Ionization Efficiency Calibration Tutorial for the ToF-AMS

AMS Users Meeting
September 17, 2006
Edward Dunlea, University of Colorado

Thanks to: Roya, Ann, Pete, Ken, Ingrid, Dara, Qi, Shane, John, Jose, Tim, Doug…

The purpose → Quantification!!!

General page: http://cires.colorado.edu/jimenez-group/UsrMtgs/

Ipf: http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg7/ams_tof_ie_calibration_v3.0.4.ipf

Data: http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg7/IE_tutorial_sample_data.zip

Definitions

- **Ionization Efficiency = ions detected / molecules vaporized**
  - In our case done on per particle basis
  - **IPP = ions per particle; MPP = molecules per particle**
  - IE = IPP / MPP
  - ***Based on NH_4NO_3: m/z 30 + m/z 46***
- IPP calculated from AMS signals
  - MS, pToF and/or BFSP modes
- MPP calculated from particles of known size and composition
  - User must introduce monodisperse distribution
  - Typically NH_4NO_3 [or $(NH_4)_2SO_4$]
  - Use of MS or pToF data require data from particle counter (typically CPC)
- **RIE = Relative Ionization Efficiency**
  - (IE of NH_4) / (IE of NO_3) * ratio of ionization cross sections
  - Ratio of cross sections approximated by molecular weights

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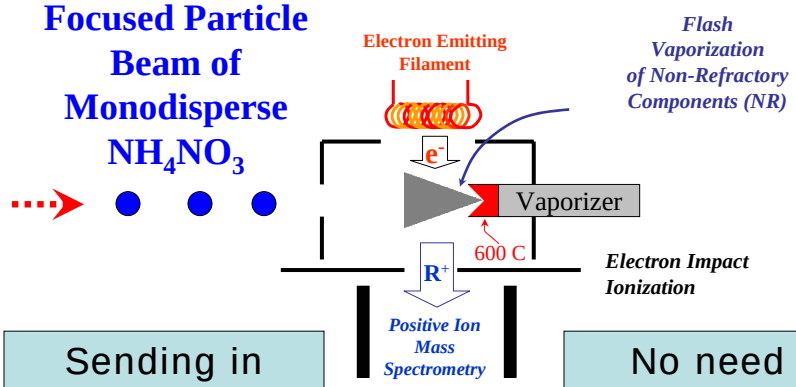
Single Particle Method

Focused Particle Beam of Monodisperse NH_4NO_3



Sending in known packet of particles

No need for external measurement

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Typical Values

- IE
  - Q-AMS 10^{-6}
  - C-ToF-AMS 10^{-7}
  - V-ToF-AMS 10^{-8} – 10^{-7}
  - W-ToF-AMS 10^{-9}
  - Means that 1 million molecules give you ~1 ion

$$IE = \frac{IPP}{MPP}$$

- RIE for NH_4
  - All instruments ~ 4
    - Ratio of $MW(NH_4)$ / $MW(NO_3)$ = 0.29
    - Expect roughly ¼ as many NH_4 ions as NO_3
    - Actually see roughly equal amounts of NH_4 and NO_3 ions
    - RIE is thus ~ 4

$$RIE = \frac{IE(NH_4)}{IE(NO_3)} * \frac{\text{Cross Section}(NO_3)}{\text{Cross Section}(NH_4)}$$

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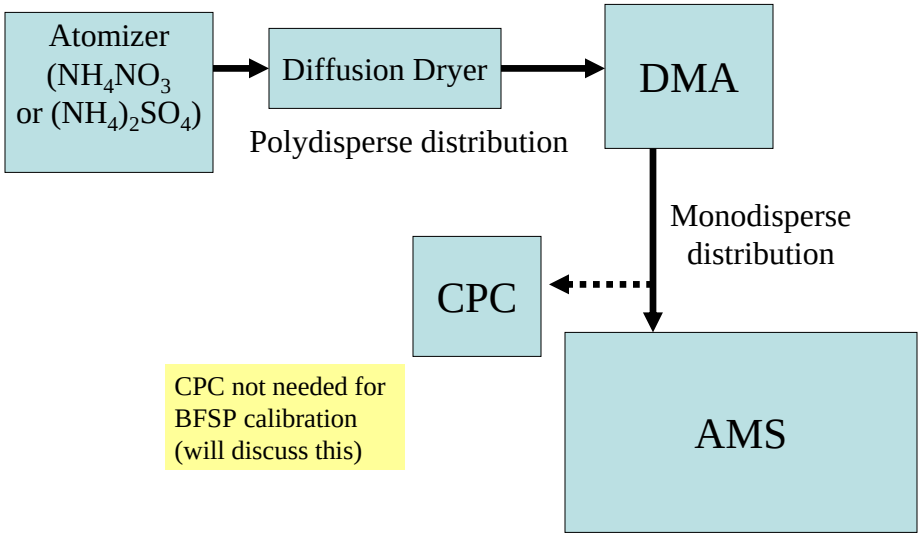
How IE and RIE Get Used

