub>4</sub>
17			X		X	X	Very noisy, avoid using
18					X		Water
28 / 32						X	Either 28 or 32
30		X					NO <sup>+</sup>
43				X			Oxidized Hydrocarbons, C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>
44				X		X	Carboxylic acids (COO <sup>+</sup> )
46		X					NO <sub>2</sub> <sup>+</sup>
48	X						SO <sup>+</sup>
53				X			
55				X			
57				X			Hydrocarbons
64	X						SO <sub>2</sub> <sup>+</sup>
81	X			X			HSO <sub>3</sub> <sup>+</sup> Can have org interference
69				X			
71				X			
91				X			Aromatic

After selecting the appropriate masses, set the thresholds for each mass with the automatic button on the bottom left of the TOF screen. You also can set the threshold manually by selecting one mass and setting the threshold for this mass by right-clicking on the automatic threshold button and pressing *u* to increase the threshold and *d* to decrease it; then go back to the m/z selection window (*F6* from TOF screen) and selecting another mass. Restart the averaging after the thresholds are set by pressing *F5*. Check the airbeam value, displayed in one of the labels, and make sure it is similar to the airbeam measured in MS mode.

In MS mode, select a mass range to be scanned from 0-300 amu, and set the display to 0-100 amu (parameter window).

Select the *Averaging & Saving* tab in the parameter window to set the desired times for data acquisition in both modes. Select the screen display update frequency (1 second if you are going to watch it, pause the screen update if you are not watching to increase the duty cycle) and the intervals to auto-save the data. You can select auto-save of the data always after a given time interval or at fixed times (e.g., every full 10 minutes after a full hour). Data will be averaged during these time intervals and the averages are saved. After the auto-save the buffers will be reset and new acquisition and averaging begins. Select the log files you want to save. At a minimum, save the main logfile, which contains the instrument parameters (the most important instrument parameters are also saved in every data file).

After setting the parameters in both modes individually and setting the saving parameters select *Alternate MS-TOF* mode in the main menu to start the measurement with alternate data acquisition in MS mode and in TOF mode.

### **Typical Correction Factors**

After the data are acquired, some species require correction factors before the final mass loading can be calculated. These are empirically determined from comparisons with other measurements at several field studies.

Sulfate: 2.5

Nitrate: 2.0

Ammonium: 0.5

Organic: 0.7

Below is a list of items meant to ensure high data quality that were discussed at the 2001 AMS Users' Meeting.

- 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 performed beyond 1  $\mu\text{m}$  to avoid ambiguity in sizing of large particles.
- 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/pressure gauge calibration: check flowmeter/pressure gauge calibration at least by closing the inlet valve and making sure that flow/pressure reading is zero. For

flowmeter/pressure gauge 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 at least daily
- 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, carefully check 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 reliably.
- Humidity: the particles should either be dried to a constant humidity or the humidity and temperature should be carefully monitored. Changes in humidity may cause significant changes in measured mass.
- Black conductive tubing: organics can outgas from this tubing – this is enhanced when organic vapors like tare sampled. Particles seem to be covered by outgassed organics. No large change in mass concentrations likely, but changes in aerodynamic behavior are possible.
- If sampling through long lines, test to determine the particle transmission since this can decrease the measured mass dramatically and may also change the aerodynamic diameter depending on environmental conditions.
- Multiply charged particles: the concentration of multiply 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 none 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).

## Troubleshooting/Diagnostics

There are not that many things that can fail on this instrument. Almost all problems are related to those items that are actively in use: pumps (pressure), airflow (inlet), and ion detection (heater, filament, QMS, multiplier).

### *Leak Test*

Typical Pressure in the multiplier chamber is in the mid to low  $10^{-8}$  torr region after a couple of days pumping. After initial pump down, a pressure of less than  $10^{-6}$  torr should be reached in about half an hour with all turbomolecular pumps running at full speed. If the decrease of pressure stops suddenly at a pressure higher than this, it's an indication of a leak at one of the seals. Note that the pressure in the multiplier chamber can increase by as much as a factor of ten when the aerosol inlet is opened. Leaks can be caused by loose bolts, bad o-rings on the flanges or chopper feed-through, dirty o-rings or dirty/scratched metal surfaces. Clean the o-rings and the flanges by blowing clean, dry air on them. Scratches can be removed by sanding the flanges with small-grinded sandpaper (400 or more). To locate the leak use the following procedure if the pressure is low enough to start the QMS.

If a leak is suspected, close the inlet valve and see if the turbo pumps return to 100%

- If they return to 100 %, there is probably no leak or it is small.
- If they do not return to 100%, use helium (He,  $m/z$  4) to check for leaks (or anything else that is distinct from normal air and will not leave a residue in the chamber)
  - Set the AMS to scan 1-10 amu in MS mode if using He
  - Decrease the display interval in MS mode to 0.5 seconds so fast changes can be observed
  - Set the  $m/z$  selection window (*F6*) for TOF to  $m/z$  4 only.
  - Slowly direct He around all possible leak locations using a small, narrow tube; an increase in the He signal indicates the location of the leak.
  - The He signal can also be detected by connecting a multimeter (200 mV range) to the analog preamplifier signal jack ('output') to directly measure the amplifier signal and then setting the AMS as above.

If necessary, make a deliberate leak to check signal size and time response.

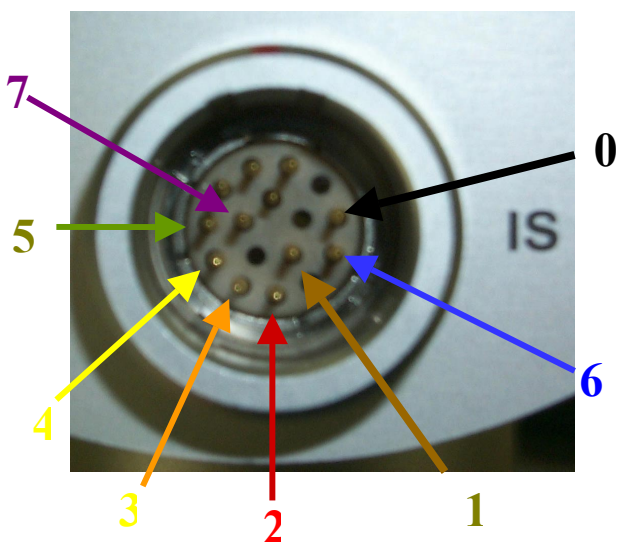
### *Very small or nonexistent signals*

**Faraday vs. SEM mode** – Sometimes the Balzers QMS control unit will start in Faraday rather than secondary electron multiplier (SEM) mode. There are two places to check this. In the Balzers control unit, go to *general/config/system* and you should see SEM under *detect*. SEM or EXTERN should also be selected under *channels/detect* on the left side of the control unit. In addition, the deflection voltage must be on (the deflection voltage is turned off when determining the Faraday signal). This can be checked either in the AMS software (*shift-B* to view all voltages and the emission current) or in the Balzers control box (*V1...V6 and V7*).

**Ion Detection** – Another cause of very small (or nonexistent) signals is the electron multiplier. It may be reaching the end of its lifetime, be set incorrectly (check this by performing the electron multiplier calibration), or be turned off (check the front of the AMS Electronics unit). Also check to make sure the ionizer filament (check visually, in software (*shift-B*), or on the Balzers control unit under *emiss*) and heater (AMS Electronics unit) are turned on. Sometimes, the ionizer filaments will turn on when initially started and then turn off almost immediately or will not return to the default setting after a multiplier calibration. The former may be a problem with the emission protection set too low (go to *emiss* on the Balzers control unit and increase *E-PROT* until the filament remains on), a bad spot weld of the filament wire to the rest of the filament assembly, or a problem with the ion source control boards.

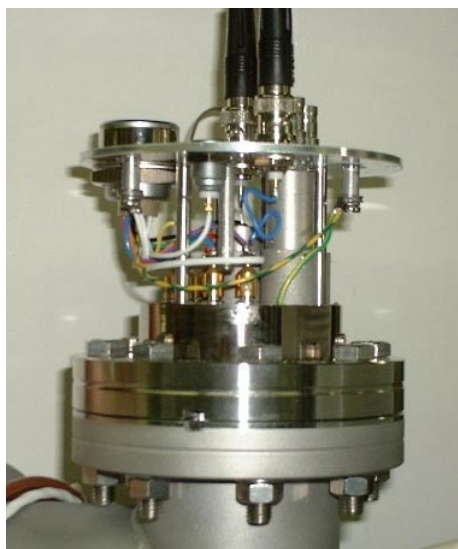
### Quadrupole Mass Spectrometer

Sometimes, there is a problem with the mass spectrometer controls or connections. The easiest way to determine if the problem is in the mass filter itself or in the control unit is to check the voltages. This can be done with everything hooked up by unscrewing and lifting up the cuff at the top of the QMS where the control cable comes in and using a



*QMS pin diagram. Voltages should be measured relative to the ion reference to get actual voltage values (i.e., if extraction is 150 V, should get 150 V measuring between ion reference and extraction pins).*

ID	Color	Connection
0	BLK	Deflection (V6)
1	BRN	Ion Reference
2	RED	Extraction
3	ORG	Filament
4	YEL	Filament
5	GRN	Filament
6	BLU	Focus



multimeter to measure the voltages (see the second picture at left). The colors on the pin diagram above should match the wire colors in the second picture.

If it appears to be a connection issue, also check continuity through the cable and through the mass filter itself if necessary (this is probably only an issue for the filaments). If the problem is not there and the configuration is set correctly on the Balzers control unit, then the problem is probably with the control unit boards and the unit may have to be sent in for repair (contact Pfeiffer Vacuum for technical assistance).

## ***Pumps***

As the turbo pumps begin to wear out, their maximum speed will decrease and the current will increase. The turbo pump bearings will wear out and a high-pitched jangling noise will be audible. The speed may also decrease under load and the current increase.

Pumps should be replaced as soon as possible after this noise is observed, as it is only a matter of time until that pump will fail. Turbo pumps can be refurbished (basically, they are cleaned and the bearings replaced), so it is not necessary to buy a brand new pump every time. It is a good idea to have a spare pump ready in case of a failure as it often takes several weeks to get a replacement. See the Hardware section for instructions on replacing pumps.

## ***Flow rate***

A decrease in the flow rate (or lens pressure) may indicate a clogged line or loose fitting (See the Hardware section for instructions on cleaning the critical orifice). Also, check that the AMS software is set to use the flow meter and not the automatic calculation.

## ***Chopper***

The ratio of MS/TOF airbeam should be approximately equal if the chopper is working properly. Comparison of the MS and TOF signal for the major fragments of interest will yield a lot of information about what is going on inside the detection chamber. For example, if the TOF signal is much lower than the MS signal for a particular fragment, there may be slow vaporization occurring.

## ***The Airbeam Signal***

Due to the continuous decrease in multiplier gain, the measured signal intensities can only be converted to the correct amount of vaporized material in the heater region immediately after a multiplier gain check. To have the possibility to calculate the “true” amount of vaporized material at any time, a quantity has to be measured which is known to be constant over time. This quantity is the airbeam signal (AB).

The airbeam is the signal measured at  $m/z$  28 ( $N_2$ ) or 32 ( $O_2$ ). The airbeam signal can be measured in the MS mode and in the TOF mode. The airbeam signals are usually 0.75-2 MHz for  $m/z$  28 or 150-400 kHz for  $m/z$  32. Sometimes the airbeam signal is smaller in TOF mode than in MS mode because the size of the chopper wheel (e.g., 1%, 2%, 3.5%) can restrict the airflow so that less air reaches the detector in TOF than in MS mode (i.e., the airbeam has a larger divergence than the aerosol beam, and it won't fit through the chopper completely).

Select  $m/z$  28 or 32 in the  $m/z$  select window ([F6](#)) to measure the airbeam in TOF mode. The airbeam signal will then be displayed automatically in one of the labels on the left side of the TOF window. It is measured as the area of the TOF signal integrated over the

flight times entered in the parameters window. The area is measured in bits \* time steps, which is converted to number of ions per time interval and to Hertz.

In the MS mode you have to toggle the chopper (*shift-T*) between the 'open' and 'closed' positions. The airbeam signal is displayed in a label in the middle of the bottom of the MS window. In this mode, the difference of the mass spectra at open and closed positions of the chopper is calculated. The airbeam signal is measured in units of bits by averaging the peak intensities over the 0.4 amu window at  $m/z$  28 or 32. This signal is converted to units of Hz by dividing by the Single Ion signal which is usually on the order of 10 bits\*Steps.

In the field the airbeam should be measured in parallel with the other masses to track the decrease in multiplier gain over time. After a multiplier gain calibration, the airbeam signal should recover to the value of the last multiplier calibration.

### ***The Baseline***

The baseline, which is used for signal intensity calculation, is measured in the TOF mode and the MS mode in different ways. In the TOF mode two 'DC markers' are displayed in the lowest window (the averaged signal window). They mark the time-of-flight range, in which the baseline is measured. Typically one of them is located at very short flight times and one at very long flight times. For most masses, using both sets of DC markers will give a much better baseline. However, any mass that has significant contamination from air (e.g.,  $m/z$  15, 16, 17, 18, 20, 28, 29, 32, 40, and 44) cannot use the first set of DC markers because the air signal will interfere and give a false baseline. The flight time region in which these markers are located is defined in the *Averaging and Saving* tab of the parameter window. In the flight time range of these markers the mass spec signal is averaged and defined as the baseline or background level.

In the  $m/z$  settings window (*F6* from TOF window) you can define the markers that are used for baseline definition for each mass individually. If only one marker is chosen, the baseline is assumed to be at the level measured at this marker, having no drift. If both markers are selected, a line approximates the baseline with a slope according to the difference in the two baseline measurement points.

In the MS mode, the baseline is measured at two mass regions at low and high masses that show very low background signal. Again these mass regions can be changed in the parameter window. The baseline is calculated as a linear fit through these two baseline points to take drifts of the baseline along the mass scan into account.



## Hardware

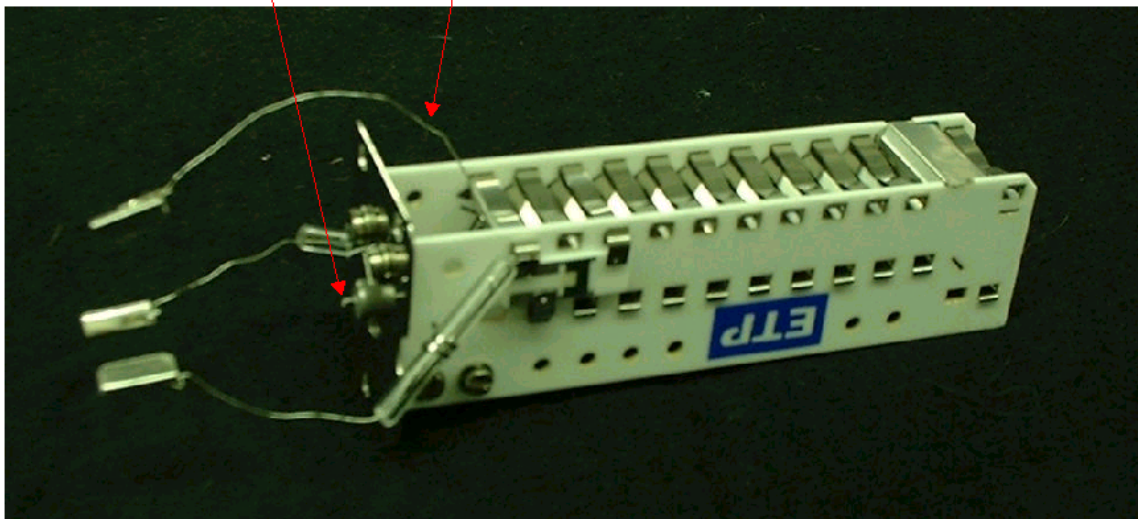
There are some hardware items that need to be replaced on a regular basis.

### ***Multiplier Replacement***

The electron multiplier must be replaced when the voltage can no longer be increased to compensate for the gradual gain decrease over time.

- Vent the AMS to atmosphere.
- Carefully loosen the bolts holding the multiplier housing by loosening a bolt slightly and then loosening the bolt opposite the first bolt. Continue loosening the bolts a little at a time symmetrically until they all turn easily by hand.
- Remove the housing and the copper gasket; the multiplier is attached to the housing, so be careful that the multiplier does not hit anything as it is pulled out.
- Disconnect the signal, high voltage, and ground leads (use gloves and tweezers and avoid touching any part of the multiplier with your bare hands).
- Unscrew the multiplier from the plate.
- If using an ETP multiplier, ensure that the signal lead does not go through the mounting plate, but around it instead. See the diagram provided by John Jayne.
- Line up the multiplier with the mounting holes and screw it into place.
- Reconnect the leads, checking the outputs on the outside of the housing to ensure the correct connections.
- Replace the multiplier housing, using a new copper gasket. Tighten the bolts carefully as above so that an even seal is achieved.

The signal lead originally coming through this feed through is cut at the "slip-on" connector, removed from this feed through and re-routed as shown. Connector is re-spot welded back on.



*Note: If the replacement multiplier has a protective metal coverplate make sure that it is removed!*

## ***Pump Replacement***

It is not difficult to replace one of the turbo pumps, but the pumps must be oriented correctly so that the backing system will work correctly.

- Shut down the AMS as described in the ***Initial Procedures*** section.
- Once the AMS is fully vented to atmospheric pressure, disconnect the turbo pump fan, control cable, and the backing line connection.
- Remove the pump by loosening the bolts evenly (i.e., loosen them in turn rather than completely removing each one before removing the next one).
- Once the pump is disconnected from the AMS, remove the screen on the front end and place it on the replacement pump (this prevents objects from falling into the pump and damaging it). Also check that the o-ring is clean (blow clean, dry air or nitrogen on the o-ring to clean it).
- Place the replacement pump against the body of the AMS and loosely fasten the bolts, ensuring that the pump is oriented correctly to make all of the connections (i.e., the backing system determines the pump orientation, so check this before tightening bolts).
- Tighten the bolts that hold the pump to the AMS, again tightening them in turn so that they form an even seal.
- Remove the turbo pump fan from the old pump by loosening the setscrews. Clean the fan (blow air through it) if necessary before fastening it to the replacement turbo pump.
- Reconnect the turbo pump fan, turbo pump control cables, and the backing line.
- Double-check that all connections are tight and then reset the turbo pump control by pressing up on the switch for that pump on the Turbo Pump Control unit until the light for that pump stops blinking.
- Start up the AMS as described in the ***Initial Procedures*** section.

