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1. Load Data

Computing Requirements:

1 GB RAM is best.

Need Igor 4.07 at least.

Start Data Analysis program.

Go to AMS Analysis Window (or James' panel).

Go to Load Data tab.

Enter pathname for data location.

Enter run numbers to load. Or enter first run, load, then load "new".

Make sure Invoke Corrections is not checked for first pass through data. (Default has no corrections checked. Defaults are in the ctrlM window.)

Make sure Plot Diagnostics and Analogue Inputs is checked.

Hit Load button.

2. Check Diagnostics

Diagnostics window shows diagnostics plotted as a function of data acquisition time.

Gaps are periods of time when no data was saved.

Multplier Voltage: Changes when an electron multiplier (EM) calibration is performed.

Multiplier Gain:

Heater Bias V: One of the voltages on the Balzers ionizer. Changes when a Balzers tuning is performed. NOTE: Do not tune the ionizer until the system has been on and pumping down for several days.

Ionization Efficiency: Changes when an NH₄NO₃ calibration is performed.

Duty Cycle: Computer processor duty cycle. Occasional small dips indicate a temporary heavy load, e.g. downloading data. If the duty cycle drops and stays low, Windows is malfunctioning and you should reboot the computer.

Flow Rate: Changes slightly with atmospheric pressure. Dips may indicate clogging of the orifice.

MS and TOF Air Beams: Tend to drift down as EM gain degrades with time. Will use to correct data for EM drift.

NOTE: Do not change the "Time Steps per Avg. Sig. point" in the parameter menu of the AMS program during a field campaign. If you do, the data analysis program will not be able to plot the TOF air beam data for the whole data set. It is ok to change the save time interval. The data analysis program can handle that change, but it does make it harder to merge with external data sets.

NOTE: Make sure you have a gap in the data when something changes, e.g., you do a multiplier gain calibration. If you manage to do it within one save cycle, you can go back and discard that run.

If you need to get rid of data points based on diagnostics, go to run list (found under Windows/Table Macros/Run_Times in the Igor menu bar. Or hit List on the Load panel.) and find run number. Enter run number in Load Data and hit Discard.

3. Check Mass Trends

Go to MS/Time Series tab.

Make sure Use MS Correction Factors is not checked for first pass through data.

Under Mass Calculations, enter species (use default initially), set Graph option to Plot single and hit Calculate.

Look at time series of masses for anything strange. For example, unexplainable spikes may indicate data that needs to be discarded, or negative water mass loadings indicate that the relative humidity was lower than predicted.

There are several ways to select a specific set of runs to operate on:

- 1) Put a box around the data points. Right click and select SetRunInterval. Select where to send the run numbers from the drop-down menu. For example, to discard data, select Load Interval. Then go to Load Data tab and hit Discard.
- 2) Look at the Run List table (found under Windows/Table Macros/Run_Times in the Igor menu bar). Or hit List on the Load panel.

Check Auto Update. Go back to Load Panel and check Do Auto Updates. Then hit Load. Now will load any subsequent data, and automatically update diagnostics and mass trends.

4. TOF Image Plot

Go to TOF/Image Plot.

Set Min Da to 10 and Max Da to 2500

Normalize to MS checked.

Plot Combined.

D Smoothing to 4

Hit Calculate.

Check Auto Update. Now when load new data, will update TOF image plot. Uncheck Plot Diagnostics so that window doesn't keep popping to the front.

The mass time trends and TOF image plot give you an overview of the data. Look for anything strange.

5. Check Average Mass Spec

Go to MS/Average tab.

Make sure Use MS Correction Factors is not checked for first pass through data.

Enter run numbers to average.

Hit Calculate.

Mass spectrum is color coded as indicated in the legend. Yellow peaks indicate unidentified species, dark green are hydrocarbons with $\Delta=0$ and 2, and black indicates a negative peak. Small black peaks show the noise level; large black peaks indicate a problem such as incorrect relative humidity.

Several things to note about the mass spectrum. First, put it on a linear scale by unchecking the Log Scale box at the top of the graph, and look at m/z 1 to 100. Notice that the dominant peaks are N_2^+ , O_2^+ , N^+ and O^+ , colored in gray. The mass spectrometer sees predominantly air. Notice that the air peak is roughly 50-100 $\mu\text{g}/\text{m}^3$. The mass of air is 1 kg/m^3 . Thus, the AMS measures 10^{-7} of the air. On the other hand, the AMS measures virtually all of the particles less than 1 micron in diameter. The aerodynamic lens allows the AMS to discriminate against the gas-phase by a factor of 10^7 while focusing the particles with high efficiency.