$$MassLoading = \frac{IonSignal * MW}{IE * RIE * N_A * Flowrate}$$

Units: $$\frac{\mu g}{m^3} X = \frac{(\frac{IonsX}{s}) * (\frac{g}{mol})}{(\frac{IonsNO_3^-}{molecules}) * (\frac{IonsX}{IonsNO_3^-}) * (\frac{molecule}{mol}) * (\frac{m^3}{s})}$$

- From Squirrel (current as of v 1.33):
  - Ionization Efficiency waves
    - root:diagnostics:ionEff
    - root:diagnostics:ionEff_logged
  - Relative Ionization Efficiencies
    - IEfac_list in Batch Table
  - Within SQ MS Concentration.ipf
    - ugfac=ug_op?((aw/Navo)*1e12/(ioneff_wave[p1]*flowrate[p1]*rie*ce)):(1)

Typical Calibration Set Up

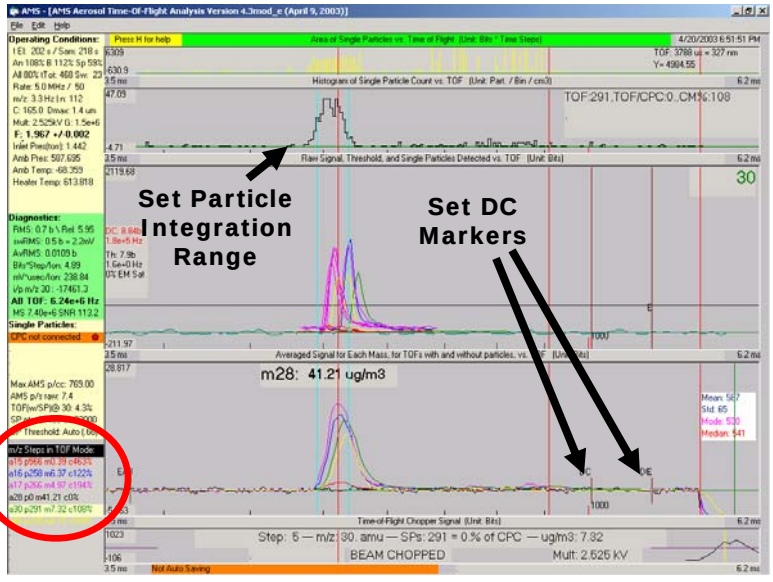


Quad

Q-AMS IE Calibration Procedure

Quad

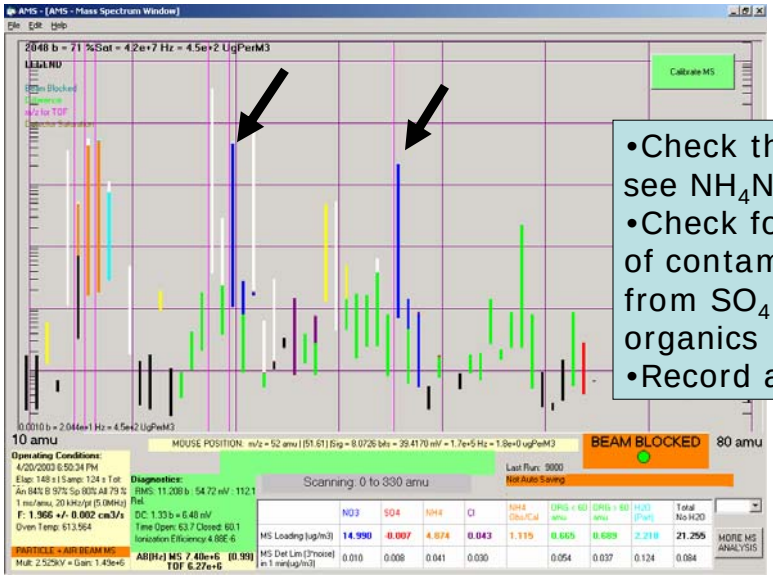