## ***Critical Orifice Cleaning***

The critical orifice can become clogged so that the flow into the AMS is reduced, which can affect the TOF distributions. Therefore, the critical orifice must be removed periodically and cleaned.

- Close the inlet valve on the AMS
- Loosen or remove the plate holding the inlet line in place.
- Loosen the ultratorr connections on either side of the critical orifice and remove the critical orifice housing.
- Remove the critical orifice from the housing with tweezers.
- There are three ways to clean the critical orifice:
  - Place the critical orifice in a small container with water or solvent and swirl it around and then take the critical orifice out and dry it. Repeat as needed.
  - Use thin (30 $\mu$ m) wire to unclog the critical orifice
  - Use a sonicator.

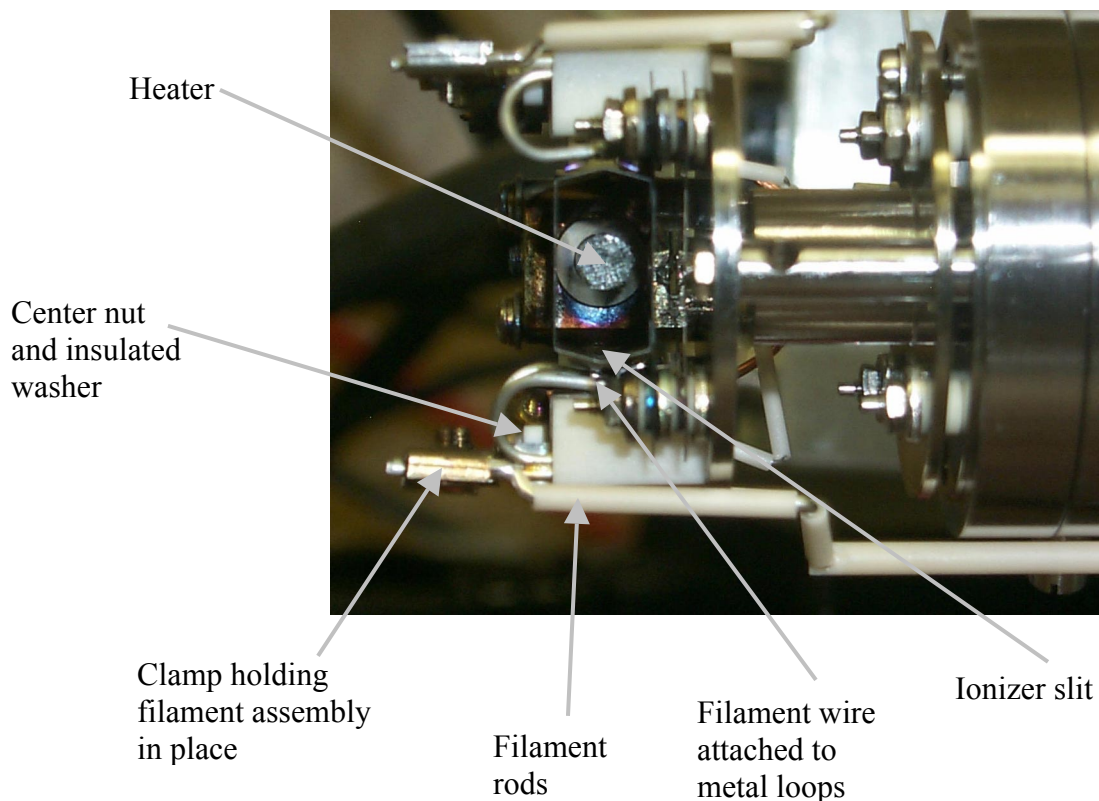
- Replace the critical orifice in the housing; making sure that the “dimple” or depression is facing out toward the incoming airflow.
- Insert the critical orifice housing and tighten the ultratorr fittings.
- Open the valve and note the change in flow rate.

*NOTE: Sometimes closing the inlet valve, waiting a few minutes and then opening the inlet valve quickly can remove the clogging. However, this is usually a temporary measure and the critical orifice should be cleaned as soon as possible.*

### ***Filament Replacement***

Over time, the filament wire becomes thinner until it breaks. When both filaments have been used up it is time to replace them. Used filaments can be refurbished for a small fraction of the cost of a new pair, so it is usually a good idea to have two complete sets available so that one set can be used while the other set is being restored.

- Vent the AMS as described in the ***Initial Procedures*** section.
- Carefully remove the QMS, being careful not to damage the rods, and place it on a clean or covered table.
  - Cover the QMS opening in the AMS to prevent anything from falling inside.
- With a small screwdriver, remove the 2 clamps holding the filament assembly to the electrical control rods (wear gloves to avoid contaminating the QMS).
- Remove the nut and insulated washer from the center of the filament assembly.
- Gently pull the filament assembly out.



- Insert new filament assembly and replace central nut/washer and holding clamps.
  - Align filament wire by the metal loops holding the wire with the ionizer slits.  
*Note: Use the metal loops because the filament wire is attached to these loops and the rest of the filament assembly may not be straight.*
  - Double check that the wire is visible through the slit (look from where the heater is located).
- Turn the QMS over and repeat for the other side.
- Replace QMS in AMS, tighten flange bolts evenly and begin the pump down procedure as described in the ***Initial Procedures*** section.
- Check that both filaments work by pressing *ion src* in the *operation* group on the Balzers control unit and setting the filament to “1”, turning on the filament (check settings in *emiss*—emission current should be set to 0.1 mA—and press *filam* in the *operation* group. Then go back to *ion src* and set the filament to “2” and repeat the process.

### ***Chopper Replacements***

There are three things in the chopper assembly that may require replacement: the chopper wheel itself, the chopper servo that moves the chopper to the open/closed/chopped positions, and the chopper motor that causes the chopper wheel to spin at a set frequency. In general, neither the chopper servo nor the chopper motor will require frequent replacement. The chopper wheel may be changed more frequently if the experiment or field study requires a different duty cycle (i.e., a chopper with wider or narrower slits). For all three of these activities, the chopper assembly must be removed from the chamber.

- Vent the instrument to atmosphere.
- Disconnect the chopper cable from the chopper flange.
- Remove the bolts holding the chopper flange in place.
- Note the exact orientation of the flange by making a mark or scratch across both the chamber body and the chopper flange if there is not already a mark (otherwise, the chopper may have to be realigned).
- Carefully remove the chopper flange from the chamber, avoiding touching the chamber walls with the chopper assembly attached to the flange.
- Follow the procedures below to replace the chopper wheel, servo, or motor.
- After replacing any of the three items mentioned above, make sure the o-rings and chamber surfaces are clean.
- Carefully insert the chopper assembly and flange.
- Line up the chopper flange with the mark or scratch on both the chamber and flange.
- Insert the four bolts holding the flange in place and tighten each one evenly so the mark or scratch on the chamber and flange remain lined up.
- Pump down the instrument and make sure there are no leaks.
- If necessary, check the servo position to make sure that everything is still lined up correctly.

Chopper wheel replacement:

- Remove the four screws holding the chopper wheel in place and then remove the wheel.
- Place the replacement wheel in place, lining up the screw holes.
- Insert and tighten the screws.
- Make sure the chopper wheel moves freely.
- Change the chopper duty cycle in the *Hardware* tab of the *Default Menu* in the AMS software.

Chopper servo replacement:

*To be added*

Chopper motor replacement:

*To be added*

## Appendix 1.1: Calibration Scheduling

There are a large number of checks and calibrations that must be performed to keep the AMS operating in peak condition. Keeping track of these can sometimes be difficult, so it may be a good idea to monitor them on a regular schedule. Below is a suggested schedule; this should be modified to account for the instrument, environmental conditions, and the experiment performed. In addition, there is software under development to track these items, particularly in field conditions. Many of these calibrations/checks produce a screen display that should be copied and pasted into a paper or electronic (e.g., power point file) logbook or a spreadsheet. Any or all of these can be performed if the instrument is not running properly as a diagnostic aid. The instructions for performing these calibrations/checks are located primarily in the *Calibrations* section.

Check or Calibration	Frequency	Output/Use	Comment
Mass Offset	Daily	Drifts with conditions	Changes signal strength
Signal Summary	Daily	Summary screen-paste into logbook	General instrument performance
Inlet Flow	Daily or more frequently if high mass loading or humidity	Determines if pinhole needs to be cleaned	~1.44 cm <sup>3</sup> /s with 100 μm pinhole –causes errors in size distribution
Turbo Performance	Daily	Tracks pump performance	Lower speed, higher current – replace pump
Chamber Pressure	Daily	Determines background	Only for older configurations
Multiplier (EM)	Every 3-4 days; when AB decreases to 70%; beginning new experiment	Determines EM gain	May be done more often, only concern is wear on multiplier
Mass (NH <sub>4</sub> NO <sub>3</sub> )	Every 3-4 days	Determines ionization efficiency	
Size	After moving or every 6 months	Determines velocity calibration	
Lens Position	After moving or inlet change	Determines where particle beam is aimed	
Collection Efficiency	After moving or every 6 months	Comparison of EM and Faraday collection	
Tuning QMS	After moving or major change in instrument	Increase in signal	Perform only when necessary; can change ionization efficiency
Resolution	After moving or every 6 months	Determines optimum peak shape	
Servo	After moving, every 6 months, TOF/MS AB <<1	Determines if chopper in correct position	

## Appendix 1.2: Technical Information

### 16 mm QMS Specifications: *To be Added*

System	Amps	Volts	Watts	Weight (pounds)	Mass (kilos)
Vacuum Chamber _ Turbo Pumps (Load) _ Cooling Fans Backings Pump					
Detection Balzers QMS Balzers Ionizer Control RF Box					
Rack Mount Boxes Turbo Control Box Chopper/Heater/Mult. Supply AC/DC 24 V Supply					
Data Acquisition Rack Mount Computer					
		<b>Total</b>			

### 8 mm QMS Specifications:

25.5" Long Chamber

Weight includes fiberglass frame (~ 12 lbs), cooling fans, and pressure gauges

Volume ~ 3'x2'x2'

Electronics fit into half rack

System	Amps	Volts	Watts	Weight (pounds)	Mass (kilos)
Vacuum Chamber <sup>1</sup> 5 Turbo Pumps (Load) 5 Cooling Fans Backings Pump <sup>2</sup>	7.2 0.625 2	24 24 24	172.8 15 48	96.5  18	43.9  8.2
Detection Balzers QMS Balzers Ionizer Control RF Box	0.9	115	103.5	28 26 11.5	12.7 11.8 5.2
Rack Mount Boxes Turbo Control Box Chopper/Heater/Mult. Supply AC/DC 24 V Supply SenTorr P. Gauge Controller	2  0.1	24  115	48  11.5	11.5 7.5 9.5 6	5.2 3.4 4.3 2.7

Data Acquisition Rack Mount Computer	0.6	115	69	29	13.2
		<b>Total</b>	<b>467.8</b>	<b>243.5</b>	<b>110.7</b>

<sup>1</sup> All DC powered components can operate with a maximum input voltage of 32 VDC.

<sup>2</sup> AC powered diaphragm backing pump (MD60) uses 2.5 amps at 115 VAC.

For optimal performance, the Balzers control unit must be set correctly. Below is a list of the important Balzers settings.

Button	Setting	Sub-Setting	Value
Detect	Type		SEM or EXTERN
Config	System	QMA	430
		Mass-R	300 (can be changed for a different mass range)
		Detect	SEM
		IS-Type	Spec+
		Option	No
	Ctrl	Mode	CS422 (panel) or ASCII (computer)
		Sem+Fil	Intern
	Simul		Off
Emiss	Emiss		2.5mA (0.25mA on modified IS-420)
	E-Prot		3.8 A to 4.2 A
V1-V6	V1 (Ion Ref)		83 V (standard is 90 V)
	V2 (Cathode)		70 eV (no change unless want softer ionization)
	V3 (Focus)		11 V
	V4 (Field Axis)		14 V (controls peak shape)
	V5 (Extraction)		282 V
	V6 (Defl. Inner)		26 V
V7	V7 (Defl. Outer)		13 V (should be ~ 1/2 of V6 voltage)
	V8		3 V
	V9		37.5 V
Ion Src	Mode		Normal
	Type		Spec+
	Filam		1 or 2
Filam			On or Off



Below is a list of most of the vendors that provide components for the AMS. This list is constantly changing, so do not expect that the prices are current – double check part numbers and request specific price and availability quotes from the vendors.

Vendor	Part Number	Part Description	Cost (USD)	Comment
<b>Varian Vacuum</b> 121 Hartwell Ave Lexington, MA 02173 800-882-7426		V250 Turbo, ISO 100 flange		
	9699365	V70LP turbo pump, ISO 63 flange	3,830.00	
	L91223010	Convectorr cable, 10 ft.	47.00	
	L91103030101	SenTorr controller UHV2c, w/degas and RS232 opt.	1,720.00	
	MSP B0387	MBA-100 gauge on 2-1/8 CCF	245.00	Special
		MBA-100 ionization gauge on 2-3/4" CFF		
	R11723010	MBA-100 cable 10 feet	105.00	
	9499411	MD60 Diaphragm pump, 120V, 60Hz	2,776.00	Required if DC pump insufficient
	9499412	MD60 Diaphragm pump, 220V, 50Hz	2,776.00	
	FG0212CI	Copper gaskets for 4-1/2" CFF, 10 pack	13.00	
FG0275CI	Copper gaskets for 2-3/4" CFF, 10 pack	17.00		
FG0450CI	Copper gaskets for 2-1/8" CFF, 10 pack	25.00		
<b>SPI Supplies</b> 509 Gay Street West Chester, PA 19381 800-242-4774	P6120-AB	Platinum aperture disc, 6.35 mm OD x 120 um hole	52.00	Inlet pin-hole disc, spares
	P6100-AB	Platinum aperture disc, 6.35 mm OD x 100 um hole	52.00	
	14140	ETP Electron multiplier, AF140 (Replaces Balzers model SEV 217)	995.00	<b>Always have spare</b>
<b>SGE, Inc</b> 2007 Kramer Lane Austin Texas 78758 800-945-6154				
		Supplier of ETP multipliers		
<b>Scientific Instruments Sales and Service, LLC</b> 2200 Spanish Oak Trail Round Rock, TX 78681 512-259-8298 (Larry Garretson)				
<b>Pfeiffer Vacuum</b> 24 Trafalgar Square Nashua, NH 03063-1988 603-578-6500	BN 845088-T	Tungsten filament set	420.00	<b>Always have spare</b>
	BG521611-X	SEV 217 CuBe electron multiplier	1,250.00	

		SEV 218 CuBe multiplier with conversion dynode	2,500.00	
<i>In U.K., Pfeiffer Vac., Bradbourne Drive, Tilbrook, Milton Keynes, MK 8AZ, UK, +44-(0)1-908-373-333</i>				
	HS-81	Hitech HS-81 servo w/Hitech connector	17.25	Spare chopper servos; can get at any RC model airplane/hobby store
<b>Servo City</b> 620 Industrial Park Winfield, KS 67156 877-221-7071				
	AL4028-2105	Hardigg polyethylene case for instrument shipping, white 42.75" L x 30.75" W x 29.24" H	701.00	
<b>Cases Cases</b> 107 Audubon Road Wakefield, MA 01880 781-245-5144				
<i>Local distributor for Hardigg cases, www.hardigg.com</i>				
	PMT-5	Analog preamplifier	654.00	
<b>Advanced Research Instruments, Corp.</b> 5151 Ward Road Wheat Ridge, CO. 80033 303-463-5500				
	MD1	Diaphragm pump 19L/min, 24 VDC	1,500.00	
<b>Vacubrand</b>				
		distributor for 80/20 extruded aluminum		
<b>Sprague Air Controls</b>				
	N726.4ANI	DC Diaphragm pump, 29 LPM, 2 amps, 24 VDC	~2,300.00	Might replace Varian MD60 AC powered pump. To be tested 8/00
<b>KNF Neuberger, Inc.</b> Two Black Forest Road Trenton, NJ 08691-9428 609-890-8600				
<b>Astrodyne</b> Myles Standish Blvd Taunton, MA 02780 800-823-8082	AS-320-24	300 Watt switching supply 24V/12.5A	169.00	AC-DC power supply for turbo pump box
	AS-60-24	60 Watt 24V/2.5A switching power supply	59.00	AC-DC power supply fro electronics box

	SP-500-24	500 Watt switching supply 24V/20A	235.00	AC-DC 20 Amp supply
<b>Pilgrim Electronics</b> 38 Union Street PO Box 311 East Walpole, MA 02032 508-668-3500	RX7-5-MB2-15- ST-P1IW	Differential pressure gauge, 0.1 inch water range	259.00	For AMS inlet flow
	RX7-5-MB2-15- ST-P5IW	Differential pressure gauge, 0.5 inch water range		
<b>National Instruments</b> 11500 N Mopac Expwy Austin TX 78759 512-795-8248	777270-01	BNC 2090 BNC termination panel	395.00	
	182419-01	SH6868 shielded cable, 1 meter	125.00	
	777475-01	PCI 6011E 5MHz, 4 input board	2,995.00	
	777743-01	PCI 6024E general purpose board	595.00	
	1525 - U - 012 - BRE	Brushless DC motor	93.83	Chopper motor
<b>Micromo Electronics</b> 14881 Evergreen Ave Clearwater, FL 33762 800-819-9516				
		Balzers ionizer filament repair	60.00/set	Takes about 3 weeks
<b>Scientific Instrument Service</b> 1027 Old York Road Ringoos, NJ 08551- 1039 908-788-5550				
	92N4765	Brushless DC fan, 3.62"x1.0", 24VDC	9.75	Turbo pump cooling fans
<b>Newark Electronics</b> 1-800-718-1998 <a href="http://www.newark.com">www.newark.com</a>				
<b>McMaster Carr</b> PO Box 440 New NBrunswick, NJ 08903-0440 732-329-3200 <a href="mailto:nj.sales@mcmaster.com">nj.sales@mcmaster.com</a>	93306A583	5/16-18 x 1" aluminum bolts, box of 50	22.40	Bolts for flanges on AMS chamber
	93306A585	5/16-18 x 1-1/4" aluminum bolts, box of 100	26.01	Bolts for flanges on AMS chamber
	95601A325	Fiber washers, 5/16"ID x 9/16OD, pgk of 100	4.76	
<b>National Instruments</b> 512-794-0100	777475-01	PCI-6110E 5 MHz 4-input board	2,995.00	
	777743-01	PCI-6024E general purpose board	595.00	

	777270-01	BNC-2090 board	395.00	
	182419-01	SH6868 shielded cable, 1 meter	125.00	

## Appendix 1.3: Issues and Upgrades

Below is a list of the current and future upgrades available for the AMS as discussed at the 2001 AMS Users' Meeting and a brief description of the reason they improve the instrument performance. This list is constantly updated, so please contact Aerodyne Research for more complete information about any of these items.

