ToF-ACSM Calibrations

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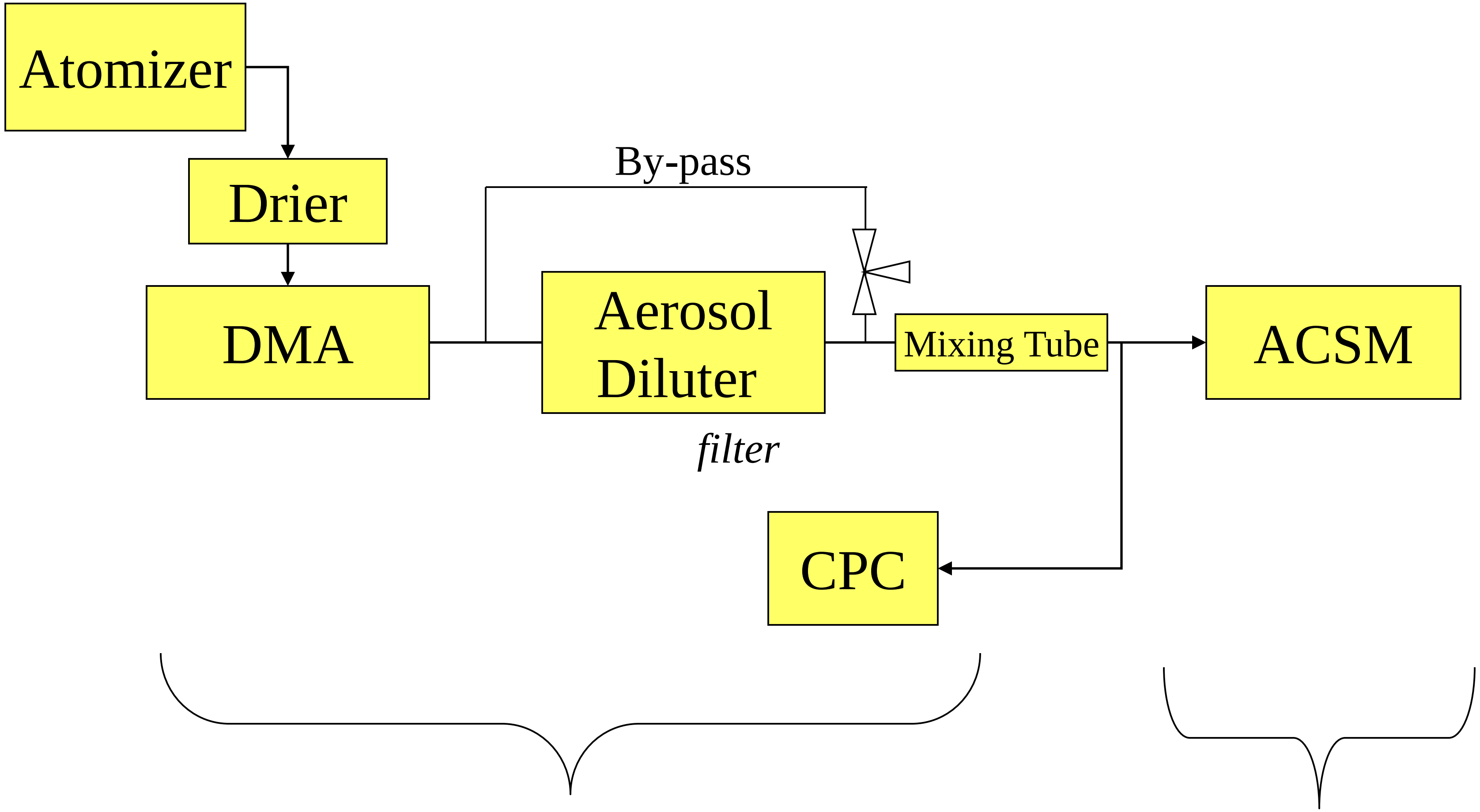
Setup for Mass Based IE Determination



