

AMS User's Meeting Notes:

Saturday: 10/9/04

Doug's Tutorial

BWP:

There is a choice for offset from the center (calibrated on the vaporizer) for when the beam is off-center. One unit = 20 μm offset at the probe (therefore an offcentering of 10 μm at the actual lens).

CE:

You can get 100% CE by increasing the RH (over 80%) for Ammonium Sulfate particles. However, if they are coated with organics, this becomes much harder/less change/increase in CE.

Velocity (Size) Calibrations:

Should add a smaller size- maybe like 70 or 80 nm, even 50- but harder to get just one PSL in the particle droplet.

Never use the 50 μs default saving resolution for the TOF (what for MS?). Also- mentioned was to use the same saving time in your calibration as your experiment/field mission. For the 1% chopper- must use the 10 μs save, and the 2% you can get away with 30 μs , but obviously the smaller the better (resolution)/more accurate!

Big Debate/Issue: Use the histogram rise time for the flight time- Doug says to use the initial first rise, not what I have done with Jose. For Doug's he says to choose that threshold and then add 0.5 x the chopper time width (in time). I think now that the averaged of the mass and histogram talked about in the next section is the way to go- it just still has the [issue of using peak/rise/initial threshold](#)- which to choose for your point.

For the best precision, Doug goes on to say that you should use the size of the smallest PSL within the error as the size to go along w/this first rise in signal (ex: for 101 \pm 2 nm, set this size to 99 nm). Another aside- can get from Duke Scientific some type of resin beads that will remove the surfactant. Also suggested was using a 50/50 MeOH/H₂O solution to make smaller droplets for use with 50 nm PSLs in order to get more droplets with just one PSL.

Katja uses the average of histogram and avg calibration lines to form the size calibration curve. They also used the AB for a "really small" (what?) size particle. (Is this correct to do?) Peak of histogram was used. Maybe can just use 51 m/z instead of 104 m/z due to faster vaporization and "ion transit time", which depends on species and size.

Water Issues/Ionization Efficiency:

RH matters. Issues with the lens drying particles: All the water starts evaporating in the lens. Particles are cooled due to latent heat of evaporation. Just remember that bounce can be optimized by increasing RH and that, well, water concentrations are jacked due to high evaporation in the lens.

THE ACTUAL TUTORIAL:

Loading the Waves:

Default the Analog input load waves. If you hit “default” it will bring up those waves/names. The default list can be found in the procedure window. Can manipulate the defaults and then “save as” to overwrite the template (.pxt).

Choose autoupdate on the specific graph and then click do autoupdates on the load menu- then all will update themselves.

Windows-Graphs-Diagnostics:

Removing bad data: 1-find the point, 2-to load data panel, 3-hit list (relates point # to run #), 4-type run number into load panel, 5-hit discard

Why the AB (can) drift(s) up with time: EM is degassing, gain is drifting up- shows AB drifting up. Therefore, expect after venting. “It is seen all the time.” As it falls down- shows the decay of the EM (multiplier).

Choosing an IE constant- use a constant time at end. Multiplier voltage plus gain- constant. A change in EM/IE = calibration.

Selecting an AB reference. Highlight the run area- click set AB ref. Autoset. Perform correction. Recalculate. Immediately unclick autoset after running. → plots correction factors (MS?) relative to IE and AB at the selected run time. It corrects for the EM degradation. Next step is to invoke the corrections. We reference to AB b/c we believe it to be relatively constant.

Corrections-(uncheck autoset)-click correct for flowrate (measure of the pressure in the lens, which is or is not proportional to ambient pressure?)-then recalculate. This corrects for mass. Does this correct for size? You can show this working by graphing AB in time before and after the corrections. Correcting for flow rate changes the AB to assume a constant volume entering the instrument- in order to get mass loadings. AB is the reference; assume it’s constant. It’s linear with the flow rate- so correcting the AB for the flow rate change makes the input volume the same. Restated: The AB is linearly dependent upon the flow rate, therefore, any change in the AB

“The AB correction is a multiplier calibration.” – Doug Worsnop

“AB calibrates ug. Flow rate calibrates ug/m3.” - Jose-Luis Jimenez; Doug supports and reiterated. (Roya gave a presentation on this last year.)

Go to MS timeseries and use the corrections (MS corrections) in the mass calculations window. Click and calculate.

Make sure you miss a save when you do any calibration. An EM calibration done without missing a save will severely decrease the duty cycle, as seen in the example experiment. You also want to have a gap in the data to make alterations easy to find. Makes glitches easy to find and correct for.

You don’t need to do an EM correction every day. It needs to be done when you lose like 20% efficiency. The example shown lost about 4%/day. Also, don’t worry about having to start one high (2.75 keV) eventhough the max is 3.5 keV. As the voltage got higher they often become more stable.