Now rescale the y-axis from 0 to 10 and notice that the next biggest peaks are m/z 40 for Argon, m/z 18 for H_2O and m/z 29 for $N^{15}N$ which are the next most abundant species in the gas-phase.

Now rescale the y-axis from 0 to 1. The gray part of the peak at m/z 44 is due to gas-phase CO_2 , present at about 370 ppm. The next most abundant species is CH_4 at 1.7 ppm which is in the noise. All other gas-phase species are present at even lower concentrations and do not show up in the AMS mass spectrum.

Note Ar^{++} at m/z 20.

Yellow peak at m/z 39 is K due to surface ionization on the vaporizer and is not quantifiable. (39 does not disappear in the difference spectrum perhaps because the particle beam enhances surface ionization.) Little bit of yellow at m/z 40 is organic. Other yellow peaks are truly unknown. Except 31 which is CH_3O^+ and should be included as organic.

Assume that there are no interferences at m/z 28, i.e., only air at 28. CO_2 is calculated relative to air, assuming 370 ppm.

What fraction of a mass spectrum peak is assigned to which species, is controlled by the fraglist. Note sulfate peaks (red), ammonia (orange), organics (green). Fragmentation patterns are typically constant, except for three values which need to be set for a particular data set (see below).

Take a look at mass resolution. Set scale so looking at m/z 27, 28 and 29. Are we sure that these three masses are really separate? Best way to check mass resolution. Should be minimal leakage of 28 into 29 – consistent with dip between 28 and 29. But on low mass side, some leakage – shows up as slight shoulder between 27 and 28. Maybe should be part of Alice's diagnostics.

29 may have real significance. But may be problematic because mostly NN15 (grey part of bar, calculated from isotopic abundance of N15.) Remaining green part of bar is organic.

This picture is also a way to check how important recalculate sticks is – peaks in average mass spec should sharpen up after mass calibration has been corrected for each mass spectrum individually.

Take a look at m/z 14 to m/z 18. m/z 14 is almost entirely N^+ . Note that 18 is not as smooth as 14 because these are difference spectra and there is a huge background at 18. 18 is H_2O^+ from 4 sources:

green: organic $H_2O=CO_2$ from organic, based on lab experiments and not exact

red: sulfate H_2O , from lab experiments and not exact

grey: gas phase H_2O , based on RH, constant for data set.

blue: particulate H_2O , calculated as residual after subtract first three.

17 is OH^+ and NH_3 . green, red, grey and blue are fraction of amounts at 18.

Remaining signal at 17 is assumed to be NH_3 .

16 is O^+ and NH_2 . Ratio of 17 to 16 for ammonia should be 1.1.

Look at another mass spectrum that is not averaged as well, from a noisy part of the data. Error is larger, so can see blanks at bottoms of sticks. Suppose make RH too big, then grey bars are too big and get black bar for particulate water signal because difference between signal and the three calculated components is negative.

NOTE: There can also be negative masses because open-closed is negative, e.g., for large masses.

Important to keep track of negative numbers, especially ones caused by frag wave calculations.

6. Corrections

Airbeam Correction

Notice on diagnostics panel that air beam drifts with time (usually down as multiplier gain decays), and jumps when perform calibrations.

Choose a run interval for the airbeam reference. Ideally, this is a set of runs right after an NH_4NO_3 calibration when the signals are stable.

Go to Corrections/MS tab.

Check Auto-Set for Reference Values. The Reference Values for the airbeam correction will be calculated from the selected run interval. It is better to use these numbers rather than the numbers obtained in the Shift-M window in the AMS program because sometimes the signal is unstable right after a calibration.

Click Perform Correction.

Hit Recalculate.

Now, uncheck Auto-Set for Reference Values so they don't get changed accidentally.

Note that the correction factor is defined as 1 for the selected run interval and scaled for all the other runs. Should drop back to 1 every time you do an electron multiplier calibration.

The analysis program assumes that the IE/AB is constant during a field campaign. Every time you do an NH₄NO₃ calibration, you should record the IE/AB in a running plot to check that it is constant. NH₄NO₃ calibrations should be done every few days. The airbeam tends to drift about 10% per day due to the electron multiplier. The electron multiplier should be calibrated every day, or less often if sensitivity decays less than 10 -20% per day.

In the long run, you should choose the best reference values for the whole field campaign and enter them manually.