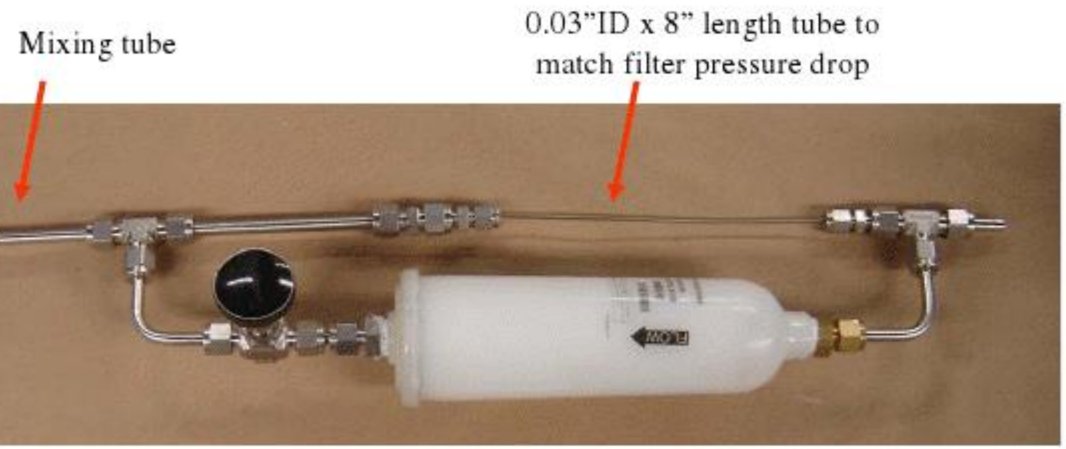
Input Mass = ρ x Volume(size) x Number

Reported Signal

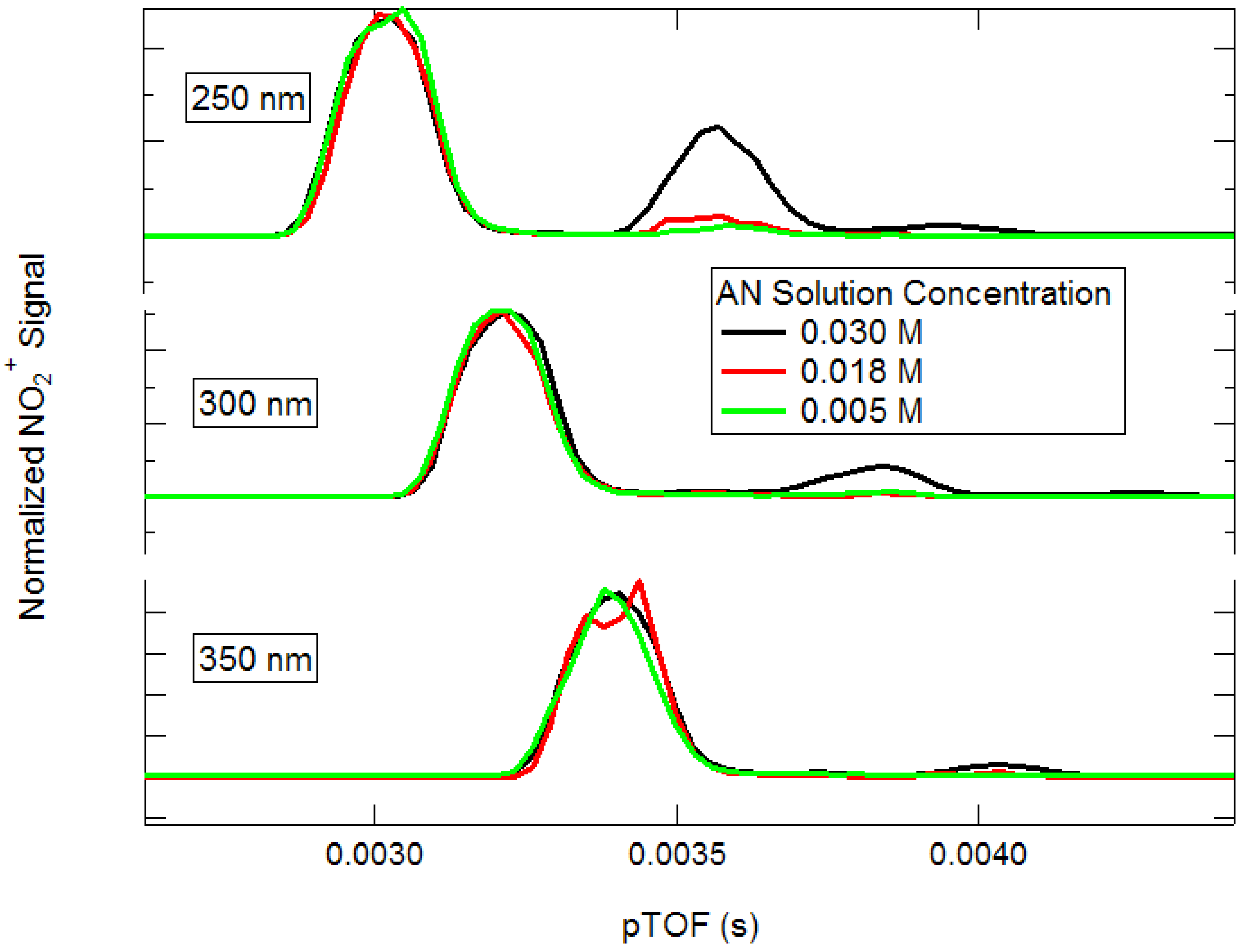
Plot Measured Mass vs Input Mass

Aerosol Diluter Parts

- HEPA filter, Pall p/n 12144 (with 3/8" FNPT ports)
- Valve Swagelok SS-1RS4
- Capillary tube .032"ID x 1/8" OD x 8" length
- Two ¼ swage TEEs, two ¼ x 1/8"swage tube stub reducer (you will probably want one of these to be a bored thru fitting), two 3/8"MNPT x ¼ swage, one ¼" union, two ¼" port connector.
- Some ¼" st. st. tubing (straight and with 90 degree bends).
- Mixing tube.McMaster 1/4"OD 3530K43 $159.31 (http://www.koflo.com/static-mixers/stratos-tube-mixers.html) 7" length