Data Used are from PToF



Record several m/z : NO_3: 30, 46 Airbeam: 28
NH_4: 15, 16, 17

MS Taken for Consistency and AB

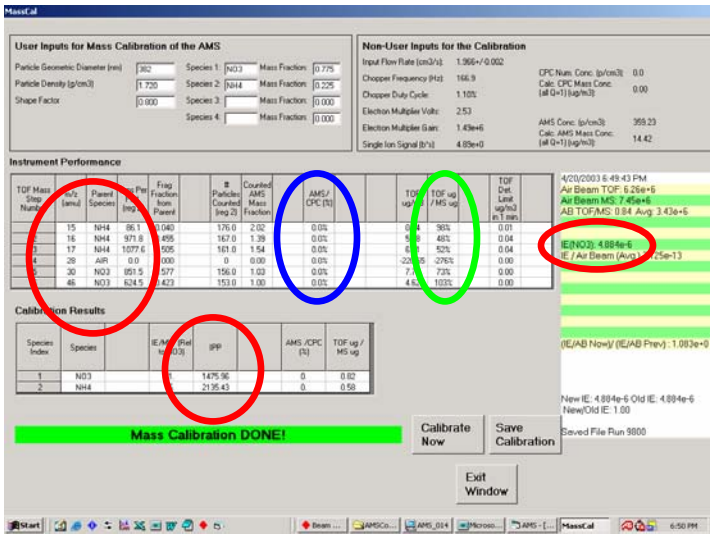
Quad



- Check that you see NH_4NO_3
- Check for lack of contamination from SO_4 and organics
- Record airbeam

IE Calibration Panel for Q-AMS

Quad



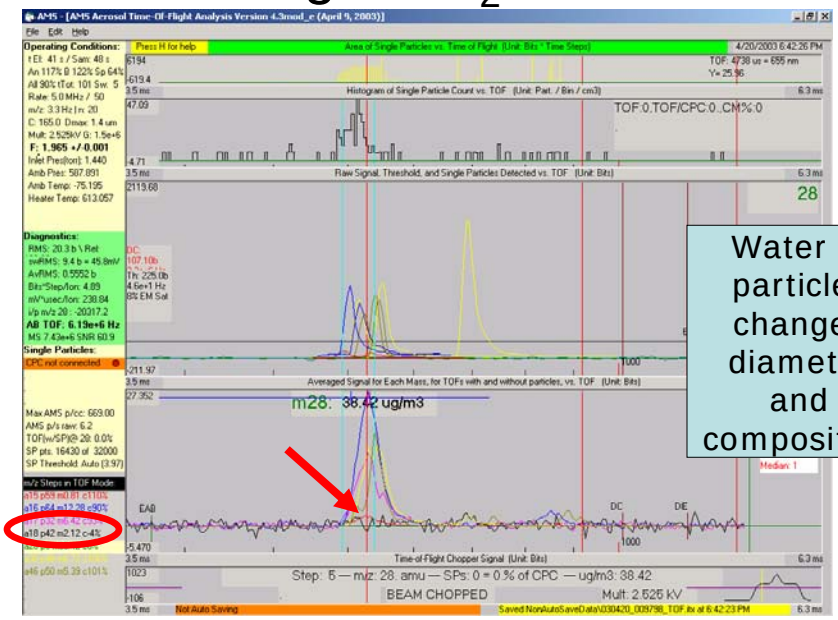
- Calculate IPP for list of *m/z*s
- Sum up IPPs for NH_4 & NO_3
- Calculate MPP (not shown)
- IE = IPP / MPP

If you have CPC, check transmission

ToF / MS should be 100%

Quad

Checking for H_2O in Particles



Water in particles changes diameter and composition

ToF

On to the ToF…

C-ToF-AMS

HR-ToF-AMS (V-Mode)

HR-ToF-AMS (W-Mode)