### 16 mm Quadrupole

- More ion transmission, especially for large  $m/z$  ( $>100$  amu)
- Not much benefits proven for low masses
- Adds ~ 30 lbs
- Price: ~ \$52,000 (Without electronics box: ~ \$42,000)

### Conical Heater with Thermocouple

- Reduces particle bounce
- "Nicer" single particle histogram
- Direct temperature measurement
- Price: ~ \$2500

### New Aerodynamic Lens and adjustable Inlet

- Better transmission for small particles, 50% cut-point shifted down to ~ 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: ~ \$2000

### Conversion Dynode Multiplier

- Eliminates the mass dependence of the multiplier gain
- Reduces ion collection efficiency (needs further investigation)
- Price: ~ \$4000

### Differentially QMS and Ionizer Chamber

- Improves water-vapor background significantly → possible to measure particle water content
- Improvement of ammonium measurement (at  $m/z$  16)
- Adds another pump to the system
- Price: ~ \$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 ~ 50 W to the power load
- Price: ~ \$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-volatilized 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

### The Conical Heater

The heater is used to vaporize the particles that come into contact with it. It is resistively heated to several hundred degrees Celsius. The heater current and voltage (and temperature on the newer instruments) is displayed on the Aerodyne Electronics unit.

The basic heater is a cylinder of about 6 mm length and with a diameter of about 3 mm. The front end, where the particles impact, is flat. To increase the deposition efficiency of the particles, a fine grid is spot welded on the heater. In theory, particles are trapped in the meshes and vaporized efficiently.

For ammonium nitrate particles the single particle counting efficiency is about 100 % for particles above approximately 300 nm. However, ammonium sulfate particles are less efficiently counted. Only about 20 % of the particles at the aerodyne instrument and 5 % at the SUNY instrument are counted as single particles (with a new lens and the 250 l/s pump at the ionization chamber, the SUNY AMS reaches now about 15 to 18 % counting efficiency for 350 nm particles.)

One explanation of this behavior is that ammonium sulfate particles tend to bounce off the heater before being vaporized. To reduce the loss due to bouncing a new heater was manufactured, which had a conical shape at the front. The heater was made from porous tungsten (80 % and 50 % density material) to provide good sticking efficiency for the particles.

After installing the new heater the sodium ( $m/z$  23) and potassium ( $m/z$  39) signals in the MS mode were very large. The large surface of this porous material contained many impurities and so produced large amounts of sodium and potassium, which were ionized on the hot heater surface without electron impact ionization. This intense background signal decreased significantly after several days.

The single particle collection and counting efficiency did not improved with this new heater, not at the SUNY instrument (80 % density material, counting eff. 5 %), nor at the Aerodyne instrument (50 % density material; counting efficiency 15-20 %). However, the single particle ion statistics were improved with the new heater design. The histogram of the number of counted particles with different ions per particle in the single particle window (press *insert* from TOF window) showed a nice gaussian distribution with the new heater. With the basic heater this distribution was always skewed – probably due to particles trapped at the edge of a mesh wire that form an evaporation plume in a certain direction.

Also the TOF distribution, and therefore the size distribution, measured with the new heater was significantly narrower compared to measurements with the old heater under the same DMA conditions. The distributions had now a much “nicer” gaussian shape than before. Obviously the particles collected on the heater “see” a more homogeneous surface at the heater (no spot-welded mesh) and are vaporized faster (no long tail in the time of flight distribution).



## Appendix 1.4: Publications and Online Resources

Aerodyne Research has created several mailing lists that are available to any AMS user. Go to the Aerodyne Research website (<http://aerodyne.com/>) or follow the directions below. There is also an ftp site available for transferring information, but you must have a username and password to use it.

### Mail Lists

- 1.ams-users: Please participate in this list for discussions that are of general interest to all Aerosol Mass Spectrometer users.
- 2.ams-igor: Select this list if you are interested in detailed discussions of the IGOR programs that are used to analyze AMS data.

You can send specific AMS software/hardware technical support questions to all appropriate Aerodyne personnel through [ams-support@aerodyne.com](mailto:ams-support@aerodyne.com).

*Note: These lists have been designed to separate the general issues of AMS users from the more specific concerns of only a few users. Please address questions/comments to the appropriate list.*

### To Subscribe

- 1.Double click on the list(s) you want to join. This will launch an e-mail from you to the request address of the list (the request address is the listname followed by: - request@aerodyne.com, example: [ams-users-request@aerodyne.com](mailto:ams-users-request@aerodyne.com)).
- 2.Include the word subscribe in the body of the message.
- 3.A message will be returned to your mailing address containing an authentication key. You will not be subscribed to the list until you return the proper authentication key.

### To Send Messages to List

Send an e-mail to the list address. The list address is the listname followed by: @aerodyne.com, example: [ams-users@aerodyne.com](mailto:ams-users@aerodyne.com).

### To Unsubscribe from List

Send an e-mail to the e-mail address [majordomo@aerodyne.com](mailto:majordomo@aerodyne.com) with the word unsubscribe followed by a space and the listname (i.e. unsubscribe ams-users)

There is also information about the AMS, as well as a lot of general aerosol information, available at the AMS Web Page: <http://www.its.caltech.edu/~jljimene/ams.html>.

Below is a list of some of the recent publications involving the AMS, a more extensive list can be found on the AMS Web Page.

- Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Technol.*, 33, 49-70, 2000.
- Jimenez, J.L., J.T. Jayne, Q. Shi, C.E. Kolb, D.R. Worsnop, I. Yourshaw, J.H. Seinfeld, R.C. Flagan, X. Zhang, K.A. Smith, J. Morris, and P. Davidovits, Ambient Aerosol Sampling with an Aerosol Mass Spectrometer. *J. Geophys. Res. - Atmospheres*, in press, March 2002.
- Middlebrook, A., Murphy, D.M., Lee, S.-H., Thomson, D.S., Prather, K. A., Wenzel, R. J., Liu, D.-Y., Phares, D.J., Rhoads, K.P., Wexler, A. S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., and Flagan, R.C. An intercomparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project. *Journal of Geophysical Research-Atmospheres*, in press, 2002.
- Morris, J. W., Davidovits, P., Jayne, J. T., Jimenez, J. L., Shi, Q., Kolb, C. E., Worsnop, D. R., Barney, W. S., and Cass, G.R. Kinetics of submicron oleic acid aerosols with ozone; a novel aerosol mass spectrometric technique. *Geophysical Research Letters*, in press (Feb. 18, 2002).
- Allan, J.D., Jimenez, J.L., Coe, H., Bower, K.N., Williams, P.I., and Worsnop, D.R. Quantitative Sampling Using an Aerodyne Aerosol Mass Spectrometer. Part 1: Techniques of Data Interpretation and Error Analysis. Submitted to the *Journal of Geophysical Research – Atmospheres* (March 22, 2002).
- Allan, J.D., Coe, H., Bower, K.N., Williams, P.I., Gallagher, M.W., Alfarra, M.R., Jimenez, J.L., Worsnop, D.R., Jayne, J.T., Canagaratna, M.R., Nemitz, E., and McDonald, A.G. Quantitative Sampling Using an Aerodyne Aerosol Mass Spectrometer. Part 2: Measurements of Fine Particulate Chemical Composition in Two UK Cities. Submitted to the *Journal of Geophysical Research – Atmospheres* (March 22, 2002).
- O'Dowd, Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Kulmala, M., Pirjola, L., and Hoffmann T., Particle Formation in the Marine Atmosphere Controlled by Biogenic Iodine Emissions. *Nature*, in press (March 20, 2002).
- Jimenez, J.L., Cocker, D.R., Bahreini, R., Zhuang, H., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., Hoffmann, T., and O'Dowd, C. New Particle Formation from Photooxidation of Diiodomethane (CH<sub>2</sub>I<sub>2</sub>). New Particle Formation from Photooxidation of Diiodomethane (CH<sub>2</sub>I<sub>2</sub>). *Journal of Geophysical Research - Atmospheres*, Submitted (April 16, 2002).

## Appendix 1.5: Basics of Mass Spectrometry

Note: Much of the following information is taken from various Balzers manuals.

### *Ionization*

Ionization refers to the process of stripping off an electron to give a positive ion. Low-energy electrons bombard gaseous atoms/molecules and a small proportion is ionized (both single and multiple positive charges). The energy of the impact electrons influences the number type of ions that are formed.

Ionization begins at a minimum electron energy (ionization potential) and the number of ions formed increases until reaching a maximum at 50-150 eV (70 eV is standard for the AMS) and then decreases again. Fragmentation of the base ion and rearrangements can occur in addition to ionization. Fragmentation can be influenced by ionization energy, temperature, and properties of the analyzer.

### *Separation*

Different ions are separated by their mass/charge ratio by an electric field. Four hyperbolic rod electrodes (approximated by cylinders) generate a high-frequency quadrupole electric field. Ions entering this region in the direction of the axis oscillate at 90° to the field axis because of the high-frequency electric field. Some ions pass through the mass analyzer to a detector (stable: those with a limited oscillatory amplitude), while others hit the rods and are neutralized and pumped away (unstable: those with a continual amplitude increase). The masses can be scanned by varying the frequency or the voltage to obtain a linear mass scale.

There is a decrease in transmission with mass number (because of the increase in resolution with mass number?), called “mass discrimination.” If the rod system of the quadrupole is sufficiently precise and the ion source produces the correct conditions for injection of ions, this can be avoided.

### *Detection*

Ions are detected electrically based on their mass/charge ratio. Since the ion currents are very small, an electron multiplier, which can amplify the current, is used for detection. Positive ions strike the initial surface (dynode) of the multiplier and an electron is released from the surface to strike the next surface, where each incident electron releases a large number of secondary electrons, which then strike the next surface, etc. The electron multiplier can give gains of  $10^4 - 10^8$  per ion. Also, since the ions are deflected into the multiplier from a straight-line path, there should be no false signals.

There are several issues to consider when using an electron multiplier. The number of electrons released from the initial surface depends on the ion mass, type of ion, and ion energy. The energy of the incident ion corresponds approximately to the operating voltage on the electron multiplier, which can cause the conversion rate for masses greater than 100 amu to decrease with increasing mass. Also, the surface of the dynodes that emit the secondary electrons can change, thus altering the output of the secondary

electrons. This issue makes the determination of the gradual drift in the gain over time essential. The measurement of the single ion signal (ions/electron) quantifies the behavior of the multiplier.

Ions can also be detected using a Faraday collector. Ions strike a collector where they give up their charge. The current is converted to voltage to form an output signal proportional to ion current. Since the Faraday collector is located on a straight line from the quadrupole, it should provide a minimum limit on the number of ions available for measurement. However, “false” ions can get through to the Faraday collector and give an inaccurate measurement. (The limit of measurement is  $\sim 10^{-16}$  A for a time constant of several seconds.)

## **QMS Voltages**

### *V1: Ion Reference (IonRef)*

“IonRef” is the nominal potential on which the ions are formed (the actual effective potential is slightly lower) and is the reference potential for all other potentials. According to the Balzers operating manual, the IonRef should be set slightly higher ( $\sim 20$  V) than the electron energy (V2 Cathode), so the Cathode is on a positive potential referenced to ground and no electrons are emitted to the environment (prevents interferences with the Faraday cup and other equipment??).

- At low values (25 – 40 V), the sensitivity for lower masses is higher (and the max sensitivity for higher masses is reached at higher values).
- The higher IonRef setting, the lower the mass discrimination (sensitivity decreases with higher mass numbers).

### *V2: Cathode*

This determines the acceleration voltage of the electrons and therefore the nominal ionization energy. The cathode is normally set to 70 eV.

### *V3: Focus*

The focus should be adjusted to maximize the peak level. The extraction and focus voltages are related and must therefore be optimized when one changes.

### *V4: Field Axis*

This is the potential in the axis of the quadrupole field. It acts as a decelerating voltage, causing the ions to remain in the rod system long enough to be resolved. It is the nominal voltage of the ions in the rod system. The field axis depends on the frequency and analyzer type: lower frequencies (higher mass ranges) or shorter rod systems require lower ion energy because the ions must stay in the mass filter longer to be resolved.

The field axis is also related to the resolution. A higher field axis value will give higher peaks, but if the field axis is too high, the resolution decreases and the peak shape deteriorates.

*V5: Extraction*

This accelerates the ions from the ionization area towards the rod system. The focus voltage is related to the extraction voltage and must be optimized if the focus is changed.

*V6 (inner plate) / V7 (outer plate): Deflection*

These voltages direct the ions through the 90° turn to reach the electron multiplier. The polarity of these potentials is opposite that of the ion polarity, so that the ions are accelerated from the mass filter and then directed toward the electron multiplier.

Deflection can be performed in two modes: one deflection voltage and two deflection voltages.

*One deflection voltage:* This mode uses only the inner plate to direct the ions to the multiplier. The outer plate is grounded to the Faraday cup. Typical deflection values used in this mode are 180 V – 220 V. The optimal deflection voltage is determined by IonRef (the ion formation potential) and also by the multiplier voltage to some extent. A higher IonRef voltage requires a higher deflection voltage.

*Two deflection voltages:*

This mode uses both the inner (V6) and outer (V7) plate voltages to direct ions to the electron multiplier. Typical settings are ~ 15 V for the inner plate and ~ 30 V for the outer plate (the voltage on the inner plate should be approximately half the voltage on the outer plate).

*Place Holder For Future Additions To Manual Part 1.*

# AMS MANUAL PART 2

## *Overview of AMS Screens*

### **The Main Menu**

The main menu/starting window appears immediately after starting the AMS program. It contains a message box to type in messages, which will be stored with the data files. The content of the two text boxes 'Researcher(s) Operating AMS' and 'Experiment Being Conducted' are also saved together with the data files. Fill in The operator's name and the name of the experiment if appropriate.

18 buttons are displayed to choose different settings, measurement, tuning or information windows. These buttons are described briefly below:

#### Settings:

- The 'Parameter Menu' button brings up the parameters window with several tabs to select all parameters concerning AMS operation (described below).
- The 'm/z Steps for TOF Mode' button brings up the 'F6 window' to select the masses that are scanned in the ToF mode (described below).
- The 'Change Default Settings' button brings up a default menu window with tabs that contain further menu parameters that control AMS operation (described below).

#### Measurement Modes:

- The 'Time-Of-Flight' button brings up the ToF window and starts the measurement in the ToF mode (described below).
- The 'Mass Spectrum' button brings up the MS window and starts the measurement in the MS mode (described below).
- The 'Alternate TOF – MS' button first brings up the ToF window and starts the measurement in the 'alternate' mode, toggling between ToF mode and MS mode with sampling intervals as set in the parameters window.
- The 'Exit Program' button ends the program.

#### Diagnostic Modes:

- The 'Raw Signal' button brings up the raw signal window for diagnostic of this signal (described below).
- The 'Tune Balzers Mass Spec.' button brings up the windows used for tuning the Balzers mass spectrometer and starts the tuning procedure to optimize the voltages at the ionizer and ion deflection system (described below).
- The 'Calibrate Electron Multiplier' button brings up the windows used for calibration of the electron multiplier and starts the calibration procedure of the gain(described below).

- The ‘Calibrate Servo Position’ button brings up the windows used for calibration of the servo position and starts the calibration procedure which sets the optimal servo positions for open, chopped and blocked beam (described below).
- The ‘Check Air Beam’ button brings up a window that contains a summary of AMS signals that are being observed (Described below)

#### Help & Information

- The ‘Command Help’ button brings up the command help windows with short descriptions of the commands that can be used in the ToF, MS and Single Particle windows (described below).
- The ‘On-line Manual’ button has no function at the moment.
- The ‘Particle Calculator’ button brings up the particle calculator window to make simple calculations of particle properties (described below).
- The ‘AMS Email List Web Page’ button brings up the Netscape Navigator and connects to the web page of the AMS Email List, which is used to connect all AMS users and helps them sharing their experiences.
- The ‘AMS Outgoing FTP Site’ button brings up the Netscape Navigator and connects to a read-only ARI FTP site where some AMS manuals can be found.
- The ‘AMS Incoming FTP Site’ button brings up the Netscape Navigator and connects to the Aerodyne read/write FTP Site. Access to this site is restricted to those with approved username/password combinations. Once the connection to the ARI ftp site is made, the login dialog can be brought up by clicking on the right mouse button.
- The ‘NIST WebBook (EI-MS Info)’ button brings up the Netscape Navigator and connects to the NIST WebBook page, which contains MS data on many compounds.

#### The TOF Mode

The TOF Mode is used when the AMS is operating to obtain chemically speciated size distributions. This information is obtained by modulating the particle beam by a chopper and measuring particle time-of-flights through the known distance from the chopper to the detector. Typically the chopper is operated around 100 Hz (time between consecutive chopper openings about 10 ms). Since the quadrupole scan rate is 1 ms/amu the quadrupole cannot be scanned through the entire 0-300 amu mass range during one period of one chopper cycle. Thus the particle signal is detected with the quadrupole set at a few (10-30) selected masses during each chopper cycle. The TOF masses can be selected in the m/z settings window which is described below. The rate at which the quadrupole switches between TOF masses in this mode is fixed at 3.3 Hz. The data is acquired at 1-5 MHz (the rate can be selected in the parameter menu- “data acquisition boards” tab) and subsequently coaveraged down to 100 kHz such that the time step for TOF data is equal to 10 us (Note: this is often referred to in this manual as TOF time step). Further coaveraging can be performed by setting time steps per avg sig point menu parameter in the “averaging and saving” tab to a number >1.