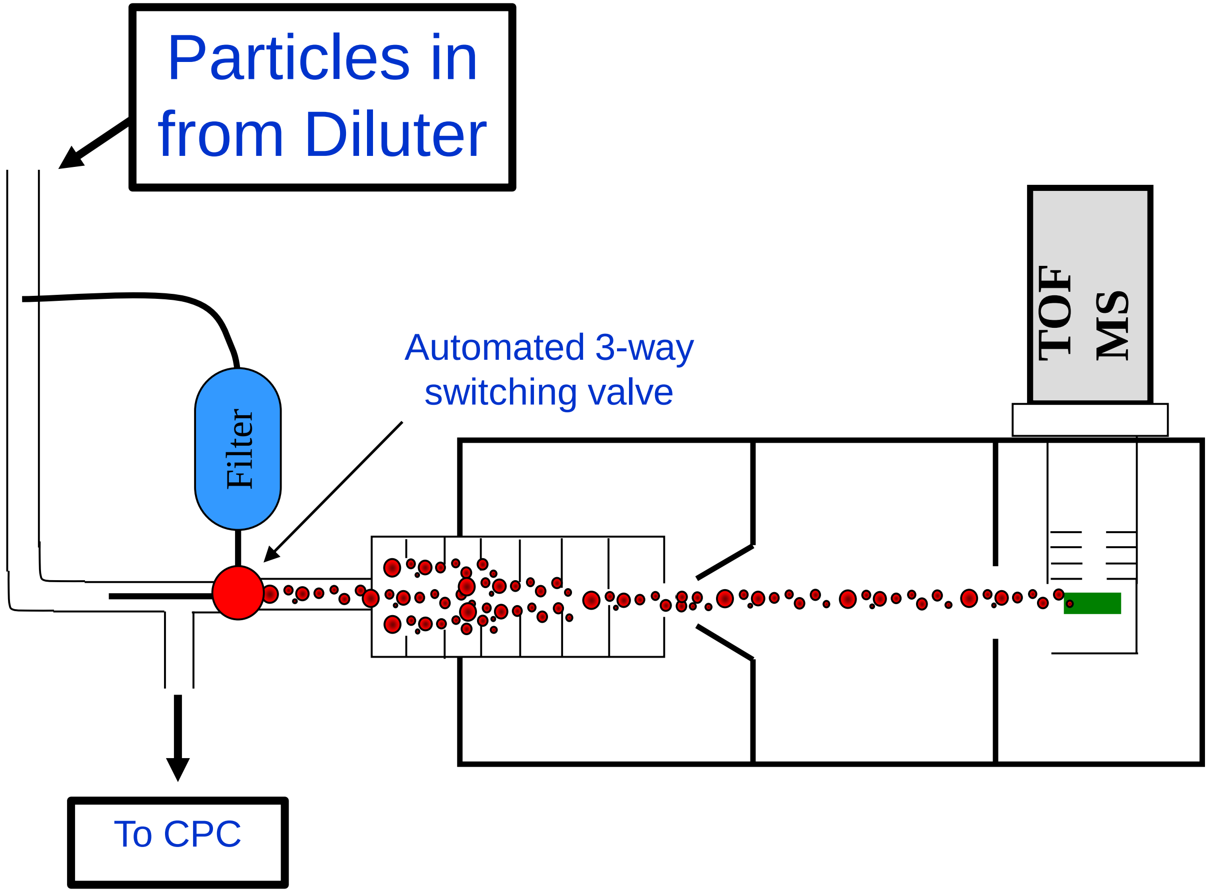


NH_4NO_3 Solution Concentration for ACSM IE Calibration
Want to minimize multiply charged diameters from DMA
Tests performed with TSI 3076 Atomizer



- Use 0.005M NH4NO3
- Aim for 1000 p/cc with diluter valve closed

Setup for calibration



What are we calibrating? Ionization efficiency (IE).

- Want response of instrument to a known amount of NO3, or how many ions (at mz 30 and 46) do we detect per pg of NO3. (For the AMS, IE is expressed as ions/molecule.)
  - NH4NO3 has CE of 1.
  - NO3 forms mostly mz 30 and 46, so easy to count all the ions.
- Use size-selected NH4NO3 (AN) particles – 300 nm is optimal.
  - Enough mass to get good signal to noise.
  - Larger sizes might not be fully transmitted by lens.
  - Smaller sizes have many more Q2 particles from DMA.
- Count particles with CPC.
  - Use Analog Input 3 on ToF-ACSM for Acquility to record CPC counts.
  - Remember that a CPC can be off by ±20%!

IE_NO3 Calculation

- $IE = \frac{\text{ions/s } (30 + 46)}{\text{pg/s (NO3)}}$
- Add the signals at mz 30 and mz 46 = ions/s (30+46).
- pg/s = CPCcnts*4/3π(Dmob/2)^3 * rho*SF*1e-9*MFAnion*Flowrate
  - rho = density (1.72 for NH4NO3, 1.77 for $(NH_4)_2SO_4$
  - SF = shape factor = 0.8 for NH4NO3, 0.85 for $NH_4)_2SO_4$
  - MFAnion = mass fraction anion = 62/(62+18) for NO3
- Plot ions/s for (30+46) vs pg/s for NO3
- Slope = IE_NO3 (ions/pg)
- Also record AB and flow rate during IE calibration.