Single Particle Based

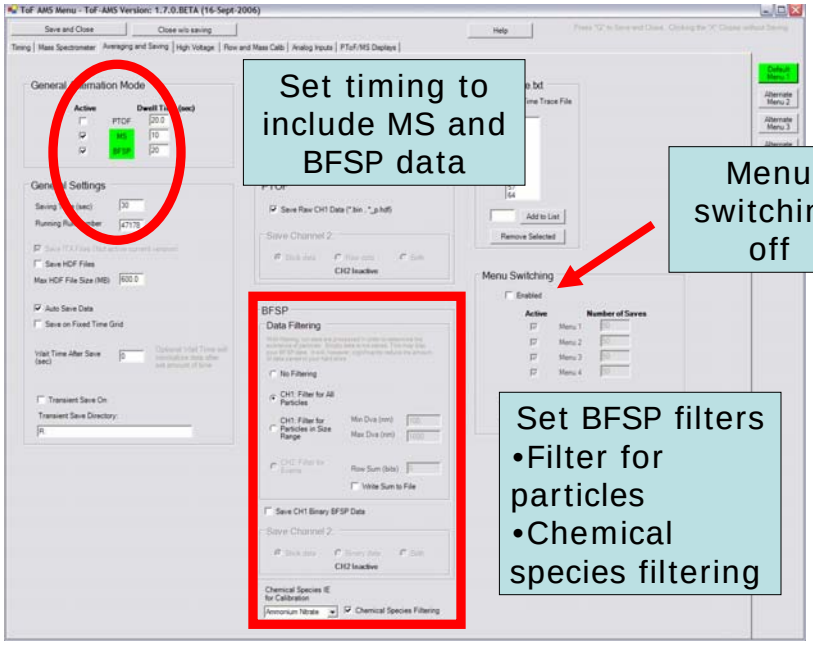
Mass Based

Mass Based Ensemble Approach
- Relies and comparison with another instrument (CPC)
- Takes time

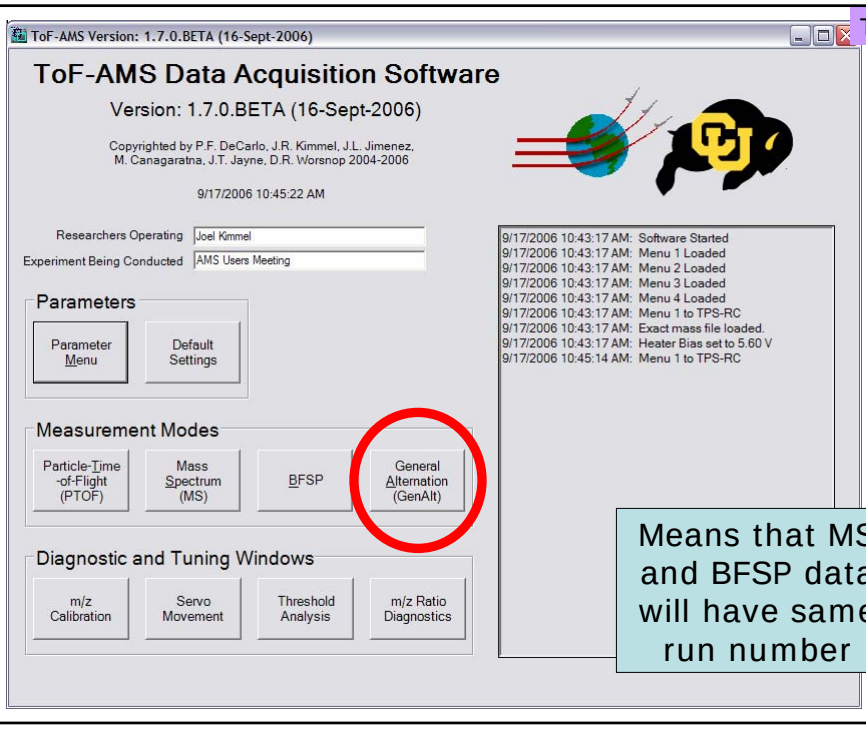
Single Particle Approach
- Can be done on all particles (above certain size)
- For both instruments (C-ToF-AMS and HR-ToF-AMS)
- Not for W mode → will discuss in later slide
- BFSP → will define in 4 more slides