One interesting thing to look at is the air beam – go to MS time series and type in air for species. When invoke MS Correction Factor, air signal should become much smoother. Now go to Corrections/MS and check Correct for Flowrate. Hit Recalculate. This takes out most of the remaining wiggles in the air signal.

Now go back to the MS/Time Series tab and check Use MS Correction Factors. (This should be checked from now on.) Set graph to Update. Use MS Correction Factors on TOF/Image Plots panel, too.

Hit Calculate.

The MS time series are now corrected for the drift in the airbeam.

Go to the Load Data tab and check Invoke Corrections so that any new data that is loaded will be corrected for the airbeam.

Go to the Corrections tab and check Apply to new only.

If you look at the correction factors, there is still some noise. If you now use the correction factor as is, it will introduce noise into the signals. Set smoothing on correction factors to remove effects of random noise.

Set MS Airbeam Smoothing to 4, TOF Airbeam Smoothing to 4, Flowrate Smoothing to 4. Hit Recalculate. (Amount you set smoothing to depends on instrument and saving time interval.)

General Comments about Smoothing

Put gaps in the data (either by discarding some runs, or by not saving for one time period) for stepwise changes that are real. The smoothing algorithm will jump over steps.

Smoothing is particularly useful for seeing trends in ratios.
Set smoothing to 4 on TOF traces and image plot because 4 points is about the same as the chopper width, so it doesn't change shape of traces very much.

Flow rate Correction

This correction assumes that the airbeam is proportional to the flow rate and will correct the airbeam for dips in the flow rate due to the orifice clogging and changes due to changes in ambient temperature and pressure.

Flowrate Offset not needed for Baratron P measurement of flow rate (zero is really zero).
Was needed for laminar flow tubes used before to measure flow rate.

Recalculate sticks

Go to graph of MS average.

Unclick Log Scale and click Width Bars and Raw Spectrum. Make sure Integer m/z Show is clicked. This plots the sticks at integer masses. (New Feature: Before, we assumed integer masses for plotting. Now taking into account actual masses.)

On Igor menu bar, go to Analysis/Smoothing. Click From Target. Chose the average MS wave and perform a 2 point, binomial smooth.

Now examine how well the heights of the bars match the heights of the peaks in the raw spectrum, and whether the width bars are centered on the peaks.

If there are problems, the mass calibration isn't quite right and needs to be recalculated.

Go to Corrections/MS/Recalculate Sticks.

Click Perform Correction.

Choose Open + Closed for Method.

Make sure the m/z's to fit are the actual molecular weights of the species associated to the selected peaks (i.e., not integer values).

Wave of nominal values is a list of nominal m/z values for other species, e.g., large hydrocarbons are off the integer mass by about 0.3. Based on isotope/multiple species contributions to peak. Non-integer correction becomes larger as go to higher masses because of number of H's in these molecules.

Use amus_alt for nominal m/z's. Used to use CnH2nPLUS2_plusAmbient_amu, but it has some organic contributions to molecular weights that are not correct for most conditions. E.g., Ar, CO2, benzene and toluene are better with amus_alt.

However, user can change this for their purposes. For example, if sampling diesel exhaust, then want to include hydrocarbon contributions to masses.

Go to MS/Average and hit Calculate. Also uncheck Integer m/z Show on graph.

The bars should now be a better representation of the raw spectrum peak heights.

Hit Graph. Every time AMS program autosaves, it does an automatic mass calibration (slope only, and only on m/z 28). This graph shows tweaks to automatic mass calibration (slope and intercept) for every run and for open and closed MS. Slight drift in slope. Drifts and big jumps in intercept. Big jumps are because automatic mass calibration routine can only change intercept by 0.05 mass units. NOTE:

Be careful in the field if you stop autosaving for a while, e.g., to do calibrations, because when you restart the mass calibration may have changed quite a bit.

Error analysis

Go to Corrections/MS and check Perform Analysis under Error Parameters and uncheck Recalculate Sticks.

Hit Recalculate.

Go to MS/Average.

Uncheck Plot New Graph.

Hit Calculate.

Now the errors are blanked out in the average MS. Bottom edge is set by electronic noise and looks slightly overestimated. Set it a factor of 10 smaller in Error Parameters. Recalculate. Go to MS/Average and hit Calculate.

On log scale, top of bar is signal, blanked out area is noise. Length of bar is signal to noise. So, for large masses, signal to noise is ~10 and for smaller masses signal to noise is ~100. On linear scale, can't even see errors.

7. Mass Spec Analysis

Fragment waves

For this part of the analysis, you should have some data with only the airbeam. Ideally, this is obtained by putting a filter in front of the inlet. This should be done once a week. Alternatively, look for a series of runs where the particle signal is very low.