RIE_NH4 Calculation

- RIE_NH4 = $\dfrac{\text{ions/pg (NH4)} = \text{CPCcnts}*4/3\pi(\text{Dmob}/2)^3*\text{rho}*\text{SF}*1\text{e-}9*\text{MFCation}*\text{Flowrate}}{\text{ions/pg (30 + 46)} = \text{CPCcnts}*4/3\pi(\text{Dmob}/2)^3*\text{rho}*\text{SF}*1\text{e-}9*\text{MFAnion}*\text{Flowrate}}$
- Note that in the calculation of pg/s, the only difference for NH4 and NO3 is the MFCation (62/(62+18)) or MFAnion (18/(62+18)).
- RIE_NH4 = $\dfrac{\text{NH4 (ion/s)/18}}{\dfrac{\text{NO3 ion/s/62}}{1.05}} = \dfrac{\text{NH4 (ions/s)} *1.05 * 62}{\text{NO3 (ions/s)} * 18}$
- Plot NH4 (ions/s) *1.05 * 62 vs NO3 (ions/s) * 18
- slope = RIE_NH4

RIE_SO4 Calculation

- (NH4)2SO4 (AS) has a low (and variable) CE. Reference SO4 to NH4 in internally mixed particles, then CE does not matter.
- RIE_SO4 = $\frac{\text{ions/pg (so4)}}{\text{ions/pg (30+46)}} = \frac{\text{ions/pg(so4)*ions/pg(nh4fromAN)}}{\text{ions/pg (30+46)*ions/pg(nh4fromAS)}}$ =RIE_NH4
- Assumption: RIE_NH4 is the same in AS and AN

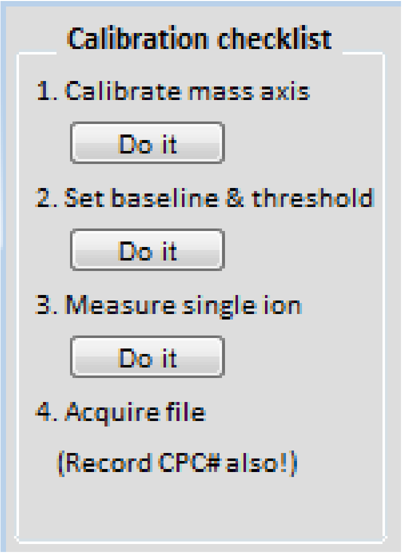
$$= \frac{\text{ions/pg(so4)} \quad \text{*RIE\_NH4}}{\text{ions/pg(nh4fromAS)}}$$

- SO4 pg/s = CPCcnts*4/3π(Dmob/2)^{3*}rho*SF*1e-9*MFAnion*Flowrate
  - rho = density (1.72 for NH4NO3, 1.77 for $(NH_4)_2SO_4$
  - SF = shape factor = 0.8 for NH4NO3, 0.85 for $NH_4)_2SO_4$
  - MFAnion = mass fraction anion = 96/(96+36) for SO4
  - MFCation = 36/(96+36) for NH4 in (NH4)2SO4

RIE_SO4 cont.

- $$RIE\_SO4 = \frac{ions/pg\ (so4)\ *RIE\_NH4}{ions/pg(nh4fromAS)}$$
- Note that in the calculation of pg/s, the only difference for NH4 and SO4 is the MFCation or MFAnion.
- $$RIE\_SO4 = \frac{SO4\ (ions/s)/96\ \ *RIE\_NH4}{NH4\ (ions/s)/36} = \frac{SO4\ (ions/s)\ *\ 36\ *\ RIE\_NH4}{NH4(ions/s)\ *\ 96}$$
- Plot SO4 (ions/s)*36*RIE_NH4 vs NH4 (ions/s)*96
- slope = RIE_SO4