## TOF Window:

The Time-of-Flight Window consists of a row of parameter labels on the left of the window and five graphs on top of each other, showing different information versus flight time, on the rest of the windows:

### ***Information labels:***

*The information labels provide status information about a variety of AMS operating parameters. The information labels are yellow or green in color when the AMS is operating within normal parameters. Label colors of orange and red signify increasingly important degrees of warning about parameter values that are outside normal operating parameters.*

- t El: Real time, elapsed since the last restart (F5) of the measurement.
- sam: Sampling time, elapsed since the last restart of the measurement. This is the real time corresponding to actual data analyzed.
- An: (% Retrieved TOF data buffers that are completely analyzed); B: (% TOF data buffers that are retrieved for analysis) ;Sp: (Spare Duty Cycle- % elapsed time that computer is finished with displays and calculations and is waiting to receive new data to analyze. When # close to 0, An and B could be <100%)
- Status of TOF mode ( Not alternating/Alternating)
- Rate/xx: Actual Sampling rate in TOF mode/Number of points covered (set in The averaging and saving tab of the parameter menu).
- m/z: Switching rate between TOF masses – this is hardwired to 3.3Hz
- n: Number of completed TOF Mass cycles
- C: Chopper frequency in Herz; SNR: Signal to noise ratio for photodiode, measuring the chopper signal.
- Dmax: Maximum particle diameter that can be measured with the actual chopper frequency. Particle diameter which corresponds to the maximum flight time, displayed in the graph.
- Inlet Flow: Inlet flow into the AMS in cm<sup>3</sup>/s. Typically about 1.5 cm<sup>3</sup>/s.
- Mult., G: Actual multiplier voltage in kV and actual multiplier gain according to the last multiplier calibration.
- P Ioniz.: Pressure in detection chamber in Torr- This is not connected for most instruments
- CT: Pressure at the two high vacuum gauges in Torr- This is not connected for most instruments
- RMS: Root mean square of the Raw Signal in bits and in mV; Rel: Raw Signal noise relative to low electronic noise benchmark of 0.12 bits.
- swRMS: Root mean square of Raw Signal in bits and in mV after it is averaged over appropriate sliding window.
- AvRMS: Root mean square of the noise in the average signal in bits.
- AMS p/cc: Average of calculated particles per cm<sup>3</sup> for the actual averaging cycle. Calculated from the number of single particle events per second and the inlet flow.
- AMS p/s raw: Actual particles per second counting rate of the AMS.

- CPC p/cc: Actual CPC reading of particles per  $\text{cm}^3$ . The colored point behind the value indicates if a CPC is connected. If a CPC is connected and this CPC seems to work properly the point is green, otherwise it's red. The label will also change colors from yellow to orange if CPC is not connected.
- CPC Avg: Average of CPC reading of particles per  $\text{cm}^3$  and one standard deviation of this value for the actual averaging cycle. The color of the label background indicates the stability of the CPC reading: If the standard deviation is less than 10 % of the average value it's green, if it is outside this range, it's red.
- n AMS/CPC: Percentage of particles counted by the AMS of particles counted by the CPC. For monodispersed aerosol of sufficient particle diameter this value should be around 100 %.
- Mass CPC: Calculated mass concentration and standard deviation for CPC reading calculated assuming test particles of size and density as set in the parameters window.
- Mass A/C m/z xy: Ratio of mass concentration measured by the AMS to mass concentration calculated from CPC reading for m/z xy.
- i/p m/z xy: Number of ions per single particle for mass xy. This number is calculated by dividing the average number of xy ions per TOF determined for an averaging period by the total number of single particles counted over that time period. Note that the average number of ions per TOF for a given mass is calculated over the ENTIRE TOF here rather than between a particular set of region markers. If the number of particles counted by CPC is not equal to zero (which it would be if the CPC was not connected), then the counted particle number used in this calculation comes from the CPC counts/cc. If the CPC counts are equal to zero, then the particle number that is used is equal to the total number of particles counted at the appropriate mass xy during the averaging time period.
- AB: Intensity of the air beam signal in Herz. This signal is only measured when the mass, typically m/z 28, which is used to measure the air beam (set in the parameters window) is scanned. If no air beam - mass is scanned, this label is displayed in red and shows: 'xy not scanned'. Since the air beam is supposed to be constant over time, changes in airbeam signal are a useful measure of changes in multiplier gain.
- T Amb. ( C ): Ambient temperature in degrees Celsius. Only a reasonable number if temperature sensor is connected.
- Bits\*Step/Ion: Peak area of single ion signal in bits (intensity) \* time steps (10 $\mu\text{s}$ , width of peak). Important for calibration of multiplier.
- mV\* $\mu\text{s}$ /Ion: The same in other units (signal intensity in mV, time in  $\mu\text{s}$ ).
- a% / b% /c%/d%: This label signifies the % of total avg TOF signal in region1,region2,region3, and region4 as signified by the region markers set in the menu.
- TOF w/SP m/z xy: Percentage of time-of-flight cycles that contain single particle events for mass xy.
- SP pts. x of y: Number of pts x out of total pts y in the single particle buffer that contain single particle information. When  $x > y$  then the single particle buffer is reinitialized. Note: When TOF mode is initialized, a single particle buffer w/ y

- pts is created to hold detected single particle signals. The number of points saved for each single particle event that crosses the threshold is determined by parameters set in the single particle tab of the menu.
- SP Threshold: Auto (.7): Button to start automatic single particle threshold setting by right mouse clicking on it.
  - m/z steps in TOF Mode: List below this label shows the masses that are scanned in the ToF mode in different colors. These colors are also used in the ToF graphs to represent the data versus flight time. Every list entry has the same form. The entry: ‘m46 p1850 m17.33 c80%’ means: Mass 46 amu is scanned, in the current averaging cycle 1850 single particles are counted, the nitrate equivalent mass loading calculated for m/z 46 is 17.33  $\mu\text{g}/\text{m}^3$ , 80% of the mass at m/z 46 is counted by the AMS.

### TOF Graphs:

**Graph # 1: Area of Single Particles vs. ToF:** In this graph the signal area (in units of bit steps) for each detected single particle is plotted as a function of the particle’s time-of-flight. On the left side of the graph the numbers at the top and bottom of the graph indicate the y-axis scaling of the graph. The label on the right side of the graph shows the actual position of the mouse as time of flight and calculated aerodynamic diameter (using to the actual TOF calibration and the particle density as indicated in the parameters window). The y-value of the mouse position is shown as well in bits.

**Graph # 2: Histogram of Single Particle Count vs. TOF:** In this graph the number of single particle events per histogram bin per cc for the different flight times is shown. Again the y-axis scaling is shown at the left side of the graph.

**Graph # 3: Raw Signal, Threshold, and Single Particles Detected vs. TOF:** This graph shows the ion signal measured at an individual m/z as a function of particle time-of-flight (Time after chopper start signal) for the most recently analyzed TOF cycle. The raw TOF ion signals are smoothed according to the sliding window prescribed in the ‘F6’ window and this smoothed signal is displayed in the graph as a green trace. Single Particle Events – all events, when the MS signal at a given mass exceeds the single particle threshold for this mass – are printed on this graph as peaks in the color which represents the mass at which they are measured. The single particles displayed can be toggled between all single particles observed for that m/z since the start of averaging or all new particles observed for that m/z since the last display by the keystroke “B”. The mass number of the active mass always is printed on the top right corner of the graph. If multiple masses are stepped, the ‘active’ mass is printed in the front of the graph in ‘it’s’ color and the single particle events of the other masses are printed in ‘their’ color in the background of the graph.

Two horizontal lined are printed in the graph. The horizontal green line indicates the zero level for this signal. The DC level, which is determined for each m/z by averaging the signal between the DC level markers ( The specific DC level markers to be used for the mass are chosen in the F6 window, and the DC level marker positions are chosen in the menu). The DC level is printed at the left side of the graph in bits and Herz (DC:). The DC level is calculated for and subtracted from each TOF trace. Thus it is very important that the DC markers are set properly. The black horizontal line indicates the

single particle threshold. This threshold should be well above the noise level to suppress single particle counts due to electronic and background noise. The level of the threshold is also printed on the left side of the graph (Th:). The y-axis scaling is again printed at the left top and bottom corner of the graph.

Many vertical lines are printed in graph: Vertical **Blue** lines: used to divide TOF into regions. These lines are particularly important during calibrations when Q=1 and Q=2 charged calibration particles need to be distinguished from each other. Region 1 is from start of TOF to 1<sup>st</sup> marker. Region 2 is between the two markers, and Region 3 is between 2<sup>nd</sup> blue marker and last TOF point. Set the marker positions in parameter menu. Vertical **Brown** Lines: 2 pairs of lines- 1 at start of TOF and other towards end. The regions within sets of brown lines are used to obtain a measure of DC level. Positions of the markers are set in the parameter menu.

**Graph # 4: Averaged Signal for Each Mass, for TOFs with and without particles vs. TOF:** This graph shows the averaged signals acquired from the different stepped masses since the beginning of the actual averaging cycle versus flight time. It shows the averaged sized distribution of the aerosol measured in the running averaging cycle. In the default mode only the averaged signal of the actual active mass (indicated at the right top of graph # 3) is printed in this screen. In this mode the averaged total signal (color, indicating the mass) is printed as well as the averaged signal due to all single particle events (in dark blue) as well as the averaged signal due to the measured non-single particle signal (the signal that doesn't exceed the single particle threshold in black). In another mode (which can be started by pressing the 'C' key) only the averaged total signals are printed, but for all masses at the same time. The active mass is printed in a textbox on the top right, followed by its measured average nitrate equivalent mass loading in ug/m<sup>3</sup>.

In this graph again a horizontal line indicates the baseline. The y-axis scaling is printed again at the left corner of the graph. Vertical lines in this graph again indicate the mean position of the size distribution and the DC areas ('DC'). The expected position of the airbeam with the current TOF calibration is indicated by the 'AB' marker. The 'EAB' marker indicates the end of the airbeam as set in the menu. Since this menu parameter is used in the calculation of the TOF AB signal, it is important that it be set properly (The AB signal area is calculated from the beginning of the TOF until the EAB timpoint). The end TOF marker which is set in the menu and is used to dimension TOF matrices that are saved ('E'). The vertical lines at the left and right corner of the graph indicate the time position of the chopper start and stop signal respectively. If the option to plot test particle is checked in the "Flow,Size and mass calibrations" tab of the parameter menu, vertical red lines appear to mark estimated TOF's for Q=1-5 particles. At the right corner of the graph a textbox shows the calculated parameters of the size distribution according to the ToF calibration and the particle density as set in the parameters window.

**Graph # 5: Time-of-Flight Chopper Signal:** This graph shows the chopper signal as measured with the photodiode at the chopper versus time. The rising chopper signal at the left side of the graph indicates the zero flight time. Also in this graph the y-axis scaling is printed at the left side of the graph.

In the middle of this graph some additional information about the actual measurement status is printed: The mass step and the actual active mass, the number of single particles counted in this mass setting, the counting efficiency for this mass setting compared to the CPC and the calculated particle mass concentration in  $\mu\text{g}/\text{m}^3$ . Below these information the actual chopper state is printed: Beam blocked, Beam chopped or Beam open. And the actual multiplier voltage is printed.

*Below these graphs in the border of the lowest graph on the left side of the boarder the saving state is printed as 'Not Auto Saving' or 'Auto Saving', depending on the saving conditions as set in the parameters window. On the right side of the boarder the last saved file (since the start of the program) and the date and time of the saving are printed.*

### The Single Particle Window

The Single Particle Window is used to display information about the average single particle events. It is particularly useful during manual calibrations of ionization efficiency and multiplier gain. The window consists of two large graphs on the top and a label area at the bottom.

**Graph # 1: Average Single Particle Signal:** This graph shows the average of single particle signals for the three Time-of-Flight regions as set in the parameters window, independent of mass at which these signals are acquired. The y-axis scale is printed as minimum and maximum value at the left side of the graph. The x-axis is divided into a couple of time steps (10  $\mu\text{s}$ ), each displayed as a vertical black line. The x-axis scale is indicated by the minimum and maximum value of the ToF below the graph. The color of the three average single particle signal shapes is the same as the color indicated below the graph for the three ToF regions. The green vertical line signifies the edge of the peak for peak width calculations. The single ion signal is shown as a yellow trace. The horizontal black line is the single particle threshold, the white line is the zero line and the blue line is the single particle bgd level calculated from a region of timepoints preceding the single particle threshold crossing event. The vertical black lines are ticks that mark TOF time points.

**Graph # 2: Pulse Height Distribution:** This graph contains a histogram, showing the number of single particle events for different pulse intensities. The red trace is the raw particle count distribution. The blue trace is the raw distribution weighted by the size of the signal. If there are no problems with the vaporization (all particles are vaporized equally) and the particles are large enough that all of them to lead to single ion signals well above the threshold, this pulse height distribution should have a gaussian shape for every particle size (for monodispersed aerosol). The x-axis scale is indicated as minimum and maximum value below the graph, the y-axis scale is indicated by these values at the left edge of the graph. Below the graph the standard deviation of the pulse height distribution and the ionization efficiency (IE) of the mass spectrometer is printed.

In the **label area** additional information about the single particle events are printed:

- Int. Time: Integration time since last reinitialization (F5).
- Ions/Part.: Number of Ions, counted by the multiplier (calculated from the multiplier signal using the multiplier calibration) per single particle event in

- region 2. If multiple TOF masses are being scanned, this will be an ions/part averaged over single particles detected at all m/z's. This number is calculated by dividing the total detected single particle ions in region 2 (irrespective of m/z) by the total number of single particles counted in region 2. The total detected single particle ions for particles in region 2 in the region is calculated by summing up the particle area for every detected single particle in region 2. The area is summed over timepoints ranging from 1/2 the single particle width (as defined in "Single Particles" tab of the menu) before the peak of the single particle threshold crossing event to the peak timepoint + single particle width. This single particle ion area is then divided by the number of single particles counted by the AMS in region 2. The ions per particle number is a measure that indicates the efficiency of the vaporization and ionization process.
- AMS/CPC(%): Percentage of particles per cm<sup>3</sup> counted by the AMS of the particles counted by the CPC.
  - Bkg: Background ion signal, calculated in units of ions/TOF time step from point before the single particle peak.
  - t1 num: 24 Width: 3 P1:18.4 (38.3) Ions (t1/t2/t3, P1/P2/P3): Number of single particles counted in ToF area #1 (#1/#2/#3), width of the average single particle signal in this area in units of TOF time steps, number of ions per particle (with range) for this area.
  - DC Level: Baseline (background) level of ion signal.
  - SigZeroAvg is the Background ion signal in units of ions per TOF time step
  - Disp. Rate: Display rate of the graphs.
  - Mult: Multiplier voltage and multiplier gain according to the last multiplier calibration.
  - StDev: Calculated to be 100\*Standard Deviation in Ions per Particle calculation/ Ions per Particle
  - Std/Exp: (Ions per Particle)<sup>2</sup> \* Ions per Particle Std Dev/ Ions Per Particle
  - IE: Ionization efficiency calculated from Ions Per Particle in region 2

### The m/z Setting Window

The m/z setting window is used to select the masses that are measured in the ToF mode. It is also used to set different parameters related to the mass spectrometric measurement of these different masses and to run the mass calibration procedure.

To call the m/z setting window, press F6 (window also called 'F6 window') from the ToF window or press the 'm/z Steps for TOF Mode' button from the main menu.

The main table of the m/z setting window consists of 40 rows for a maximum of 40 different mass steps, measured in the ToF mode, with 16 columns for each row, containing the different measurement parameters for the single masses.

The mass number in front of the first column has no meaning than to distinguish the different rows. Press one of these mass number buttons to select or unselect the mass, represented by this number button (first row) for ToF measurement. The last pressed

number button appears in red. The mass to which this button refers is displayed in the preview window on the right top of the window. The rows of the selected masses appear in green. Pressing 'ENTER' first reorders the table with all the selected rows at the top, saves the selection and closes the m/z selection window. Pressing of the 'INSERT' key only reorders the table without saving and exiting the window.

If you want to select a mass for measuring in the ToF mode that is not represented in the table, you have to change an unused nominal mass (m/z nominal (amu))' in the first row of the table to the desired value. You can't add more than 40 masses to the table. The maximum amu that can be entered in the table is indicated by the text in red on the right hand side of the table "Mass for 10 V Out ....."

The top right corner of the window contains a mass spectrum in the region about the m/z of the fragment whose mass number column is highlighted in red. This graph is useful in determining whether the quadrupole mass calibration is set properly for the TOF mode. The calibration is set properly when the mass peak in the middle of this window is located between the two black sticks rising into the window from the bottom. The rightmost black stick denotes the selected mass and the right edge of the signal peak should line up with this stick. Since the TOF measurement for a particular m/z is only obtained at one point along the signal peak, the quadrupole should be set to the point that coincides with the maximum of the signal peak. This can be done by varying the offset (in column 2 of the table).