Acquisition Software Parameter Menu

ToF

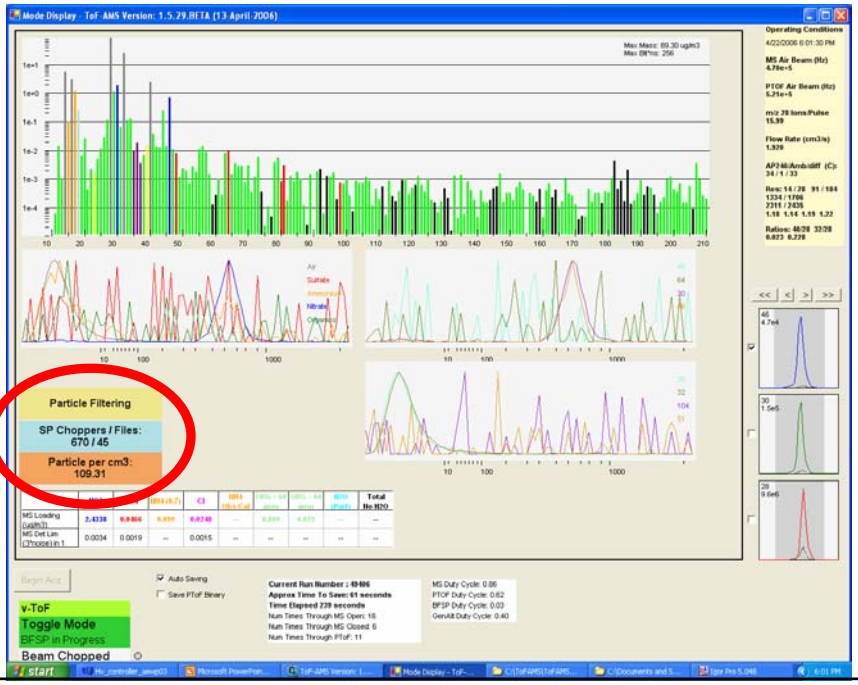


ToF



ToF

Screen shot during IE calibration

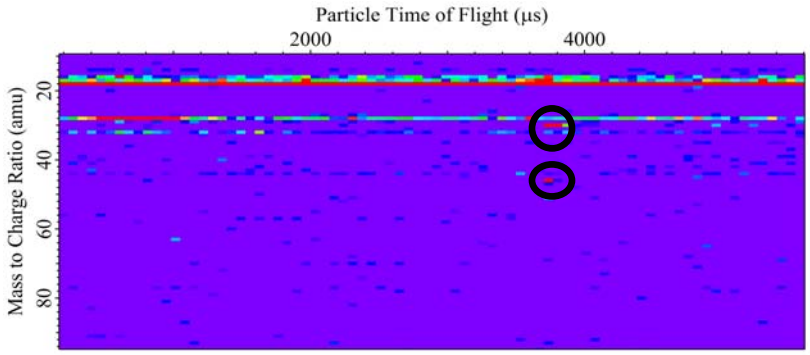


ToF

BFSP

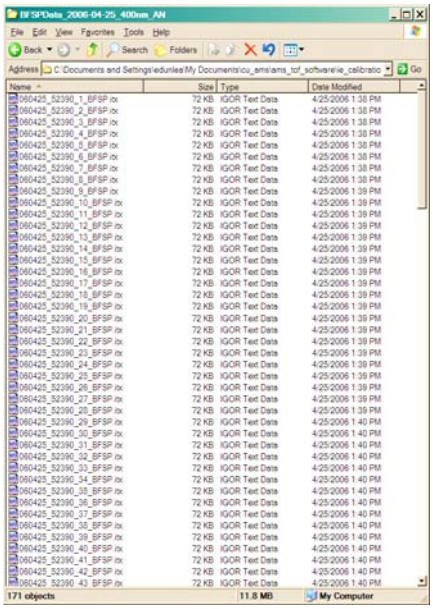
Difficult to get BFSP signal in W-ToF mode

- BFSP = Brute Force Single Particle
- BFSP = single pToF file
- Save of BFSP particle file triggered when 2 *m/z*s from same compound > 10 bit*ns
  - E.g., NH_4NO_3 → *m/z* 30 and 46



ToF

BFSP Files



- Stored as individual itx files
  - Saved under C:/ToFAMS/ToFAMSData/BFSP/
  - MS data saved in as itx files C:/ToFAMS/ToFAMSData/AutoSaveData/
- Each contains one pToF matrix
- No info or parameters included
  - Important to run in Gen Alt mode in order to save MS and pToF info files
  - Also allows checking of IE values through Squirrel
    - Will explain near end of talk

ToF

BFSP Software Versions

- Version 1 – Created by Roya Bahreini
- Version 2.0.1 - Created by Edward Dunlea
  - Making the panel
- Version 2.1.0 - Updates from Ed
  - Functional and cosmetic updates to panel
- Version 2.2.0 – Updates from Ed
  - More updates to panel
- **Version 3.0.4 – Critical updates from Ed**
  - **Inclusion of duty cycle correction to IPP calculation**
  - **Inclusion of proper definition of RIE**
  - **Must use this version of code or later**

Stop. Open Igor and go through panel.