One last correction: Correction Factor Graph- assume AB trend is “noise”- don’t want to add to the data. In the Correction Window- can MS AB smooth and TOF smooth. The example was arbitrarily set to 4 for each (=40 min) for 10 min data.

Now going to recalc the MS timeseries and image plots. So- correct for MS in the image plot. Then need to modify the color scheme.(NH4-1, Org-9,NO3-1, SO4-2)

Go to MS AVG- set an interval and average. Expand a region and go to a linear scale. Look at about 10-120 m/z. *Assume 28 is ALL AB. Yellow is unknown (?). CO2 is done assuming a constant percentage of atmospheric concentration. Gas phase CO2 will always be 50 ug/m³. Argon- Methane is next highest concentration and is within the noise. So- 44 is mostly from particles. The ratio of 17:16 should be 1.1 for ammonia- some water will often interfere and need to be corrected.

Click on review fragmentation waves- look at air and CO2. Assume 28 is only N₂- at this point no corrections. The correction of 29 is just the isotopic abundance of N₁₅ x 2. 40 is the same thing- 0.9% Argon atmosphere, and account for relative ionization a little larger than N₂- and then 0.92 is it's fraction in the atmosphere. At 44 predict CO2 mixing ratio of 370ppm and a relative ion factor, composition of air and N₂ signal at 28 = CO2 gas phase signal is predicted. 3 parameters to be determined by the user: 16 signal due to O⁺ is done by referencing to 14 (N⁺); frag_RH (for m/z 18) fits the gas phase water vapor and is defaulted at 0.017*28signal ← it should be the gas phase percentage of water in the atmosphere. So a constant RH is being referenced. So 0.017 is high and was set for Pittsburgh, Doug thinks a normal one is more like 0.01 Ideally, would want to reference the changing RH, but this has not been defaulted into the program yet. 3rd- set the CO2 mixing ratio. Reiterate- you set those three, the rest is (pretty much) set up for you, therefore, relatively constant (?). Those 3 values can be set from an estimate made from the data.

Look at the raw spectrum and width bars. Mass Calibration Calcs: Used to assume integer mass units. Actual masses deviate from measurable AMUs by amounts that are significant. Jose says the fragmentation window does not conserve mass- Doug will get to later. Correction- Recalculate Sticks- Perform Correction Method- default is open + closed (can change- these are the masses it will use for the mass calibration, non-integers, 14,18, 128, 149, 182, 183, 184,- N⁺, H₂O⁺, phthalate⁺, 4 tungsten isotopes) A least squares fit is done to these peaks that have good SNR- explicitly fit to the non-integer mass units of those fragments. Then, all other peaks to analyze can be found at their non-integer values. This can be viewed in the "CnH2nPLUS2_plusAmbient_amu" wave. The non-integer correction becomes larger and larger with AMU. Unclick AB correction and hit recalculate in the ms correction window. Now the non-integer masses are being used to calculate our "sticks". Wave "amus_alt" is identical until we get to mass 40- some new differences depending on dominance for you (the original wave is HC fragments). 40 was C₃H₄⁺ and in the newer one is (?). 44 should be CO₂ not HC's. 77 is also different- primarily benzene. 91- same but for toluene. Recalculate with the "amus_alt" wave as the selected nominal value wave. FYI- the default is the HC wave/original. The key- this is and should be a user-definable wave. The importance is that this changes the signal. So the number chosen is the chosen peak that will be used to form the stick- that's why it's IMP. The user can search for whatever mass he/she thinks is present in the sample.

An aside- get max within each AMU region- trouble with noise on top of the signal. An averaged spectrum this could be done for- NOT a timeseries. Look for 1 or 2 peaks within each amu region to determine what you're seeing instead of looking to see

how the signal changes as you change the chosen mass to use. Could also increase the resolution of the quadrupole but at a loss of SNR/sensitivity- not being done at present.

Now expand m/z 200-220 to check the calibration at larger fragments. 215 has a decent amount of PAH- and should be almost a tenth of an AMU off. Can we average more and get better than 1 AMU resolution to get better PAH sensitivity? The answer is and will be the TOF.

Corrections- error analysis (perform analysis under error parameters)– unclick correct sticks. Auto update MS average. Top is signal, whited out is the noise (Poisson statistics). Therefore, the length of the stick is the SNR. (ex: SNR for Sulfate is about 500.) This estimates ion-counting statistics, a lower limit to the noise. For long averages it is a good estimate. (This can be double checked by sampling through a filter. -JJ)

Diagnostics:

Data Diagnostics window- only looks at relations. Smooth at 4, calc standard batch, and plot all DD.