The different columns of the table contain following information:

- Column 1: 'm/z nominal (amu)': Mass of the selected mass number in amu. Change this box to 'create' a new mass to be scanned in ToF mode.
- Column 2: 'Offset (amu)': Offset (in amu) of the mass peak maximum relative to the exact mass number (right edge of the peak). Represented in the preview window by the green line between the two black sticks. Set the offset so that this green line is at the maximum of the peak. Typically offset = -0.5 to -0.7 amu.
- Column 4: 'SP Threshold (b)': Single particle threshold in bits as set in the ToF window. This threshold can be set in this box or (the better way) by setting it in the ToF window while scanning this mass (automatically or manual setting, see section ToF window).
- Column 5: 'Sliding Window #': Width of the sliding window in time steps (10  $\mu$ s) that is displayed in the raw signal graph of the TOF window and saved around every single particle event. Typically a sliding window of 4 is used for m/z's that will be used to monitor particle TOF's. A sliding window of 2 is recommended, however for m/z's that will be used to monitor single ion signals during multiplier calibrations.
- Column 6: 'DC Mark (0: Front, 1: back, 2: both)': Indicates which DC markers should be used to measure the baseline for this mass. For example for m32 which is part of the air beam, only the back DC marker can be used, since the front DC marker is located at the air beam. Only DC markers should be used, that are located in a ToF-area without signal.
- Column 7: 'Species': Species designation is used during the ionization efficiency

- Calibration to identify all m/z fragments that arise from the same parent species. The species names “NO<sub>3</sub>” should be reserved for nitrate m/z’s (typically 30,46) and “AIR” should be reserved for airbeam peak m/z’s (typically 28,32).
- Column 8: ‘Group Member’: Indicates the membership of the mass to a particular group. The group member designation is used to select m/z for use in the automatic multiplier calibration and the automatic servo calibration. The multiplier calibration is performed w/ the first m/z in the table that contains the letter “I” in its group member code. The servo calibration is performed w/ the first m/z in the table that contains the letter “B” in its group member code. The group member code is also used for selecting multiple m/z’s that belong to the same species. All those m/z’s that belong to the same group can be selected at once by entering the group name at the bottom right hand side text box and clicking the “process” button.
- Column 10: ‘m/z set (amu): the actual m/z in amu at which the quadrupole is set after the offset is taken into account. This value is automatically calculated by the Program using the current quadrupole mass calibration parameters. Do not change these values- They are displayed purely for troubleshooting purposes if the quadrupole is not being set to the appropriate mass.
- Column 11: ‘m/z set (bits)’: Same as above, but in units of bits
- Column 12: ‘Resol. Set (b)’: Shows resolution setting for the mass in col. 1 in bits. This setting is calculated from the resolution setting parameter. Don’t change it.

NOTE: Most of the table cells needn’t be changed. Some of the cells only have to be changed (or are changed by the program) after a calibration. The offset cell has to be changed if the peak form has changed and the offset doesn’t represent the maximum of the peak. The nominal m/z cell has to be changed to measure masses in the ToF mode, not represented in the table. To change a cell content, click the cell and type in the new value. For some cells keys can be used (see below the table). After changing cells or changing the mass selection press enter to save the new settings and return to the previous window (normally the TOF window).

### **The MS Mode**

In this mode the quadrupole is scanned to obtain chemical information about sampled aerosol. The mass spectra can be obtained in two ways. The basic MS spectrum is obtained with the chopper in a single fixed position (Typically open). The toggle MS spectrum is obtained while toggling the chopper between open and closed positions (Toggle with by pressing the letter “T”). In the closed position the MS spectrum measured the background chemical species in the AMS. In the open position, the MS spectrum that is obtained contains information about both the instrument background as well as chemical species entering the instrument from the atmosphere. Thus, in the toggle mode when the closed MS spectrum is subtracted from the open MS spectrum, the contribution of the instrument background is removed.



In the MS mode the quadrupole is scanned at the rate of 1amu/1ms. Thus, a 0-300 amu scan is acquired in 0.3 s. The data is acquired with a sampling rate from 1-5 MHz (sample rate can be set in the parameter menu). The acquired data is then averaged down to a fixed rate of 20 kHz so that there are 20 data points/ amu.

### The MS Window

The MS Window consists of a large mass spectrum graph at the top of the window, containing the mass spectrum in the actual mode and a label area below this graph, containing additional information about AMS parameters.

*The Mass Spectrum graph has vertical lines every 10 mass units, dividing the mass scale in smaller parts, easier to overview. The mass range is indicated by the maximum and minimum displayed mass printed at the right and left below the graph. The y-axis scaling is indicated by the minimum and maximum value (in bits and Hertz, the maximum also in Torr and % detector saturation) at the left bottom and top corner of the graph.*

The m/z's in the mass spectrum are colored according to the likely chemical species from which they originated. Air beam masses (m14, m28, m32, m40) are in white, Water fragments (m16-m18) in light blue, nitrate masses (m30, m46) in dark blue, sulfate masses (m48, m64, m80, m81, and m98) in red, ammonium (m15) in orange, PAH masses (m202, m226, m252, m276, m300) in light blue, Tungsten peaks (m182, m183, m184) in yellow, and the rest of the masses in green.

The mass peaks are divided by small yellow lines every mass unit. In the default mode, the mass spectrum is in the linear mode: The y-axis is scaled linearly. In this linear mode, the stick mode doesn't work. Pressing the 'L' key shifts the display to the log mode. In this mode the stick mode (press 's') shows a single stick for every mass, representing the signal intensity, averaged over the central part of this mass peak. See the description of the quadrupole mass calibration below for more details about how the stick signal intensity is determined. The sticks are printed in the same colors as the mass lines are printed in the other modes.

Below the mass spec graph, a label shows the actual mouse position: The mass of the mass line at the mouse position in integer mass units and in fractional units and the signal intensity at the mouse position in bits, mV, Herz and Torr. This label can be used to read the intensity of a mass peak by pointing on its top with the mouse pointer. The green label below this field contains information about possible substances that can be found at this mass.

### **The other labels:**

- The first label on the top left hand side shows the actual date and time.
- Elap: .. Samp: This label shows the time that elapsed since the last reinitializing (F5) and the actual time spent corresponding to the MS data analyzed.
- An: (% RetrivedTOF data buffers that are completely analyzed); B: (% TOF data buffers that are retrieved for analysis) ;Sp: (Spare Duty Cycle- % elapsed time that computer is finished with displays and calculations and is waiting to receive new data to analyze. When # close to 0, An and B could be <100%)

- 1 ms/amu, 20 kHz/pt, S: 1 MHz: Sampling at 1 MHz, with post-sampling averaging to get down to rate of 20kHz/pt and 1ms/amu
- Pionizer: Pressure in detection chamber. This label is printed in red, when pressure is above warning level (see parameters window).
- F: Flow reading (typically around 1.5 cc/s)
- Averaging status/Not Averaging status –appears in basic MS Mode and is toggled w/ F4 key. This label reads “Particle+Air Beam MS” in toggle mode
- Subtraction on/off: Held signal can be subtracted as new Mass Spectra are obtained. Subtraction can be toggled with F6 key. This label reports status of subtraction.
- DC Offset: calculated from regions for zero specified in the MS tab of the menu
- DC: Average signal level of scanned Mass Spec Signal
- Root Mean Square for MS signal
- Multiplier KV setting and gain in MS mode. Shift-V/V keys can be used to change multiplier votage by +/- 0.025 kV
- Amps/Torr: Calculated amps signal at Faraday cup from ionizer Bgd/ P ionizer
- Far cup: Calculated amps signal at Faraday cup. Calculated from airbeam signal (OH+N+H2O+N2+O2+Ar+CO2)\*0.001/(Amplifier gain\*multiplier gain)
- Mult: Calculated amps signal at Multiplier ( =Far cup amps\*mult gain)
- Ion Eff: Ions Per Second from calculated Faraday cup signal/ molecular flux calculated from ionizer pressure; Diam: Ionizer Diameter in m
- Air Beam: MS and TOF airbeam signals (m/z to use for airbeam is selected in menu). This label is active only in Toggle MS mode
  
- Last Run: Shows the run number of the last saved datafile.
- The 2 yellow boxes with text m/z: 46 ... show the masses that are actually scanned in the ToF mode with calculated mass loading for that amu in nitrate equivalent mass for MS mode. . The bottom 4 labels on the rightmost yellow box Contains estimated nitrate equivalent mass loadings in ug/m3 for sulfate, nitrate, ammonium, and organic. Sulfate loading is calculated from m/z 48,64,80,81, and 98. Nitrate loading is calculated from m/z 30,46. Ammonium is calculated from m/z 15. The total mass is calculated from all m/z's except for airbeam masses m/z 16,17,18,28,32,40,29,39,44, and 14. All m/z's not identified as sulfate, nitrate, ammonium, or airbeam are included in the organic mass calculation.
  
- The Label: ‘Not Auto Saving’ or ‘Auto Saving’ shows if the auto-save mode is set or not in the parameter window. If a data file is saved, the name of the file is shown below this label.
- The Text on the right side below the MS graph shows the status of the chopper: Beam Closed, Beam Chopped or Beam Open.

## *User control of AMS Operating Parameters*

### **The Parameter Menu**

This menu is accessible from the initial AMS window by pressing the 'Parameter Menu' button. This menu contains parameters that are changed often by the user during regular operation of the AMS in its default MS, TOF, or Alternate TOF-MS modes.

The Parameters Window contains 9 Tabs in which all the parameters are selected that are used to drive the AMS. The parameters window is selected by pressing the 'Parameter Menu' button in the main menu or by pressing the 'Return' key in the MS of ToF window. Pressing 'Return' in the Parameters Window closes the window, saves all changes made in the tabs and returns you to the window from which you started the Parameters Window. The same happens after pressing the 'Save & Quit' button at the top of the Parameters Window. After pressing the 'Quit w/o Saving' button the Parameters Window is closed without saving the changes.

### Averaging & Saving tab

#### Averaging of TOF and MS Data

- Time Steps per Avg Sig point: This controls the final coaveraging of the 1-5 MHz avg TOF data.
- Reinitialize after Each Display: Selecting 'yes' yields to a reinitialization (F5) of the average data after every display. Used to only measure the actual size composition with virtually no averaging. Normally set to 'no'.
- Dead Time in MS Mode after Chopper Move: Time (in s) after moving the chopper in which no data are measured. Especially used in the toggle mode.
- Dwell Time in MS Mode for Each Chopper Position: Time (in s) for which data are measured in every chopper position in the toggle mode. After this time the chopper is moved again.
- Time in TOF Mode in Alternate TOF-MS mode(s): Measurement time (in s) in the ToF mode before program is switching to MS mode, when measuring in Alternate mode.
- Time in MS Mode in Alternate MS-TOF mode (s): Measurement time (in s) in the MS mode before program is switching to ToF mode, when measuring in Alternate mode.

#### Saving of TOF and MS Data

- Run Number for last Data Files Saved: 4-digit number that is used as part of the file names for auto- and non-auto-saved data. Number is increased by one after every saving. This number shows the run number of the last saved file.
- Format of Saved Data: ITX= Igor Text Files- this is currently the typical saving format for Ambient sampling and lab experiments. HDF= Hierarchical Data Format- this format is currently being used only for data intensive AMS modes like the Eddy correlation mode.
- Save TOF Size Dist. vs dLog10Da: If "Yes", saves an extra column in TOF.itx which contains ion intensities converted to units of  $d[\mu\text{g}/\text{m}^3]/d\text{Log}10\text{Da}$

- Efficient Data Saving: Not Implemented yet.
- Fixed Time for Next Save in min: This value sets fixed saving times to every x minutes after a full hour. For example the setting 5 sets saving times to 10:00, 10:05, 10:10, 10:15, ... normal setting for field measurements when defined sampling intervals are desired. Negative number turns this saving mode off.

#### Markers for TOF Mode

- Markers for TOF Mode, positions of DC Level Markers: Input for the time positions (in  $\mu\text{s}$ ) between the front and back DC level marker is located. These markers mark the time interval in which the DC level of the ion signal is measured in ToF mode to get the level of the baseline. These markers should be located in time-of-flight areas in which no particle signal is measured. In the F6 window the markers that are used for every single mass can be selected.
- Number of Time-of-Flight Region Markers: Selection of the number of ToF-Region markers in the ToF-Scale. These markers are used to separate the single particle ion measurements for different parts of the size distribution.
- Position of TOF Marker: Position (in  $\mu\text{s}$ ) of the ToF markers to separate different parts of the size distribution.
- Marker for End of Airbeam: The value of this parameter is important in the calculation of the magnitude of TOF airbeam signal. The airbeam signal area is calculated from the beginning of the TOF to the end of airbeam marker.
- Marker for End of TOF: This marker sets the number of timepoints that will be saved in the 2D TOFlogfile matrices described below. It does not affect the number of TOF points saved in the normal TOF igor text files.

#### Saving of Log Files

- Saving of Log Files: Pressing 'yes' buttons for the different log files selects these log files to be saved at every auto- or non-auto-saving. These log files contain data that are also contained in the data files. The log files only allow faster access to these data.
- *MainLog.dat*- Daily logfile that contains TOF data and MS data

*TOF SizeDistLog*- Three Daily logs per mass are saved with one in raw units vs. TOF, one in converted units vs  $\log_{10}\text{Da}$ , and one with the run number (to be able to map to times). These files are in a matrix format that can be easily read and plotted in an image plot in Igor.

*MSDifferenceStickLog*- Daily logfiles of MS stick difference (named MSSD) and MS stick backgrounds (named MSSB) files saved in form that can be easily read into and plotted as a matrix in IGOR.

- AutoSave Interval of Slow Board Inputs: Saves all Slow Board inputs after set number of seconds. Useful when additional measurement devices are connected to the analog input of the slow board. Negative number turns this saving feature off.

## Data Acquisition Boards tab

- Data Acq Rate for TOF Mode (MHz): Pick desired rate at which sampling is to be done. Note that data sampled at this rate is coaveraged down to a rate of 100 KHz or less depending on the value selected for 'time steps per Avg Sig Point' in the Averaging and Saving Tab of the parameter Menu. The "oversampling provided by the faster DAQ rate allows for improved S/N.
- Data Acq Rate for MS Mode (MHz): Pick desired rate at which sampling is to be done. Note that data sampled at this rate is coaveraged down to a rate of 20 KHz. The "oversampling provided by the faster DAQ rate allows for improved S/N.
- A/D Input Gain: Gain of slow board amplifier for signals, typically set to 1.
- DC Offset of Slow Board Rel. to Fast: DC Offset (in V) of one board relative to the other.

Typical DAQ Channel Assignment is as follows:

Fast Board (NI PCI-6110E)

Analog Input 0: Mass Spec Signal

Analog Input 1: Chopper Signal

Analog Output 0: m/z Control of Quad

Analog Output 1: Resolution Control of Quad

Counter 0: Chopper Servo Control

Counter 1: Special Purpose (Generate 10 Hz Sq Wave for Anemometer; Read 100 GPS Clock in Twin Otter)

Slow Board (NI PCI-6024E)

Analog Input 0: Ambient Temperature

Analog Input 1: Heater Temperature

Analog Input 2: Inlet Pressure

Analog Input 3: Inlet Flowmeter

Analog Input 4-7: Available as extra data inputs

Analog Output 0: Heater Bias Control

Analog Output 1: Multiplier HV Control

## Multiplier & Chopper tab

Electron Multiplier Parameters

- Maximum KV (for Protection): Maximum voltage to which the multiplier is to be set. This is set to prevent errors in which the multiplier is set to too high a voltage unwittingly.
- C0, C1, C2 for Multiplier Gain Curve: The multiplier gain, dependent on the multiplier voltage is calculated from this gain curve as:  $G = SF \cdot 10^{(C0 + C1 \cdot U + C2 \cdot U^2)}$ . These factors are measured once with the new multiplier. With aging of the multiplier the gain curve doesn't change its shape, it only decreases which is taken account of by adjusting the scale factor SF of the gain curve.

- Scaling factor of Multiplier Gain: Factor to adjust aged multiplier gain to initially measured gain curve. This is the parameter that should be changed during manual multiplier calibrations. It is changed automatically when multiplier gain is checked with software(described above).
- Emission Current for Multiplier Calibration: Emission current setting of the filament (in mA) for automatic multiplier calibration procedure. This current has to be adjusted to the background level at the mass which is used for the calibration so that the ion signal is below 2000 Hz. Typical current settings are between 0.2 and 1.5 mA.

#### Chopper Parameters

- Chopper Trigger Threshold: Threshold (in bits) for chopper trigger signal.
- Target Chopper Speed (Hz): Typically this value will be negative to indicate manual control. If computer control is desired, then the number should be positive and reflect desired chopper speed. NOTE: Computer control of the chopper is achieved with an additional analog board (PCI-6703). The output calibration for this board can be set in the 'Analog In Out Calib' Tab of the menu.

#### Servo Parameters

- Block/Chop/Open Position of Servo: Position of the servo motor for the different positions of the chopper (open/chop/closed). Minimum is 0, maximum is 70 ( For older versions of the program, this corresponds to a minimum setting of 110 and maximum setting of 180). The optimum servo motor positions for these chopper positions are delivered by the 'Calibrate Servo Position' procedure (main menu, see below). They have to be typed in these textboxes. Negative numbers in the block position text box will result in a step by step movement of the chopper servo upon each press of the 'G', 'Shift-G' keys.
- Time Per Servo Position Iteration: Value is in units of seconds. Control time spent averaging data at each chopper positions during the automatic servo calibration routine. Typically 2-3 seconds is reasonable for this parameter.

### Mass Spectrometer tab

#### Mass Calibration

- Mass Calibration Intercept: Intercept of QMS mass calibration. This value is automatically changed when the quadrupole mass calibration is performed via the 'calibrate MS' button in the MS window. This value is also changed when the mass scale is moved with the 'A' key in the MS mode which does a quick automatic calibration based on the m/z 18 peak to correct the mass calibration offset. This value can also be changed by pressing 'Y' and 'Shift-Y' in the MS window.
- Mass Calibration Slope: Slope of the mass calibration. This should be set by doing a quadrupole calibration via the 'calibrate MS' button in the MS window.

#### Mass Resolution Control

- Resolution Setting: Parameter that describes the mass resolution of the QMS. This value is inversely proportional to the mass resolution. Set this value via the routine accessed with the 'calibrate MS' button in the window.

- Slope of Rel Resolutions: Set w/ the quadrupole calibration routine described above.

#### Ionizer and Quadrupole Controls:

- Default Em.: Default emission current setting (in mA). The filament emission current is set to this value when pressing the 'default' button in the Balzers Control Window. Typically 2.5 mA.
- Voltages at the ionizer and at the deflection plates. These voltages are set and displayed with the Balzers Control Window (see below). Optimize these voltages with the Balzers Tuning procedure (see below).