Acquility Calibration Interface

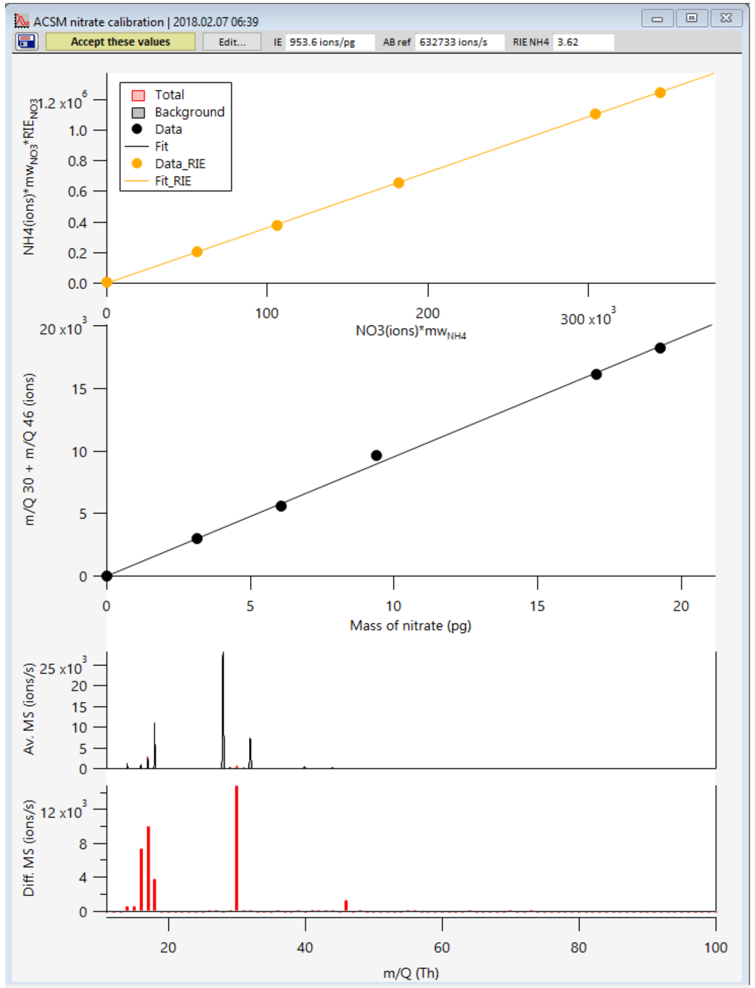


Chose ACSM Calibration profile
Follow steps 1 to 3, then hit Start.
After data collected, will ask for CPC counts (if not recorded on AI3), mobility diameter, and species.
Then will ask if want to start a new graph or add to existing graph.

Timing should be the same as for ACSM_Aquisition mode.

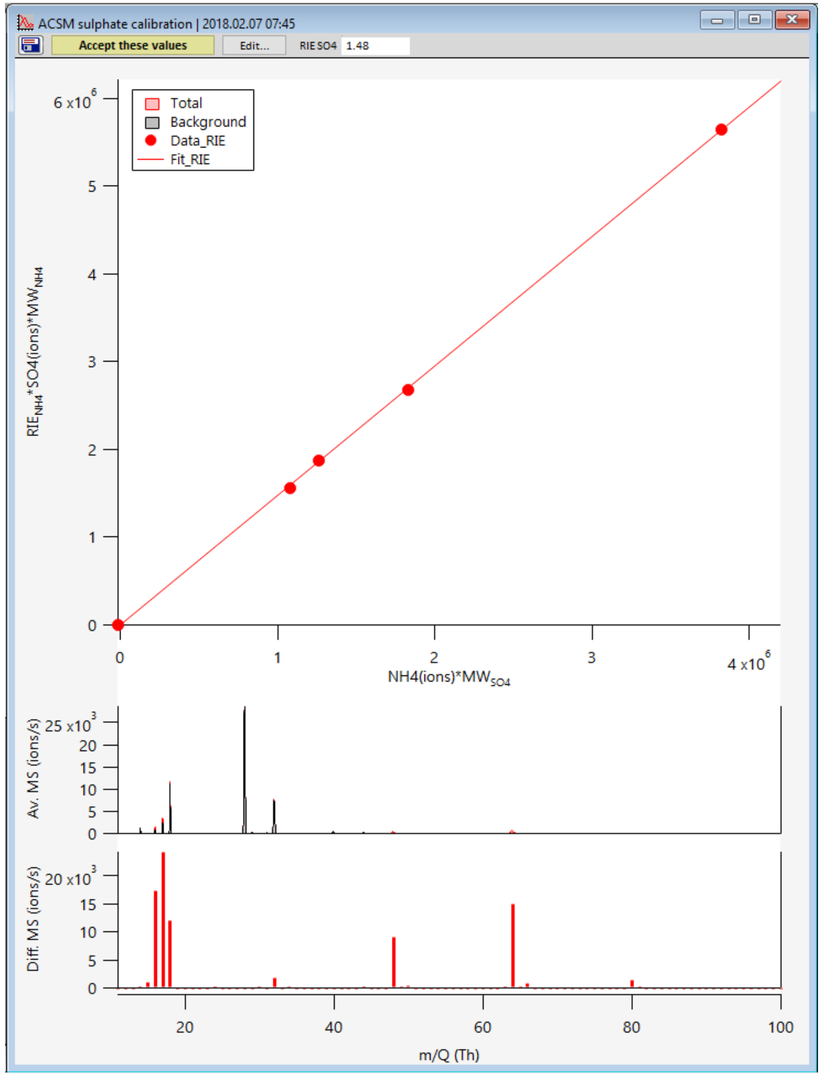
- Switch filter/sample valve every 20 sec.
- Save 2 to 5 minute data file.
- Multipoint NH4NO3 calibration
- Multipoint RIE_SO4 calibration.