Will be done with version 3.0.4 of code

Points to Discuss During Tutorial

- 1) Need Igor 5.0 or higher
- 2) Explain that there are 2 panels:
- small screen version (show this, then close)
- regular screen version
- 3) Sample data is from INTEX campaign, HR-ToF-AMS run in V-mode
- 350 nm AN particles, sheath to sample ratio of 5:1 on DMA
- from 4/25/2006
- saved in gen alt mode (show BFSP and MS/PToF data folders)
- 4) Do Browse for BFSP and MS data
- explain that run numbers are being filled in for you
- explain data folder name
- 5) Explain all load variables
- show how you can toggle back and forth between compounds
- explain "clear all on load" and "save raw" check boxes"
- 6) Hit load button
- point out run # and particle # counters
- show data browser and look inside data folder
- 7) Explain Particle Time of Flight Traces graph
- show how to set ranges with marquee - can be done by hand as well
- particle arrival range = filter; if either anion trace max occurs outside this range, particle ignored
- baseline #1 = baseline for anion traces only
- baseline #2 = baseline for cation and anion traces
- summation of particle signal done between front edge of particle arrival range and front edge of baseline#2
- 8) Explain rest of input variables
- SI, Dm and Co-adds
- 9) Hit Do It button
- 10) Maybe go back to power point to show full IE equation
- 11) Explain IPP histograms
- Minimum IPP values are there if you wish to test, not recommended at current time
- 12) Explain IE / RIE plot
- line is running average
- dashed lines are +/- 1 std dev
- point out # of particles in final count
- noisy measurment of stable value
- 13) Show example of blacklisting
- show label on PToF plot for "particle kept"
- blacklist a couple particles
- reload data and highlight difference in final particle count
- 14) Explain view calc inputs button

IE Calculation

Duty Cycle Correction

$$\text{Ion Per Particle} = \frac{\Sigma(RawMSsig(bit \cdot ns) * \sqrt{\frac{28}{m/z}})}{SingleIon(bit \cdot ns)}$$

Sum for *m/z*s in molecule

$$PartVol = \frac{4}{3}\pi(\frac{D_{mob}}{2})^3$$

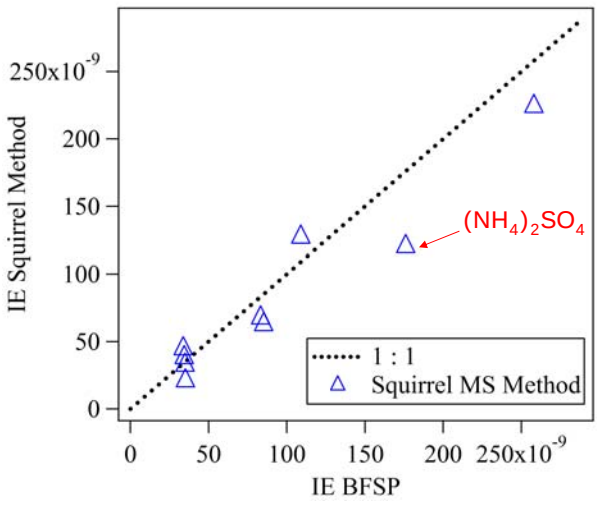
$$\text{Molecules Per Particle} = \frac{\rho(g \cdot cm^{-3}) * S * ParticleVol(cm^3) * N_A(molecule \cdot mol^{-1})}{MW_{NH_4NO_3}(g \cdot mol^{-1})}$$

$$IE = \frac{\text{Ion Per Particle}}{\text{Molecule Per Particle}}$$

Mass Based Method

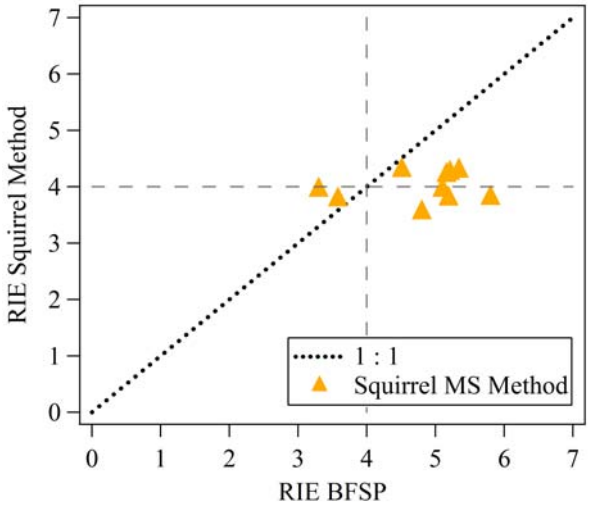
- We're working on writing up method for a web site
  - Not that hard, just haven't gotten to it
- Comparisons shown below from mass based method:
  - Use Squirrel to calculate mass loadings with assumed IE
  - Calculate mass loadings from CPC numbers
  - Use ratio to calculate real IE