#### Ionizer Tuning Parameters:

- Mass Peak for Signal Optimization: For automate QMS tuning this mass peak is used to measure the signal intensity. This peak should be intensive to get good statistics.
- Number of Spectra to Average: Number of Spectra that are averaged in QMS tuning procedure for every setting. A reasonable value is 20.
- Interval (min) for AutoTune: *MAKE SURE THAT THIS IS TURNED OFF BY SETTING IT TO A NEGATIVE NUMBER UNLESS AUTOTUNING AT REGULAR INTERVALS IS REALLY DESIRED!!*
- Tune All or only one parameter: Typically choose All
- Tuning Routine: Slow Tuning displays MS, fast routine does not.

#### Parameters Related to Ionization Efficiency

- Estimated ionization and Transmission Efficiency: Efficiency of ionization and ion transmission through QMS to multiplier. This value is essential for aerosol concentration calibration. It is set when the calibration is conducted.
- m/z (amu) for AirBeam in TOF: Mass which has to be measured for the air beam signal in the ToF mode, typically 28 or 32 amu.

#### M/z Range in Mass Spectrum

- Lower and Upper limits for MS Scan and Display
- Peak Width to Calculate MS: Width of the integration region (in amu) for every mass peak over which the peak intensity is averaged. Typical value 0.40 amu.
- Threshold for Aerosol Signal in MS: No longer in use.

#### Calculation of Zero Level in Mass Spectrum

- Lower/Upper Limit of First/Second Zero Region: Lower and upper limits of the mass range, that is used in MS mode to measure the MS baseline for every Mass Spec. These limits should range over masses that contain only electronic noise and no real aerosol signal. Typically, the first zero region can be in the range from 7-10 amu and the second can be in the 290-300 amu range.

#### Noise Calculation

- Estimated Electronic Noise: Used in the noise calculation used to blank out the noise in the MS display when the “N” key is pressed.

### Flow, Size & Mass Calibration tab

#### Flow Calibration

- Alarm FlowRate (cc/s): low limit for flow that controls if a warning is displayed

#### Particle Aerodynamic Diameter Calculation

- Gas Velocity after Particle Lens: Gas velocity in the flight chamber as obtained by the fit parameter  $v_{\text{gas}}$  from the TOF calibration.
- Gas Velocity inside Particle Lens: Gas velocity in the high pressure region of the aerodynamic lens. This parameter in the size calibration becomes important for larger particle sizes. It can be set to ‘0’ for sizes below 1 micron.
- $D^*$  for Particle Velocity Calculation: Fit parameter  $D^*$  from ToF calibration.
- $b$  for Particle Velocity Calculation: Fit parameter  $b$  from ToF calibration.

#### Particle Mass Signal Calibration

- Particle Geometric Diameter: Geometric Diameter (DMA diameter, mobility diameter in nm) of the particles that are used for the mass signal calibration.
- Particle Density: Density of the particles (in  $\text{g/cm}^3$ ) used for mass signal calibration. For  $\text{NH}_4\text{NO}_3$ : 1.72.
- Shape Factor: Shape factor of the particles used for this calibration, for  $\text{NH}_4\text{NO}_3$  typically 0.85 used.
- Mass Fraction of Species: Ratio of the mass of the parent molecule for the measured masses to the molecular mass of the species. If  $\text{NH}_4\text{NO}_3$  is used the total mass is 80 amu while the mass of the parent molecule that is detected,  $\text{NO}_3$  is 62. The mass fraction in this case is  $62/80 = 0.775$ .
- Plot Test Particle: If “yes” is selected, red lines for the predicted TOF positions of the  $Q=1$  to 5 charges of the calibration particles will be plotted in the TOF window.

### Analog In and Out Calib. tab

#### Calibration of Slow Board Inputs

- The 8 channels of the slow data acquisition board are listed in this tab. Text boxes are available for denoting the intercept and slope for calibrating input voltage with the value of the signal measured. The first 4 channels are setup to measure Ambient temperature, Heater Temperature, Inlet Pressure, and Flow Rate. The last 4 channels are available to the user for input of any other analog signals. For convenience, descriptive string for the signals input into these channels can also be entered in the text boxes in the first column and saved with the menu.
- Instantaneous readings of the analog inputs can be achieved by pressing the “Read AI” Button. This can be especially useful when calibrating the inputs.

#### Analog Output board parameters



- A PCI-6703 can be used to generate an output voltage to control the Chopper Speed. If this board is to be used, the linear calibration of the speed vs analog voltage can be input in the appropriate text boxes.

### Serial Ports tab

- Port for TSI CPC: Select from the pull up menu the serial port number to which the CPC is connected. 'Zero' means no CPC connected.
- Port for Varian SenTorr: Select from the pull up menu the serial port number to which the pressure gauge controller is connected. 'Zero' means no pressure gauge connected.
- Port for Balzers QMG 422: Select from the pull up menu the serial port number to which the Balzers Control Box is connected. 'Zero' means no Balzers control box connected.
- Port for Other Info: Select from the pull up menu the serial port number to which additional instruments are connected. 'Zero' means no additional instruments connected.
- Use of the "Other Info" Port: If the other info port is nonzero above, then the appropriate function of the port must be selected.

### Single Particles tab

#### Automatic Single Particle Threshold

- Automatic SP Threshold: Select if automatic single particle threshold is available

#### SP Averaging and Saving

- Points to Save with SP Before/After Peak: Number of 100 KHz datapoints that are saved in the datafile for every single particle TOF event before and after the area where signal is larger than the threshold.
- Points on either Side of Peak for SP Average: Number of Points on both sides of the SP peak that are used to get an appropriate "Average Single Particle" from multiple single particle events that is displayed in the Single Particle Window graph.
- Save all SP to File: Select 'Yes' to save all single particle events to a file. This file which has an extension of \*.spd is saved in the C:/AMS:/AMSData/ folder. For 'no' only the most recent 1000 events are saved to the TOF.itx file.

### Graphs tab

- Display Interval in TOF/MS Mode: Time interval in ToF/MS mode after which the display is refreshed. Should be as large as possible to save computing time used for the display refreshment for sampling.
- Display after each TOF or MS analyzed: Select 'yes' to refresh display after every measurement cycle.
- Display after each Buffer in TOF Mode: Select 'yes' to refresh display always when buffer is full, about every 20 ToF cycles.

- Y: Maximum Level/Min as Frac. Of Max: Shows the maximum displayed level for every of the 5 windows in the ToF window (Single Particle Window, Histogram, Raw Signal Window, Average Signal Window and Chopper Signal Window) and the minimum for these displays as fraction of the maximum. These values change when the display scale is changed in the ToF window by pressing the up/down keys.
- Minimum X-Scale/Maximum X-Scale: Minimum and Maximum of the x-scale of the ToF window in time steps of 10  $\mu$ s.
- Current Graph for Scaling: Shows the currently active graph, the graph that is highlighted in green and for which the scaling can be changed by pressing the up/down keys.
- Scale for Average Single Particle Graph: Y Maximum/Minimum: Shows the maximum level for the single particle graph in bits and the minimum level as fraction of the maximum.
- X-axis Scale for Graphs vs. Time: Select the scaling of the x-axes of the time-series graph (F10, Shift F10, F11 and Shift F11 from MS window).

### **The Default Menu**

This menu can be accessed by pressing the ‘Change Default Settings’ button in the initial AMS window. This menu contains parameters that changed very seldom if at all. This menu contains “factory settings” that need to be changed only if instrument hardware is changed. The user can also access software debugging tools in this menu and operate the instrument in non-standard modes like the eddy correlation and airplane mode. *Be cautious when changing these parameters. Instrument operation and performance will be negatively affected if inappropriate menu parameters are used !!!!!*. The Default Menu contains 4 tabs. Each tab is described in detail below. The default menu can be exited by pressing either the “save changes and exit” or the “Exit without Saving” button on the top left hand side of the menu.

### AMS Operating Mode

- The default setting is “NO” for all the option boxes in this tab. If a non-standard operating mode like Eddy Correlation, Airplane, or NYC Alternate mode is desired, select the appropriate one by setting it to “YES”. Note, that currently only one of these special modes can be active at a given time.

### Data Acquisition

- Fast Board (PCI-6110E) Device number: This should have been set appropriately when the NIDAQ software was installed. The appropriate number for the board can be determined by running Nat. Inst. automation explorer to see what device number is assigned to the 6110E.
- Slow Board (PCI-6024E) Device number: see above
- Slow Board Installed: Should be set to yes unless slow board has been taken out
- Board used to control chopper servo: Typically set to Fast board. If this is changed in the software to slow board, make sure that the appropriate hardware connections have been made between the board and the chopper
- Analog Output Board (PCI-6703) number: If this board has been installed to control the chopper speed via computer, then the number can be obtained by running Nat. Inst. Automation explorer.

- A/D Gain for Mass Spec Channel (ch.0): Usually set to 1
- A/D Gain for Chopper Signal (ch1): Usually set to 1

### Hardware

- Particle Flight Distance (m): Typically 0.39
- Duty Cycle of Chopper: Set this to appropriate number especially if chopper is changed after instrument delivery.
- Chopper Signal Trigger Direction: Usually set to up. The direction of the chopper signal can be determined by clicking the “raw signal” button in the main AMS window.
- Quadrupole in Use: This must be set to Balzers QMA 430
- Multiplier High Voltage Control: This should be set to Aerdyne 4kV
- Resistance of Multiplier (Ohm): 18 MOhm

### Software

- Macro Language Control: Used to turn on/off external AMS control by a macro language. This function uses the file ‘AMSMacro.dat’. Function is not yet fully installed.
- Automatic Start Alt Mode: Typically this is set to No. However, this is useful if computer is running unattended and reboots on its own. For this mode to work the AMS program needs to be in the startup menu.
- Simple External Control: Turn on/off simple external AMS control with the file ‘AMSControl.dat’. Normally not used.
- Averaging time: Time in seconds after which an automatic initialization (F5) is made and averaging restarts. Normally set to a very large time, so it never happens.
- Reinitialize after AutoSave: ‘Yes’ means that after every AutoSave of the data the average data are reinitialized to start another averaging interval. Normally set to ‘yes’.
- Run without Data Acquisition: Select ‘yes’ to run the program without AMS, for example to test the program. Fake raw data are read from files to simulate the AMS. THIS MUST BE SET TO NO UNDER NORMAL OPERATING CONDITIONS
- Noise in Simulated Data: Gives the noise level (in bits) for these simulated data.
- Simulate Chopper Signal: Select ‘yes’ if running program with fake raw data. THIS MUST BE SET TO NO UNDER NORMAL AMS OPERATING CONDITIONS
- User Flow Meter For AMS Inlet: Should typically be set to ‘Yes’ unless working with fake data.
- Averaging Time(s): This is the timescale after which all the variables in the program are cleared (as occurs when the user presses F5 in the MS or TOF window). This should typically be very large (i.e. 30000) so that it does not conflict w/ MS or TOF saving times which typically set the averaging time period. If repeated clearing of variables is required for some troubleshooting operation is needed, then it is useful to use this variable to accomplish that.

- Reinitialize After Each Display: This refers to restarting averages every time a display is updated. This should typically be set to “No”
- Save Raw Buffer for Each m/z and Saving Cycle: Saves the content of the raw buffer of the fast board at every saving interval. The Raw Buffer contains the most recent chunk of the data grabbed from the data acquisition board. It can be useful to save raw buffers especially when troubleshooting data acquisition software. The default mode is to set this parameter to a negative number i.e. turn this feature off.
- Display After Each TOF or MS Analyzed: Usually set to No to increase duty cycle. If set to “yes”, the display will be updated each time the most recent raw buffer (see above) is analyzed.

## ***AMS Software Shortcuts and KeyStrokes***

### **The Help Window**

After pressing the ‘H’ key in any window or the ‘Command Help’ button in the main menu, the Command Help window appears. It contains three help tabs: ‘Time-Of-Flight’, ‘Mass Spectrum’ and ‘Single Particle’. When calling the help window from the ToF, the MS or the Single Particle window, the according tab is in the front.

### The ‘Time-Of-Flight’ tab

- ‘RETURN’ key: Displays the parameters window.
- Space key: Selects the next graph in the ToF window for scaling. Active graph has a green frame.
- Up Arrow key: Compresses the y-axis of the active graph: All signals in the graph are printed larger.
- Down Arrow key: Expands the y-axis of the active graph: All signals in the graph are printed smaller.
- ‘Insert’ key: Opens the Single Particle Window to show single particle related data.
- ‘F1’ key: Toggles between the ToF and the MS window. Opens MS window and starts measurement in MS mode.
- ‘Shift F1’ key: ?
- ‘F2’ key: Auto-scales the y-axis of the active window. Sets the y-axis scale to a value that the largest signal fills the scale.
- ‘Shift F2’ key: Auto-scales the x-axis of the active window.
- ‘F3’ key: Saves the actual size distributions (with actual parameter readings) to disk in ‘non-auto-save’ folder.
- ‘F4’ key: ?
- ‘F5’ key: Reinitializes all variables and restarts the size distribution averaging.
- ‘F6’ key: Opens the ‘m/z Settings’ Window to select masses that are stepped in the ToF mode (see above).
- ‘F7’ key: Writes the content of the buffer of the data acquisition board to disk. Normally this content is read by the computer, averaged and displayed on the screen. Only for diagnosis purpose.

- 'F8' key: Toggles the 'hold mode': Holds the actual size distribution in the background of the ToF window. This size distribution is printed in purple.
- 'Shift F8' key: Opens a category plot with the number of single particles for the different mass settings.
- 'F9' key: Saves the single particle data to disk.
- 'F10' key: Toggles the printing of a plot of CPC number concentration and ions per particle reading versus time.
- 'F12' key: Displays the raw signals in the 'oscilloscope mode'.
- 'Shift A' key: Toggles the plotting of all masses at a time in the histogram graph.
- 'B' key: Toggles between the plotting of all single particle signals since the beginning of the averaging period and plotting of only the single particle signals in the actual measurement interval.
- 'Shift B' key: Opens the Balzers Control Window (described below).
- 'C' key: Toggles between plotting the average signal (only total signal) of all selected masses at a time in the average signal graph and plotting only the average signal of actual active mass (single particle signal, non single particle signal and total signal).
- 'D/U' keys: Decreases/increases the single particle threshold by 10 % (Shift D/U: 20 %) when doing the manual threshold setting procedure.
- 'Shift E' key: Toggles between the plotting of the sum of all masses in the histogram graph and the plotting of only the histogram of the actual mass.
- 'F' key: Brings up the particle calculator (described below).
- 'G' key: Moves the chopper in the direction: Open – Chopping – Closed.
- 'Shift G' key: Moves the chopper in the direction: Closed – Chopping – Open.
- 'I' key: Opens a textbox to type in a comment.
- 'H' key: Opens the Command Help Window with the ToF tab in the foreground.
- 'M' key: Jumps to the next mass setting immediately. Only useful when for every mass setting the integration times are long.
- 'O' key: Toggles between printing the active graph enlarged to fill the whole ToF window and printing the five different graphs on top of each other.
- 'P' key: Toggles the pause function to freeze the window.
- 'Shift P' key: Prints the actual ToF window to the default printer.
- 'Q' key: Quits the ToF mode and opens the main menu.
- 'R' key: Restarts in the automatic single particle threshold setting process the process. Press 'F5' additionally to restart averaging.
- 'Shift V' key: Increase multiplier voltage by 0.025 kV.
- 'V' key: Decrease multiplier voltage by 0.025 kV.
- 'Alt V' key: Emergency shutdown of the multiplier, set multiplier voltage to zero.
- 'Ctrl V' key: Sets the multiplier voltage to that value that, according to the latest multiplier calibration, the multiplier gain is equal to the default gain (as set in the parameters window).
- Click Right Mouse Button: Moves the ToF Region delimiters to the time of flight where the mouse actually sits.
- Click Left Mouse Button: Selects the graph on which the mouse button actually sits as active graph.

### The 'Mass Spectrum' tab:

- Up Arrow key: Expands the y-axis. All peaks are drawn larger. For larger expansion steps press the 'shift' key additionally.
- Down Arrow key: Compresses the y-axis. All peaks are drawn smaller. For larger compression steps press the 'shift' key additionally.
- Left Arrow key: Moves the displayed mass range down by 10 amu. Pressing the 'shift' key additionally moves the displayed mass range down by 50 amu.
- Right Arrow key: Moves the displayed mass range up by 10 amu. Pressing the 'shift' key additionally moves the displayed mass range up by 50 amu.
- 'A' key: Corrects mass calibration offset.
- 'Shift B' key: Brings up the Balzers Control Window (described below).
- 'F' key: Brings up the particle calculator.
- 'L' key: Toggles between logarithmic and linear plot of the mass spectra.
- 'P' key: Toggles the 'pause' function to freeze the screen.
- 'Shift P': Prints the MS window to the default printer.
- 'Q' key: Quits the MS mode and brings up the main menu.
- 'S' key: Toggles the MS display between normal and stick mode. In normal mode every mass peak is printed as the shape of all 20 signal readings per mass unit. In this mode the shape of the mass peaks can be checked. In the stick mode every mass peak is displayed as a single stick, representing the area of the mass peak, integrated over a central part of the peak as set in the parameters window. In this mode the mass spectra are much less complicated and it's much easier to determine the signal intensity at a single mass.
- 'T' key: Toggles the 'toggle' mode of the MS mode: In this mode the chopper moves in block position and in open position alternately to allow a measurement of the difference between the background and the aerosol beam signal.
- 'Shift V' key: Increase multiplier voltage by 0.025 kV.
- 'V' key: Decrease multiplier voltage by 0.025 kV.
- 'Alt V' key: Emergency shutdown of the multiplier, set multiplier voltage to zero.
- 'Ctrl V' key: Sets the multiplier voltage to that value that, according to the latest multiplier calibration, the multiplier gain is equal to the default gain (as set in the parameters window).
- 'X' key: not in use.
- 'Y'/'shift Y' key: Increases/decreases the offset of the mass calibration to 'move' the mass peaks in the proper m/z range.
- 'F1' key: Switches to the ToF window and starts measurement in the ToF mode.
- 'F2' key: Auto-scales the y-axis of the mass spectrum to full range for the largest peak.
- 'Shift F2' key: Auto-scales the x-axis of the mass spectrum to the range, set in the parameters window.
- 'F3' key: Saves the actual mass spectrum (with actual parameter readings) to disk in 'non-auto-save' folder.
- 'F4' key: Toggles the averaging mode. In this mode mass spectra are averaged until 'F4' or 'F5' is pressed.
- 'F5' key: Reinitializes the mass spectrum. Averaging of mass spectra restarts.