IE_NO3 and RIE_NH4 in Acquility



- Do multiple concentrations of NH4NO3, including 0
- IE_NO3 and RIE_NH4 are recorded in workspace profile
- Saved in h5 file
- Imported to Tofware

RIE_SO4 in Acquility



- Do multiple concentrations of $(NH_4)_2SO_4$, including 0
- RIE_SO4 is recorded in workspace profile
- Saved in h5 file
- Imported to Tofware

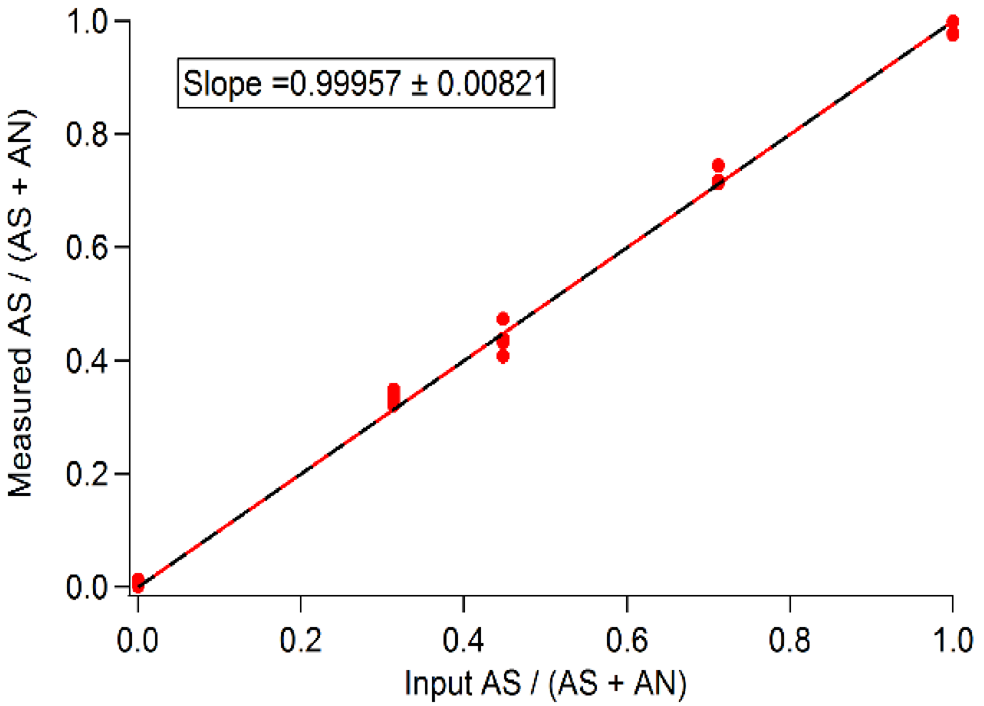
Manual IE Calibration

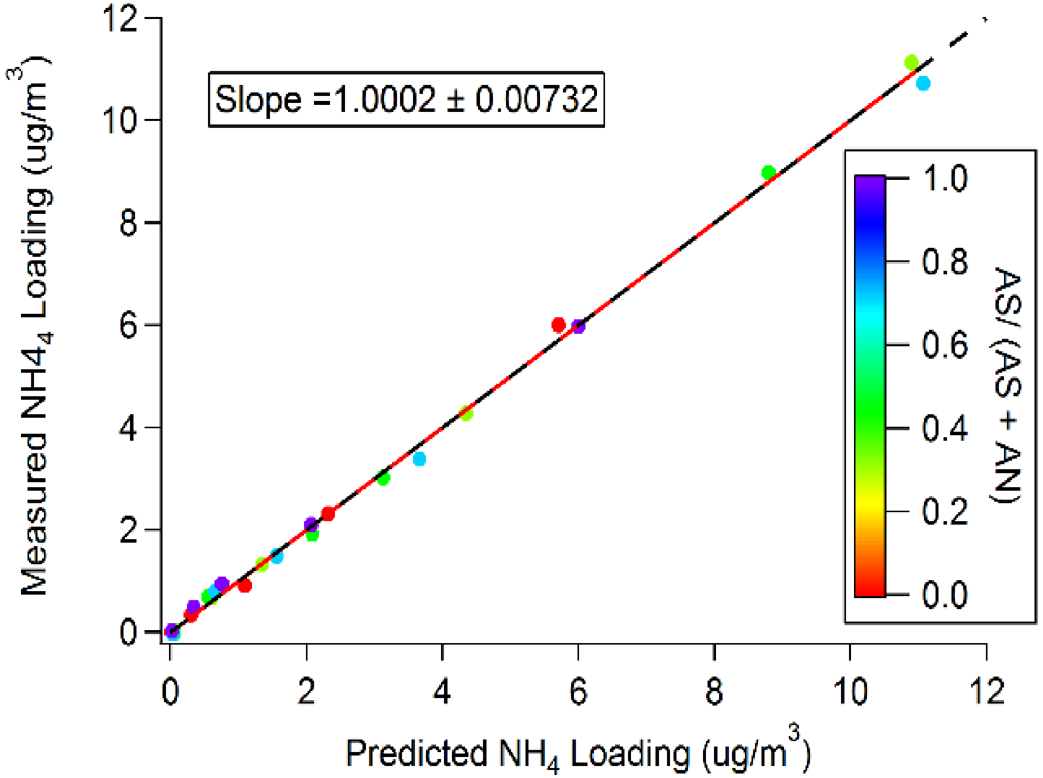
- Highly recommend that users collect calibration data in ACSM_Acq mode and analyze in Tofware to confirm that get same answer as Acquility auto calibrations.
- Detailed instructions in ToFACSM_ManualIECalTutorial_COST.ifn (open notebook in Igor Tofware experiment).
- Acquire data in ACSM_Aquisition mode, i.e., with filter/ambient switching the same as you will use for data acquisition.
- Take data for several number concentrations of 300 nm NH4NO3 particles and several concentrations of 300 nm (NH4)2SO4 particles, including 0 particles.
- Load into Tofware. Be sure to UNCHECK Correct plots for airbeam (in ACSM Settings).
- Calculate species with ug/m3 UNCHECKED. This will give you ions/sec without RIEs applied.
- Equations for IE_NO3, RIE_NH4 and RIE_SO4 are on slides 7, 8 and 10. Also in notebook.

Notes on cleaning TSI atomizer

- Slow way
  - Use a bottle of pure water, run atomizer until CPC counts get to zero
    - This takes ~10 minutes when you're size and/or mass selecting particles
- Faster way
  - Remove top fitting, flush with water
  - Push water through small tube with a rinse bottle
  - Still need to run pure water after, but not for long.

Tested that RIE_NH4 same for NH4NO3 and (NH4)2SO4 using mixtures (Xu et al., AST, 2017).





RIE_NH4 is consistent across range of mixtures, i.e., no matrix effects.