Go to MS/Average and plot the average MS for these runs.

Click on Review Frag Waves to see a table with the fragment waves. These contain the fragmentation patterns for the different species.

Three values in the fragment waves must be set by each user. First, look at frag_RH[18]. The default value of $0.01 * \text{frag_air}[28]$ is equivalent to about 60% RH. Adjust this to reflect the actual RH during the campaign. Check the setting by going to MS/Time Series and hitting Calculate. The particulate water should now be zero for the particle-free time period. Currently, this is a constant for a given data set. Really, it should be referenced to ambient RH. Could do this with a macro.

Second, look at frag_O16[16]. This fraction depends on the Balzers ionizer and will not change unless you tune the ionizer. If there is a black bar at m/z 16, adjust this fraction until the black bar is gone. If this is particle-free data, the ammonium residual (orange part of the stick) should also be gone. Or if there are particles, the 17:16 ammonium should be about 1.1. Another consistency check is that the ammonium $\mu\text{g}/\text{m}^3$ should be about 1/3 of the (nitrate+sulfate).

Third, look at frag_CO2[44]. The first number (0.00037) is the mixing ratio of CO2 in ppm. The other numbers are the relative ionization efficiency for CO2 and should not be changed. To set frag_CO2[44] you need filter data. Set the mixing ratio so that there is no black bar at m/z 44.

8. Data Diagnostics

Go to Data Diagnostics Panel (Alice's under Panels).

Set Smooth pts to 4, Diagnostics to all and Color By to time.

Hit Calc Std Batch.

Hit Plot Data Diagnostics. 6 plots will appear.

Time Series Plot

The first plot is the time series trend for the major species.

NH4_Fragment Plot

The top panel shows the mass loading of ammonium and the second panel shows the ratio of ammonium m/z 17 to m/z 16. The third panel shows m/z 17 plotted versus m/z 16. The points should lie on the line which indicates a ratio of 1.1:1. If points are offset from line, then need to adjust O16+ in frag wave. Do a linear fit to the data and correct the O16+ accordingly. Doug thinks this is more accurate than filter method described above because this technique averages over much longer time.

NH4_Meas_Pred

This plot shows the extent of neutralization of the aerosol. Measured versus predicted NH4 goes below the 1:1 line if the aerosol is acidic, e.g. NH4 is limited and there is lots of SO4. Can indicate a particle growth event.

Take a look at the batch waves for calculating mass loadings (go to James' panel, MS tab, Review Batch button). These waves contain the relative ionization efficiencies for different species obtained from laboratory calibrations, as well as calibration factors obtained from comparisons with other field instruments. The relative ionization efficiency for NH4 is obtained every time you do an NH4NO3 calibration and should be around 4.5.

SO4_Fragment

This plot shows the ratios of the different ion fragments from sulfate. The lines in the lower panel show the ratios typical for ammonium sulfate. Pure sulfuric acid has a much larger m/z 81 signal.

Ratios can vary a bit from instrument to instrument.

NO3_Fragment

This plot shows the ratio for m/z 46 to m/z 30. This ratio varies from instrument to instrument and is not as robust as the SO4 fragmentation pattern because it depends on both vaporization and ionization processes. If the 46 to 30 ratio points lie mostly on a line, then probably have mostly NH4NO3. For organic nitrates and inorganic nitrates, the ratio drops below the line because these molecules give more NO fragments and therefore more signal at m/z 30. Other nitrate compounds also give more scatter.

Org_Fragment

The bottom left panel shows m/z 44 plotted versus total organic mass loading and indicates the extent of oxidation of the organic aerosol. A ratio of 0.15 is indicative of completely oxidized aerosol, while a ratio of 0.08 is the minimum for secondary organic aerosol. Observed secondary aerosol lies somewhere between these two lines. A ratio of 0.025 is indicative of fresh primary emissions.

The bottom right panel shows m/z 43 plotted versus m/z 57. Instead should be m/z57 vs m/z 44. Slope should be 0.03 for completely oxidized organic.

9. Check Size Distributions

Got to Image Plot to choose a run interval that looks interesting.

Go to TOF/Traces tab.

Under Trace Averaging, check Normalize to MS. At bottom of panel, check Use MS Correction Factors. Set smoothing to 4. Set Data to Plot to DMDlogDa vs logDa, size range 10 to 3000 nm.

Hit Calculate.

Problems with zeros indicate that the DC markers were not set correctly.