- 'F6' key: Toggles the Subtraction mode of the MS mode: ?
- 'F8' key: Toggles the Hold mode: The actual mass spectrum is kept in the background of the mass spectrum window, printed in purple. – For comparison of different settings.
- 'F10' key: not in use.
- 'Shift F10' key: Shows a time plot of single masses. Used for diagnosis purposes.
- 'F11' key: Shows a time plot of the MS DC level and RMS, what means a time plot of the MS baseline.
- 'Shift F11' key: Only used for diagnosis purpose.
- 'Shift 1' key: Sets scan range to 0-100 amu.
- 'Shift 2' key: Sets scan range to 50-100 amu.
- 'Shift 3' key: Sets scan range to 0-300 amu.
- 'Shift 4' key: Sets scan range to 100-200 amu.
- 'Shift 5' key: Sets scan range to 0-200 amu.

### The 'Single Particle' tab

- 'F' key: Brings up the particle calculator (see below).
- 'H' key: Displays the Help window.
- 'Q' key: Quit program to main menu.
- 'Shift P': Prints the Single Particle Window on default window.
- 'Shift Q':
- 'Shift V': Decreases the multiplier voltage by 0.025 kV.
- 'V' key: Increases the multiplier voltage by 0.025 kV.
- 'Ctrl V': Sets the multiplier voltage to that value that, according to the latest multiplier calibration, the multiplier gain is equal to the default gain (as set in the parameters window).
- 'Alt V': Emergency shut down of the multiplier, sets the multiplier voltage to zero.
- 'Y' key: Saves the pulse height distribution to disk in the file phd.itx.
- 'RETURN' key: Opens the Parameters Window.
- 'Insert' key: Toggles between the ToF window and the Single Particle Window.
- 'F2' key: Autoscales the y-axis of the average single particle signal window.
- Right Arrow key: Compresses the x-axis of the average single particle signal window.
- Left Arrow key: Expands the x-axis of the average single particle signal window.

## ***Diagnostics and Tools***

### **Check AirBeam**

Continuous monitoring of the airbeam intensity is an important means of observing decays in multiplier gain. Clicking the check airbeam command operates the AMS in the alternate TOF/MS mode and brings up a summary window which displays airbeam intensities in the two modes. In addition, the state variables, mass loadings for m/z selected in TOF and MS signal levels for typical background peaks are displayed. As in

the servo calibration procedure, the first m/z in the F6 window belonging to a group with the letter "B" is automatically chosen as the airbeam for these measurements. TYPICALLY m/z 32 is used as for the airbeam measurements.

### **Raw Signal**

This mode displays the MS and chopper signals in the acquisition buffer together with the chopper threshold that has been selected in the menu. If the TOF signal is not normal and chopper behaviour is suspected, this mode can be useful in diagnosing the exact nature of the problem.

### **The Particle Calculator**

The particle calculator can be used to make simple calculations for single particles as aerodynamic diameter, particle time-of-flight, mass of a single particle, molecules per particle, mass concentration and volume concentration for given number concentration. In the upper part of the particle calculator different particle parameters as number of particles per cm<sup>3</sup>, particle diameter, particle density, particle shape factor and molecular weight of particle material as well as information about the ionization and fractionation process are typed in textboxes. In the lower part of the window the output values are printed. In the middle a 'Calculate' button is used to update the output text and a 'Quit' button is used to quit the particle calculator.

## ***Description of Saved DataFiles***

The main data files saved by the AMS software are mass.itx and tof.itx files which are saved in IGOR text format. These files are described below

### ***G.1. Mass.itx Files (Example for Run #2777)***

str\_info\_R2777: String that describes General Operating Parameters

info\_R2777: Values for the Operating Parameters described in Str-Info

ParStr\_R2777: String that Describes Menu Parameters

Par\_R2777: Values for the Menu Parameters described in ParStr

Str\_Mass\_R2777: String that describes following operating parameters:

masses scanned in TOF

no of steps: No of masses scanned in TOF

m/z nominal: Integral values of m/z scanned in TOF

m/z setting: Actual m/z setting at which TOF masses were scanned

Bits of Step x (x=1 to no of steps): Analog output in bits that is required to set quad to the desired mass

Resol Set of Step x

SP Thres Mult. of Step x

n sliding window of Step x

Rel. Dwell Time of Step x

Rel. Resolution of Step x

MW of Step x: Molecular Weight of Parent that gives rise to fragment observed at step x

Frag. Frac. of Step x: Fraction of Parent fragmentation that yields



fragment observed at step x  
 Species of Step x  
 Calibration Factor of Step x  
 DC Type of Step x: Number of DC markers used for TOF  
 Future Info  
 Mass\_R2777: Values for the parameters described in Str-Mass  
 Amu\_R2777 AMUs in MS scan  
 MS\_R2777 MS info for last mass spectrum taken before save  
 MSAvg\_R2777 Should only be present if MS NOT Toggled between Open and  
 Closed positions. When present, it contains the Average of the mass  
 Spectra  
 MSClosed\_R2777 MS when chopper in Closed position  
 MSDiff\_R2777 Difference in MS between Open and Closed  
 AmuS\_R2777 Integral Amu values for Stick MS spectrum  
 MSSClosed\_R2777 Stick Spectrum with Chopper Closed  
 MSSDiff\_R2777 Stick Spectrum showing difference between Open and Closed  
 positions

**TOF.itx Files (Example for Run # 2777)**

str\_info\_R2777: String that describes General Operating Parameters  
 info\_R2777: Values for the Operating Parameters described in Str-Info  
 Str\_Mass\_R2777: String that describes following operating parameters:  
 masses scanned in TOF  
 no of steps: No of masses scanned in TOF  
 m/z nominal: Integral values of m/z scanned in TOF  
 m/z setting: Actual m/z setting at which TOF masses were scanned  
 Bits of Step x (x=1 to no of steps): Analog output in bits that is  
 required to set quad to the desired mass  
 Resol Set of Step x  
 SP Thres Mult. of Step x  
 n sliding window of Step x  
 Rel. Dwell Time of Step x  
 Rel. Resolution of Step x  
 MW of Step x: Molecular Weight of Parent that gives rise to  
 fragment observed at step x  
 Frag. Frac. of Step x: Fraction of Parent fragmentation that yields  
 fragment observed at step x  
 Species of Step x  
 Calibration Factor of Step x  
 DC Type of Step x: Number of DC markers used for TOF  
 Future Info  
 Mass\_R2777: Values for the parameters described in Str-Mass  
 ParStr\_R2777: String that Describes Menu Parameters  
 Par\_R2777: Values for the Menu Parameters described in ParStr  
 tsig\_R2777: Time of Flight axis for average signal

dsig\_R2777 Particle Diameter axis for average signal

*THIS PART DEALS WITH AVG SIGNAL SECTION OF TOF SCREEN*

sig\_np"x"\_R2777 "x" is the integral value of the TOF mass fragment being monitored. np refers to an average of all TOFs where no single particles were detected

sig\_p"x"\_R2777 "x" is the integral value of the TOF mass fragment being monitored. p refers to an average of all TOFs (with and without particles)

If in the "Averaging and Saving" Tab of the menu the "Save TOF Size Dist vs. dLog10Da" option is selected, an analogous set of waves corresponding to Ion intensities converted to units of d(ug/m<sup>3</sup>)/dLog10Da and separated according the m/z are saved. These waves have the prefix sigd-\*

*THIS PART DEALS WITH CHOPPER DISPLAY IN TOF SCREEN*

tref\_R2777 Time axis for chopper signal  
ref\_R2777 Chopper signal

*THIS PART DEALS WITH SINGLE PARTICLE DISPLAY IN TOF SCREEN  
(Contains info about all the single particles seen in the most recent TOF cycle)*

tpart\_R2777 Time axis for single particles. Different single particle events are separated by a pair of negative numbers. The first of the 2 negative numbers in 'tpart' gives the single particle threshold in bits (This is a menu parameter in the single particle tab). The second negative number in 'tpart' gives the # of TOF cycles that have elapsed between the start of the TOF averaging process and the detection of the given particle.

Part-R2777 Particle signal in bits. Different Single particle Events are separated by pair of negative numbers. The first of the 2 negative numbers in 'part' identifies the m/z at which the particle was observed (round up to get the appropriate integer amu). The second negative number in 'part' (when multiplied by 10) gives the index of this m/z within the list of all the masses selected for TOF.

dpart\_R2777 Diameter axis for single particles. Different Single Particle Events are separated from each other by two consecutive zeros.

*THIS PART DEALS WITH HISTOGRAM SECTION OF TOF SCREEN*

thist\_R2777 Time axis for histogram  
dhist\_R2777 Diameter axis for histogram  
hist"x"\_R2777 Number of particles for histogram of TOF species "x"

*THIS SECTION DEALS WITH THE SINGLE PARTICLE INFO SHOWN IN INS WINDOW:*

spart-t1-R2777: Avg single particle signal w/o mass discrimination in First TOF section  
tspart\_t1-R2777: Single particle time axis (ranges from some time pts before the single particle peak to some time pts after the peak. The number of time pts before and after the peak are determined by settings in the single particle tab of the menu  
nspart\_t1\_R2777: Number of single particles in first TOF section  
spart-t2-R2777: Same info as above for second TOF section  
tspart\_t2-R2777:  
nspart\_t2\_R2777:  
spart-t3-R2777: Same info as above for third TOF section  
tspart\_t3-R2777:  
nspart\_t3\_R2777:

Single Particle Info is saved according to regions designated by the TOF markers. IF SINGLE PARTICLES ARE FOUND in a particular region, then the avg single particle w/o mass discrimination is given. In addition SPs in that region averaged according to m/z is also given. tpart is the time axis for the particle signal. # of time points before and after signal depends on settings in the single particle tab of the menu. The example below shows single particle signals found in region 1. The number of particles in each section is found in the Info Wave.

### **LogFiles**

In addition to the itx files, a variety of log files that document instrument performance are also saved. These files are in the form of normal text files.

#### Log files that are automatically saved:

- 1) history.dat – Daily log of keystrokes/actions performed by user
- 2) menu.prm \_ Daily copy of the menu in format that can be read directly by the AMS program. The menu is saved when the program is started. If the program is started many times, this file is continually overwritten. This will allow recovering from menu-related problems more easily.
- 3) menulog.dat \_ Daily log of menu parameters- log is updated whenever the menu is entered by user
- 4) mzcal.dat – Continuous log of changes in m/z calibration intercept
- 5) splog.dat – Daily log of observed single particles (in the format of Part\_R, tPart\_R, dPart\_R) in a file like "010421\_SPlog.dat". This is a daily sum of all the similar waves saved in all files during that day.
- 6) calibrate\_log.dat - log of calibration results. This log is updated each time the "calibrate" button is updated.

Log files that are saved depending on Averaging and Saving menu settings:

- 1) MainLog.dat- Daily logfile that contains TOF data and MS data
- 2) MSDifferenceStickLog- Daily logfiles of MS stick difference (named MSSD) and MS stick backgrounds (named MSSB) files saved in form that can be easily read into and plotted as a matrix in IGOR.
- 3) SizeDistLog- Three Daily logs per mass are saved with one in raw units vs. TOF, one in converted units vs log<sub>10</sub>Da, and one with the run number (to be able to map to times). These files are in a matrix format that can be easily read and plotted in an image plot in Igor.

## ***Appendix 2.1. Information Saved in Info and Par Waves***

### **InfoString Waves**

"Time Saved: "  
"Elapsed Time, s";  
"Sample Time,s";  
"No. TOF Mass Scans (1 scan = step thru all m/z)";  
"Dead Time, s";  
"Dwell Time, s";  
"No. of m/z steps in TOF Mode";  
"nTOF periods total ";  
"nTOF periods without particles";  
"Chopper Frequency, Hz";  
"Particles per cm<sup>3</sup> Detected by AMS (Avg. all m/z)";  
"Julian Day";  
"Seconds After Midnight";  
"Saving Interval Time (s)";  
"Electron Multiplier Gain";  
"Electron Multiplier Voltage";  
"AMS Inlet Flow Rate (cm<sup>3</sup>/sec)";  
"Chopper Duty Cycle";  
"Avg. Single Ion Signal in Bits \* Time Steps (1 step = 10 us)";  
"Pressure of Ionization Region (Torr)";  
"DC Offset of the Fast AD Board";  
"Last CPC Reading (p/cm<sup>3</sup>)";  
"Average of the CPC (p/cm<sup>3</sup>)";  
"Pressure of ConvecTorr Gage #1 (Torr)";  
"Pressure of ConvecTorr Gage #2 (Torr)";  
"Outside Temperature";  
"Room Temperature";  
"Number of CPC Readings";  
"Time in Microsoft Format";  
"TOF Air Beam in Bits \* Steps";  
"TOF Air Beam in Ions";  
"AMS VB Code Version " + AMSVERSION\$;  
"Secs Per Avg. Signal TOF Bin";  
"Amps / Torr";  
"CPC Standard Deviation (p/cm<sup>3</sup>)";  
"Mass (ug/m<sup>3</sup>) calc. from CPC Number and Menu part: "

"Std. Error of CPC Mass (ug/m3)";  
 "TOF Air Beam in Hz (w/o chopper)";  
 "MS Air Beam in Hz (w/o chopper)";  
 "DataFile Format Version Number";  
 "SNR of Chopper Signal";  
 "SNR of TOF Air Beam";  
 "Version of Error Codes String";  
 "Error Codes String: " *See Next Section For Description of this String*  
 "Single Particles in TOF Region 1 (all m/z)";  
 "SPs in TOF R2 (all m/z)";  
 "SPs in TOF R3 (all m/z)";  
 "SPs in TOF R4 (all m/z)";  
 "Fut. Par. 22";  
 "Fut. Par. 23";  
 "Fut. Par. 24";  
 "Fut. Par. 25";  
 "Fut. Par. 26";  
 "Fut. Par. 27";  
 "Fut. Par. 28";  
 "Fut. Par. 29";  
 "Fut. Par. 30";

IDInfoText\$(iid%) (Array that holds info about hardware used in Particular AMS Instrument)

"Researcher: "  
 "Experiment: "  
 "File for Model Back: "  
 "File for Model Diff: "  
 mSt.Species\$(1), (Species 1 used for mass calibrations)  
 mSt.Species\$(2), (Species 2 used for mass calibrations)  
 mSt.Species\$(3), (Species 3 used for mass calibrations)  
 mSt.Species\$(4), (Species 4 used for mass calibrations)  
 mSt.p9, (Future string parameters)  
 mSt.p10, (Future String Parameters)

### **Error Codes String**

**(String of 1's and 0's that gives status about the following parameters)**

LowTOFDutyCycle  
 LowMSDutyCycle  
 LowChopperFreq  
 HighChopperFreq  
 LowChopperSNR  
 LowInletFlow  
 NotConnectedPIonizer  
 NotConnectedP\_CT1  
 NotConnectedP\_CT2  
 HighIonizerP  
 LowP\_CT1  
 HighP\_CT1  
 LowP\_CT2  
 HighP\_CT2  
 DiffMultkVTOFMS  
 LowMultGainTOF  
 HighMultGainTOF  
 LowMultGainMS

HighMultGainMS  
AirBeamNotIN  
NotAutoSaveTOF  
NotAutoSaveMS  
NoN2Signal  
FlowNoisy

## Parameter String Waves

ParamString\$(1) = "(1) Off Line Run (1: Yes 0: No) If Yes reads raTOFAnalBuffer.dat"  
ParamString\$(2) = "(2) Chopper Trigger Level digital value (non-Integer) 30"  
ParamString\$(3) = "(3) TOF Graph 5 (Chopper Signal) Y Axis Delta"  
ParamString\$(4) = "(4) Maximum kV Allowed for the Multiplier (To avoid burning it out, Set as Low as Possible)"  
ParamString\$(5) = "(5) Active TOF Graph Y Scaling"  
ParamString\$(6) = "(6) Logging interval (sec) for Slow Board and RS232 inputs (Temp RH CPC...)"  
ParamString\$(7) = "(7) Display Update rate for TOF mode (sec)"  
ParamString\$(8) = "(8) TOF Graph 5 (Chopper signal) Y axis Min."  
ParamString\$(9) = "(9) External Control of the AMS with a File (1:yes 0:no)"  
ParamString\$(10) = "(10) Averaging time (sec)"  
ParamString\$(11) = "(11) X Min. (DAQ Time Steps = 10 us) for TOF Graphs"  
ParamString\$(12) = "(12) X Max. (DAQ Time Steps = 10 us) for TOF Graphs"  
ParamString\$(13) = "(13) Variable for Testing purposes (1: test 0: don't)"  
ParamString\$(14) = "(14) Threshold for Q = 2 single particle detection when Chopper is Open (> 2048 for turning off)"  
ParamString\$(15) = "(15) Threshold for single particle detection"  
ParamString\$(16) = "(16) Duty Cycle of the Time-of-Flight Chopper"  
ParamString\$(17) = "(17) Points to Save for a Single Particle Before Threshold Crossing (Backup%)"  
ParamString\$(18) = "(18) Points to Save for a Single Particle After Threshold Crossing (Forward%)"  
ParamString\$(19) = "(19) Display Update Rate for Mass Spectrum Mode"  
ParamString\$(20) = "(20) TOF Graph 1 (SP area vs TOF) Y axis Max."  
ParamString\$(21) = "(21) TOF Graph 1 (SP area vs TOF) Y axis Min as Fraction of Max"  
ParamString\$(22) = "(22) TOF Mark for the end of the Air Beam Signal (Used in Air Beam Calculation)"  
ParamString\$(23) = "(23) Run Number for Last Data File Saved (0 to 9999)"  
ParamString\$(24) = "(24) Use Higher Resolution for H2O+ (m/z = 18) (1: same as other peaks >1: higher)"  
ParamString\$(25) = "(25) Resistance (Ohm) of Electron Multiplier (18e6 Balzers, Used to Calc. EM Satur.)"  
ParamString\$(26) = "(26) Slow Data Acquisition Board (NI PCI-6024E) Installed (1:Yes 0:No)"  
ParamString\$(27) = "(27) Single Part. Points Used for Averaging Single Particles on Either Side of Peak, Must be Even"  
ParamString\$(28) = "(28) Average Single Particle Graph Y axis Max."  
ParamString\$(29) = "(29) Average Single Particle Graph Y axis Min. as Fraction of Max."  
ParamString\$(30) = "(30) Average Single Particle Graph X axis Compression Factor (Relative to Averaged Particle Width)"  
ParamString\$(31) = "(31) Particle Density Used for Mass Calibration and Size Display"  
ParamString\$(32) = "(32) Particle Shape factor Used for Mass Calibration and Size Display"  
ParamString\$(33) = "(33) Particle Flight Distance (m) from Chopper to Particle Heater"  
ParamString\$(34) = "(34) Serial Port for TSI CPC (0: Not Connected)"  
ParamString\$(35) = "(35) Save Differential Log Files to be read from a Separate Igor Program (1:Yes 0:No)"  
ParamString\$(36) = "(36) Reinitialize After AutoSave (1: yes 0:no)"  
ParamString\$(37) = "(37) Flow into AMS (cm3/sec) (100um Crit. Orifice: ~1.5, 120um: ~2.0)"  
ParamString\$(38) = "(38) Auto Save Interval for TOF Mode (sec.) Negative turns it off"