IE Comparisons



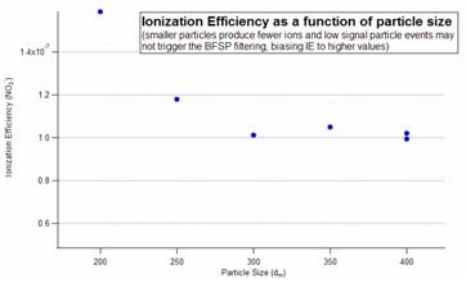
- Comparisons generally pretty good
  - Within 30% or so
  - This plot for 300 – 400 nm NH_4NO_3
- We currently believe BFSP IE calibrations are valid
  - More data points welcomed
  - For now, send to Ed

RIE Comparisons

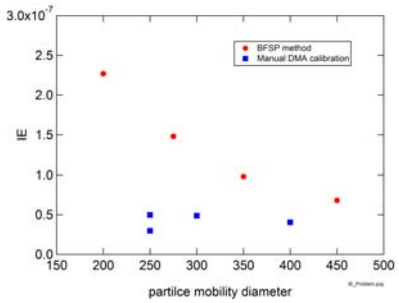


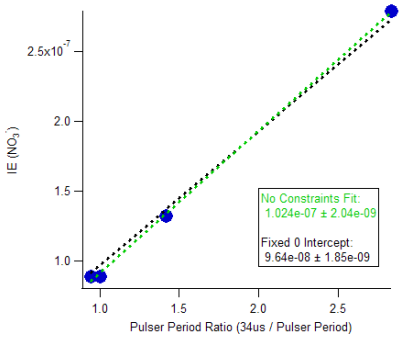
- RIE from Squirrel ~ 4 consistently
- RIE from BFSP ~ 5 for many calibrations
  - BFSP "threshold" too high

IE as Function of Size and Pulser Period



- Stable IE down to certain size particle
- Threshold biases towards larger particles (higher IE)
- Ion signal scales with pulser period





Recommendations

- All instruments
  - Monodisperse dried NH_4NO_3
- Q-AMS
  - Use of IE calibration window
- C-ToF-AMS & V-ToF-AMS
  - Record in BFSP
    - For same pulser period as your data
  - Check with more than one particle size
    - Make sure no thresholding bias
  - Check IE using MS data with calibration particles
- W-ToF
  - Calibrate in V mode
    - Use ratio of AB in W and V modes
  - As check, record in MS mode
    - Method to be described on web site

$$\mathrm{IE\,(W)} = \mathrm{IE\,(V)}\frac{\mathrm{AB\,(W)}}{\mathrm{AB\,(V)}}$$

Where We Are Going

- For the moment, still good idea to look at both BFSP and Squirrel data
  - Will have instructions for processing IE data in Squirrel posted on web in near future
- More feedback on BFSP code welcomed
  - Please email Ed at edward.dunlea@colorado.edu
    - Especially wish to know about bugs
    - Will **NOT** entertain requests/complaints/suggestions if you have not read the "Read Me" file contained within the code
  - Will try to compile suggestions from this meeting and release new version within next couple weeks
    - Do not expect calculations to change
    - Only expect small feature/aesthetic upgrades

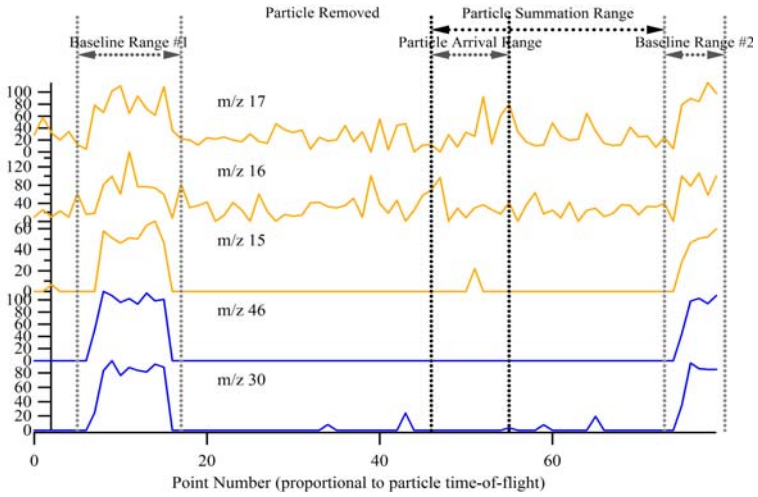
Coding To Do

- Improve blacklisting
  - Will interact with DoIt button instead of load step
  - Add blacklist button to IE / RIE window
- Include dateTime as one of the parameters saved in the info waves
- Add ability to use different run number for MS data??