Dips in the signal at around 0.1 nm are due to the chopper signal leaking into the data signal channels.

With Normalize to MS off, the signals are shown as nitrate equivalent $\mu\text{g}/\text{m}^3$. When Normalize to MS is on, the signals are actual $\mu\text{g}/\text{m}^3$ for each species.

If the size distributions don't look right, then look at the raw signals.

Go to TOF/Traces tab.

Change Data to Plot to Signal vs TOF.

Hit Calculate.

Now you can see the clear separation in time between gas-phase species (TOF<2ms) and particle-phase species (TOF>2ms). Note that the water, "ammonium," and organic traces have both gas-phase and particle-phase peaks in the TOF. The water gas-phase peaks corresponds to the water vapor mixing ratio and is noisy because of background water in the vacuum chamber. The "ammonium" gas-phase peak is due to $^{16}\text{O}^+$ ion from O_2 in the air, and the "organic" peak is due to gas-phase CO_2 . The gas-phase mixing ratios for H_2O and CO_2 can be determined from the gas-phase peaks in the TOF. Also interesting to look at m/z 28 – air beam dominates.

Baselines are calculated from regions where DC markers in TOF are set in data acquisition program. If there is any signal there, then baselines will be set incorrectly. For example for ammonium and water, only use DC markers at long times.

Clean TOF Signals

Go to Corrections/TOF panel.

Check Clean TOF signals

Check Override DC Markers

Use cursors to pick regions on TOF trace for new baseline calculations.

Pick which masses should have baseline calculated with Region 1 only or Region 2 only.

Default is to have all masses with significant gas phase peaks with Region 2 only.

If signals have significant tails and no gas phase peaks, then set those to Region 1 only.

Hit Recalculate.

Now go back to Image Plot. If baselines are set properly for TOF signals, then will see equal amounts of white and purple in regions of no signal.

GP/PP Boundary

When normalize to mass spec, integrates TOF between 2rd and 3rd DC markers. But sometimes have a large gas-phase contribution, e.g. ammonia and 2nd DC marker isn't in the correct place.

On TOF/Traces panel, can include a size for the boundary between gas-phase/particle-phase contributions for specific species, e.g. ammonia.

Integrate checkbox. Put in a diameter interval. Then integrates that diameter interval on image plot. To graph this, you have to find the created wave and plot it manually.

10. Misc. Panel

Remap Time Series: For cases where need to put your data on a different time base, for example to compare with another instrument that has a different averaging time.

Wave to remap: org,uglog_msig_org (matrix of massloading versus Dva that is used to make image plot).

Time Period: Time base that you want to put it on. Enter start time-end time and whether time stamp is start, center or end of time period. Have to specify center to get image plots to look right. Need to find out how other instruments specify time stamp. Enter time step, units.

If you are looking at a size distribution matrix, then also need to specify dva range and number of bins. 20 to 2000 with 40 bins (evenly spaced in log space). Check dM/dlogD if want standard AMS data. Uncheck if want total mass over the bin, e.g. for comparison with impactor data. Note that 20 bins per decade is a good setting considering the size resolution of the AMS.

Remapped time/size distribution can be higher or lower than AMS data. But, recommend that do not check Use Interpolation unless mapping onto higher resolution data, and do it carefully because you could artificially create data.

Mask Wave(s): Performs remapping for each mask.

Hit Remap.

Creates new data folder call remapped. Creates new waves with same names as originating waves (with mask name appended if using a mask). If size binning, creates d_bins wave to set d limits for plotting.

Notes on image plots: Igor assumes time step is in the middle of the data point. Set colors to rainbow and invert the colors, so that blue is low signal and red is high signal.

Frank Drewnick: Instrument Data Averaging Toolbox: Tool for Remapping AMS data for comparison with other instruments. Allows inclusion of a wave of times for other instrument.

Raw Data: Enter names of raw data waves, time wave. Can set cycle length, and difference between time stamp and start of cycle length.

If comparing to something with higher time resolution than AMS, then puts same AMS value into all the times between AMS save times.

Averaged Data: Can enter a Time Wave with exact times for other instrument.

Gaps: How to handle gaps in AMS data.

Correlations: Make correlations considering errors in both x and y directions (James' program only considers errors in 1 direction.)

Cannot do matrices.

Frank is willing to put this code in the template. Question is whether Frank will support it, or whether user is on their own. Or should it be an add on that people can use if they need it.

Procedure Window:

Contains the default values for James' panel and an Aerodyne function that overrides some of James' defaults. Can change this for your own needs.