ParamString\$(39) = "(39) Auto Save Interval for MS Mode (sec.) Negative turns it off"  
 ParamString\$(40) = "(40) Control of AMS Software Through Macro Language (1:Yes 0: No)"  
 ParamString\$(41) = "(41) Automatic Re-Start of AMS software (1:Yes)"  
 ParamString\$(42) = "(42) Save a copy of the menu with each TOF, MS, or JMS file"  
 ParamString\$(43) = "(43) Save All Individual Single Particles Detected to File? (1 = Yes 0 = No)  
 Otherwise saves the last ~1000 SPs to \_TOF.itx file"  
 ParamString\$(44) = "(44) Auto SP Threshold (1: Yes 0: No = Manual Th.)"  
 ParamString\$(45) = "(45) Use Flow Meter in AMS Inlet (1:Yes 0:No) (Otherwise Use Flow Value in  
 Menu)"  
 ParamString\$(46) = "(46) Gas Velocity After Expansion Into Vacuum (For Size Calibration)"  
 ParamString\$(47) = "(47) Position of DC Level Marker 1 in DAQ Time Steps (us/10) (DC Level for  
 each m/z is the Avg. Signal btw Markers)"  
 ParamString\$(48) = "(48) Position of DC Level Marker 2 in Time Steps (us/10)"  
 ParamString\$(49) = "(49) Input GAIN for channel 0 (signal) of Fast DAQ Board NI PCI-6110E  
 (Possible: 0.2 0.5 1 2 5 10 20 50)"  
 ParamString\$(50) = "(50) Input GAIN for channel 1 (chopper) of Fast DAQ Board NI PCI-6110E  
 (Possible: 0.2 0.5 1 2 5 10 20 50)"  
 ParamString\$(51) = "(51) X-axis scaling for plotting variables vs Time (sec)"  
 ParamString\$(52) = "(52) Use Higher Resolution for K+ (m/z = 39) (1: same as other peaks >1: higher)"  
 ParamString\$(53) = "(53) Quadrupole Mass Spectrometer Used (1 = UTI 2 = Extranuclear 3 = SRS 4 =  
 Balzers)"  
 ParamString\$(54) = "(54) TOF Signal Plotting (0 = with DC Level 1= without DC Level)"  
 ParamString\$(55) = "(55) Gain of External Amplifier(s) Between Electron Multiplier and DAQ Board  
 (Typical 10<sup>6</sup>)"  
 ParamString\$(56) = "(56) Voltage on Electron Multiplier (kV) for Time-of-Flight Mode"  
 ParamString\$(57) = "(57) Voltage on Electron Multiplier (kV) for Mass Spectrum Mode"  
 ParamString\$(58) = "(58) Input Gain of the Slow Data Acquisition Board (NI PCI-6024E) (Possible: 0.5  
 1 10 100)"  
 ParamString\$(59) = "(59) Lower Limit of m/z SCANNED in the Mass Spectrum (amu)"  
 ParamString\$(60) = "(60) Upper Limit of m/z SCANNED in the Mass Spectrum (amu)"  
 ParamString\$(61) = "(61) Balzers Ion Reference (V)"  
 ParamString\$(62) = "(62) Balzers Cathode (V)"  
 ParamString\$(63) = "(63) Balzers Focus (V)"  
 ParamString\$(64) = "(64) Balzers Field-Axis (V)"  
 ParamString\$(65) = "(65) Balzers Extraction (V)"  
 ParamString\$(66) = "(66) Balzers Inner Deflection (V)"  
 ParamString\$(67) = "(67) Balzers Emission Current (mA)"  
 ParamString\$(68) = "(68) Heater Bias (V) Relative to Ion Reference Voltage"  
 ParamString\$(69) = "(69) Serial Port for Balzers QMG 422 Controller (0: Not Connected)"  
 ParamString\$(70) = "(70) Peak in the Mass Spectrum to Use for Signal Optimization"  
 ParamString\$(71) = "(71) Simulate Chopper Signal (1:Yes)"  
 ParamString\$(72) = "(72) Chopper Signal Trigger Direction (0: Up 1: Down)"  
 ParamString\$(73) = "(73) Reinitialize after every display (1: Yes 0: No)"  
 ParamString\$(74) = "(74) DC Offset of the Board Channel for Main Signal in bits (Fast DAQ Board,  
 Channel 0)"  
 ParamString\$(75) = "(75) Fraction of the Mass for Calibration Species 1"  
 ParamString\$(76) = "(76) Scaling Factor for Electron Multiplier Gain (Used to Keep Track of Gain as  
 Multiplier Ages)"  
 ParamString\$(77) = "(77) TOF Graph 3 (Raw signal and Single Particle Plot) Y axis Max."  
 ParamString\$(78) = "(78) TOF Graph 3 (Raw signal and Single Particle Plot) Y axis Min. as Fraction of  
 Max."  
 ParamString\$(79) = "(79) TOF Graph 4 (Signal Average) Y axis Max."  
 ParamString\$(80) = "(80) TOF Graph 4 (Signal Average) Y axis Min. as Fraction of Max."  
 ParamString\$(81) = "(81) Default Gain of Electron Multiplier (CTRL + V to Set)"  
 ParamString\$(82) = "(82) Sign of the Main Signal (1: Positive -1: Negative)"  
 ParamString\$(83) = "(83) Fraction of the N2 and O2 to be used in the Amps/Torr Measurement (To

Account for Air in Ar Flow)"

ParamString\$(84) = "(84) TOF Graph 2 (SP Histogram) Y Axis Max."

ParamString\$(85) = "(85) TOF Graph 2 (SP Histogram) Y Axis Min. as Fraction of Max."

ParamString\$(86) = "(86) Display after every single buffer in TOF Mode"

ParamString\$(87) = "(87) Display after every single time of flight or Mass Spec analyzed"

ParamString\$(88) = "(88) D\* for calculation of Particle Velocity vs Part. Size (p. 12 our AS&T paper)"

ParamString\$(89) = "(89) b for calculation of Particle Velocity vs Part. Size (p. 12 our AS&T paper)"

ParamString\$(90) = "(90) Time Interval to Grab DC Offset in TOF mode (sec. Negative turns it off)"

ParamString\$(91) = "(91) Efficient Save Mode (1: ON, 0: OFF)"

ParamString\$(92) = "(92) Relative Change when Setting Single Particle Thresholds (>1, Typical ~1.15)"

ParamString\$(93) = "(93) Slow Board (NI PCI-6024E) Output Offset in Bits Relative to Fast (NI PCI-6110E) (1 bit = 5 mV)"

ParamString\$(94) = "(94) Coupling of the Main Signal (0: DC 1: AC)"

ParamString\$(95) = "(95) Magnitude of the Random Noise in the Simulated Data"

ParamString\$(96) = "(96) Particle Geometric Diameter (nm) for Calibration and Size Display"

ParamString\$(97) = "(97) Ionization Efficiency of Electron Impact Ionizer (for Calculation of ug/m3)"

ParamString\$(98) = "(98) Save a Raw TOF Buffer (~ 20 TOFs) for every TOF mass setting and saving cycle (1:yes 0:no)"

ParamString\$(99) = "(99) Dwell Time for Chopper ON/OFF or Valve Mass Spectrum Scanning (sec.)"

ParamString\$(100) = "(100) Dead Time for Chopper ON/OFF or Valve Mass Spec. (sec.) No less than 0.5 sec."

ParamString\$(101) = "(101) Use of 'Other Info' Serial Port (0: NYC Time Stamp 1: Simplified Status Info)"

ParamString\$(102) = "(102) Maximum Electron Multiplier kV for Large Mass Spec Peaks (To Protect Multiplier)"

ParamString\$(103) = "(103) m/z for Air Beam Calculation"

ParamString\$(104) = "(104) Dwell Time (sec.) in TOF Mode when Alternating TOF and MS"

ParamString\$(105) = "(105) Dwell Time (sec.) in MS Mode when Alternating TOF and MS"

ParamString\$(106) = "(106) Balzers Quadrupole Resolution Parameter #1 (Typical Res. ~20-30 Min. Res.: 254 Max. Res.: 0)"

ParamString\$(107) = "(107) NOT USED"

ParamString\$(108) = "(108) Block Position for the Chopper Servo in Digital Steps (< 0: Single Step)"

ParamString\$(109) = "(109) Chopping Position for the Chopper Servo in Digital Steps"

ParamString\$(110) = "(110) Open Position for the Chopper Servo in Digital Steps"

ParamString\$(111) = "(111) Number of DAQ Time Steps (10 us) Per Average Signal (or Histogram) Point"

ParamString\$(112) = "(112) Quad Mass Calibration Slope (UTI .0124656 Ex 0.011721 Bal 0.0152801)"

ParamString\$(113) = "(113) Quad Mass Calibration Offset in amus (UTI 0.58559 Ex 0.3 Bal - 0.782731)"

ParamString\$(114) = "(114) C0 for Multiplier Gain BALZERS (Gain = 10^(c0 + c1 \* kV + c2 \* kV^2))"

ParamString\$(115) = "(115) C1 for Multiplier Gain BALZERS"

ParamString\$(116) = "(116) C2 for Multiplier Gain BALZERS"

ParamString\$(117) = "(117) Number of Time-of-Flight Markers"

ParamString\$(118) = "(118) Position of TOF Marker #1 (in DAQ time steps: 10 us)"

ParamString\$(119) = "(119) Position of TOF Marker #2"

ParamString\$(120) = "(120) Position of TOF Marker #3"

ParamString\$(121) = "(121) Number of MS to use in each optimization step"

ParamString\$(122) = "(122) Device Number for NI PCI-6703 Board (Assigned by NI Measurement and Automation Explorer)"

ParamString\$(123) = "(123) Device Number for NI PCI-6110E Board"

ParamString\$(124) = "(124) Device Number for NI PCI-6024E Board"

ParamString\$(125) = "(125) Pressure Alarm Level (Torr). Multiplier is Turned Off for Larger Pressures"

ParamString\$(126) = "(126) Fixed Time (Minutes) to Save Data Files (e.g: 15 will save at 5:00 5:15 5:30 ..."

ParamString\$(127) = "(127) Alarm Level for Sample Flow (cm3/sec.)"

ParamString\$(128) = "(128) Position of DC Level Marker 3 in DAQ Time Steps (us/10) (DC Level for



each m/z is the Avg. Signal btw Markers)"

ParamString\$(129) = "(129) Position of DC Level Marker 4 in DAQ Time Steps (us/10)"

ParamString\$(130) = "(130) m/z Above Which Resolution is Reduced"

ParamString\$(131) = "(131) Resolution Setting Multiplier for Large m/z"

ParamString\$(132) = "(132) Single Ion Threshold for MS Mode"

ParamString\$(133) = "(133) Default Emission Current (mA)"

ParamString\$(134) = "(134) Minimum m/z Displayed in Mass Spectrum Mode (amu)"

ParamString\$(135) = "(135) Maximum m/z Displayed in Mass Spectrum Mode (amu)"

ParamString\$(136) = "(136) Serial Port Number for SenTorr #2 (Ionizer Pressure)"

ParamString\$(137) = "(137) Ionizer Pressure Warning Level (displays turn red if exceeded)"

ParamString\$(138) = "(138) Signal Threshold for Reporting AMU in the Difference Mass Spectrum"

ParamString\$(139) = "(139) Peak Width (amu) to be Averaged for each m/z in MS Mode"

ParamString\$(140) = "(140) Offset of Relative Resolution Function for Balzers Quad (Rel. Res = Offset + amu \* Slope)"

ParamString\$(141) = "(141) Slope of Relative Resolution Function for Balzers Quad (Rel. Res = Offset + amu \* Slope)"

ParamString\$(142) = "(142) 1: Use Balzers Multiplier Power Supply (0: Aerodyne Multiplier Power Supply)"

ParamString\$(143) = "(143) 1: Use CPC to Calculate Total Mass during Mass Calibration (0: Use AMS Count Rate to Calculate Total mass)"

ParamString\$(144) = "(144) Special Saving Mode in Which Saving interval Determined by the Number of TOF Mass Scans in Alternate TOF-MS Mode"

ParamString\$(145) = "(145) Serial Port Number for Input of Additional Information"

ParamString\$(146) = "(146) Save a DateStampLog when synchronizing with other instruments(0:no,1:yes)"

ParamString\$(147) = "(147) Start AMU for Region1 of MS"

ParamString\$(148) = "(148) End AMU for Region1 of MS"

ParamString\$(149) = "(149) Start AMU for Region2 of MS"

ParamString\$(150) = "(150) End AMU for Region2 of MS"

ParamString\$(151) = "(151) RMS noise Region1 of MS"

ParamString\$(152) = "(152) RMS noise Region2 of MS"

ParamString\$(153) = "(153) RMS noise Calculated from MS Regions (1: yes; 2: no, user inputs RMS noise)"

ParamString\$(154) = "(154) Approx. Gas velocity inside the lens, used in new velocity calibration"

ParamString\$(155) = "(155) Low Limit of LOW amu Region Used to Calculate Zero Level (DC Offset) is MS"

ParamString\$(156) = "(156) High Limit of LOW amu Region Used to Calculate Zero Level (DC Offset) is MS"

ParamString\$(157) = "(157) Low Limit of HIGH amu Region Used to Calculate Zero Level (DC Offset) is MS"

ParamString\$(158) = "(158) High Limit of HIGH amu Region Used to Calculate Zero Level (DC Offset) is MS"

ParamString\$(159) = "(159) Slope for Ambient Temperature Calibration ( $T(C) = T\_Offset + V1 * T\_Slope$ )"

ParamString\$(160) = "(160) Offset for Ambient Temperature Calibration ( $T(C) = T\_Offset + V1 * T\_Slope$ )"

ParamString\$(161) = "(161) Slope for Inlet Flow Measurement (Flow (cm<sup>3</sup>/s) =  $F\_Offset + V3 * F\_Slope$ )"

ParamString\$(162) = "(162) Offset for Inlet Flow Measurement (Flow (cm<sup>3</sup>/s) =  $F\_Offset + V3 * F\_Slope$ )"

ParamString\$(163) = "(163) Synchronize AMS measurements w/ Sonic Anemometer. Generate 10 Hz Square wave"

ParamString\$(164) = "(164) Save TOF Size Distribution Log File for Each m/z Setting"

ParamString\$(165) = "(165) Save MS Difference Stick Log File"

ParamString\$(166) = "(166) Save Size Distributions vs dLog10Da"

ParamString\$(167) = "(167) Save Main (ugPerM3\_log.dat) Log File"

ParamString\$(168) = "(168) Last TOF Used for Data Analysis and Reporting"  
ParamString\$(169) = "(169) Emission Current Used While Calibrating Electron Multiplier (mA)"  
ParamString\$(170) = "(170) Save Reduced Data Set"  
ParamString\$(171) = "(171) Low Lens Pressure (CT1) Warning Limit"  
ParamString\$(172) = "(172) High Lens Pressure (CT1) Warning Limit"  
ParamString\$(173) = "(173) Low Skimmer Pressure (CT2) Warning Limit"  
ParamString\$(174) = "(174) High Skimmer Pressure (CT2) Warning Limit"  
ParamString\$(175) = "(175) Optimize All or Only One Parameter"  
ParamString\$(176) = "(176) Force same Mult. kV for TOF & MS"  
ParamString\$(177) = "(177) Time w/o Crossings Before Quitting SP Thres. Set Mode"  
ParamString\$(178) = "(178) Tuning Mode (1:Fast)"  
ParamString\$(179) = "(179) Interval (min.) for AutoTuning Ionizer"  
ParamString\$(180) = "(180) TOF Data Acq. Rate (Hz)"  
ParamString\$(181) = "(181) MS Data Acq. Rate (Hz)"  
ParamString\$(182) = "(182) Balzers Outer Deflection (V)"  
ParamString\$(183) = "(183) Balzers Filament Used (1 or 2)"  
ParamString\$(184) = "(184) Time Per Servo Position Check Iteration"  
ParamString\$(185) = "(185) Target Chopper Frequency (Hz) (< 0: Manual Control)"  
ParamString\$(186) = "(186) Slope of Chopper Speed Control (Hz/V)"  
ParamString\$(187) = "(187) Offset of Chopper Speed Control (V)"  
ParamString\$(188) = "(188) Plot Diameter of DMA Test Particle (Q=1-5)"  
ParamString\$(189) = "(189) Fraction of the Mass for Calibration Species 2"  
ParamString\$(190) = "(190) Fraction of the Mass for Calibration Species 3"  
ParamString\$(191) = "(191) Fraction of the Mass for Calibration Species 4"  
ParamString\$(192) = "(192) Format for Data Saving (0:ITX, 1: HDF, 2:BOTH)"