Ammonia: Best way to set the O+ correction is to do so (done earlier) and then set to zero- claims more accurate than a filter since this averages over all the data. Make the O+ fragment 0.32 instead of 0.335 and recalculate the batch/plot in DD. This corrected the offset and lined up the 1.1:1 (ammonia identification ratio of 17:16) line to maintain self-consistency of the fragment list. This is the accuracy w/which we can determine the acidity of the particles.

Sulfate: Well-defined fragmentation pattern.

Nitrate: The 1:2 line is typical of (some) instruments for the 46/30 ratio. This ratio is lower than what he's used to seeing. The ratio is always lower in the atmosphere than in the lab (more NO than NO₂)– no clue why. Each instrument seems to be self-consistent. Plot 57/44 and it should be 0.03 for oxidized species (Qi Zhang- submitted paper).

General FYI:

32 is contaminated with sulfate- why we use 28 for AB (CO) and not 32.

*Do not tune the ionizer until the system has pumped down for several days so that it can have time to outgas.

Don't leave 28 selected in TOF if "not taking data"- can degrade the multiplier quite quickly in the shorter chamber.

"Closed MS should be identical to a filtered air MS spectrum." – Doug Worsnop
Always do a MS cal right before and IE cal. – Jose-Luis Jimenez

To do: TOF zeroing

Sunday: 10/10/04

Doug's Tutorial continued

Analyzing signals at 27, 28, 29 m/z:

Calibration is the most important at 27 and 29 due to the magnitude of 28. The signal at 29 includes the isotopic abundance of the N15 isotope from 28, the remainder is other signal attributed to organics. Look at the MSD graph with the raw signal. Check that there is a dip between 28 and 29 to make sure there is no 28 signal in 29– best to check your tuning of the quadrupole. Expect a tail at 27.

Analyzing 15, 16, 17, 18: NH_2^+ , O^+ , OH^+ , H_2O^+ :

All the spectra are the difference between the open and closed. The signal at 18 is noisy due to the huge background (low SNR). Organic water is determined from the fragmentation pattern; sulfate water estimated from the fragmentation pattern of SO_3 how much evaporated in water and based on lab experiments- neither is precise. The grey is the relative humidity (gas phase water) that is set by the user. Doubtful it can be made quantitative. The blue is the particulate water= total – 3 other components = the residual. Do we believe the residual? You can create/destroy mass by entering incorrect isotopic abundances/altering the fragmentation wave. You can get negative water (black bar) by inputting higher abundances to get more signal than there actually is.

Negative numbers both due to noise and bad math calculations. Talk of a new panel for the average MS (MSD) graph to show the negative numbers, and possibly the time trend. The negative mass needs to be taken track of – mention to James to add to the code. All of the organic corrections assume the presence of the delta series, and this works for a first-order approximation for atmospheric samples, NOT lab experiments- these require your own organic corrections. The moral is do not blindly trust the default fragmentation patterns.

Baselines in TOF Sizing Averages:

Plot the raw signal versus TOF. The baseline is determined by the placing of the DC markers. Ammonium always has a nonzero baseline due to the tail of the $\text{O}16^+$ signal that extends into the particles. (Qi has a routine for subtracting the $\text{O}16^+$ signal out.) Important to double check the baseline numbers by looking at the raw signal. Then go to corrections-TOF-click clean TOF signals and override DC markers- place them yourself on the graph at the start of time and before particle signals (ex: 1200 – 2000 us, and 6.75 and 8.25 ms). If there is a tail to the end- choose region one only. Imp to set the frequency of the chopper to get a good baseline in any field mission (check some time during). Hit recalculate.

The image plot should be 2/3 white (blanked out) with +1/6 of negative around that. (Return to the TOF trace of signal vs. time) FYI: 150K is the approximate temperature of our weak supersonic expansion, which can be determined from the Boltzman distribution of gas-phase ammonia signal.

PSL distributions from size calibration (reference to yesterday):

The time resolution is controlled by the chopper- 160 us is the chopper with 30us saves, so chopper (2%) is 5 steps wide- expect a top hat five channels

wide (the half width is). 4 (binomial) channels of smoothing was chosen yesterday- ok to smooth by the chopper width = an almost negligible effect and ok to go higher in the smoothing. (6 was too much- distortion occurring).

GP/PP Boundary- can be affected and is different for each instrument.

The integrate button- creates a time series within the size distribution to approximate ?. This is useful for all m/z in trace averaging- removes the gas-phase component on the respective image plot.

Miscellaneous window- going to reband the TOF image plot. Type in `uglog_msig_org` in the remap time series- James will show us this tomorrow.

Next issues on CE with more discussion of flow rates.