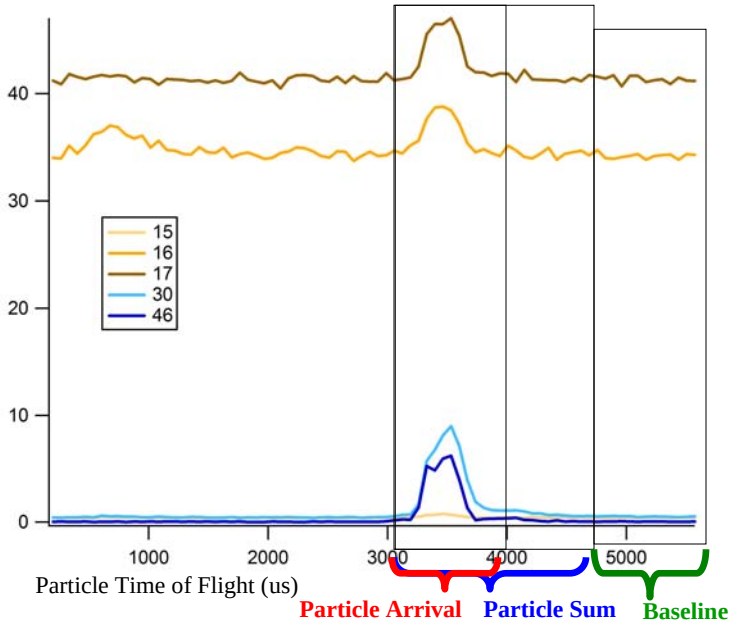
Extra Slides

Screen Shots and Further Explanation Slides

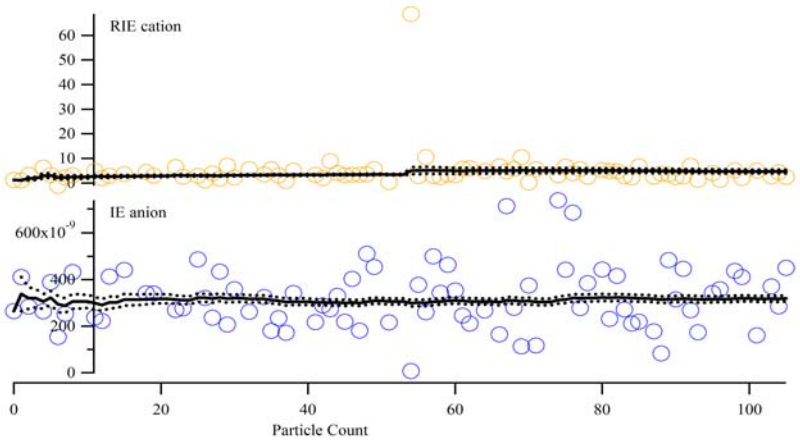
Particle Time of Flight Graph



Particle Time of Flight Ranges



IE and RIE Results Graph



"MS Method" – Used in This Tutorial

- Calculate mass loadings based on CPC number
- Compare to mass loading calculated by Squirrel (with assumed IE & RIE)

$$NO_3(\mu g \cdot m^{-3}) = CPC(part \cdot cm^{-3}) * S * PartVol(cm^3) * \rho(g \cdot cm^{-3}) * \frac{MW_{NO_3}(g \cdot mol^{-1})}{MW_{NH_4NO_3}(g \cdot mol^{-1})}$$

$$NH_4(\mu g \cdot m^{-3}) = CPC(part \cdot cm^{-3}) * S * PartVol(cm^3) * \rho(g \cdot cm^{-3}) * \frac{MW_{NH_3}(g \cdot mol^{-1})}{MW_{NH_4NO_3}(g \cdot mol^{-1})}$$

$$IE_{MS} = \frac{MassLoad(NO_3)_{AMS}}{MassLoad(NO_3)_{CPC}} * IE_{AMS}$$

$$RIE_{MS} = \frac{MassLoad(NH_4)_{AMS}}{MassLoad(NH_4)_{CPC}} * \frac{IE_{AMS}}{IE_{CPC}} * RIE_{AMS}$$

Typical Calibration Set Up

Atomizer and DMA

CPC

AMS