

Ionization Efficiency Calibration Tutorial for the ToF-AMS

AMS Users Meeting

September 17, 2006

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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

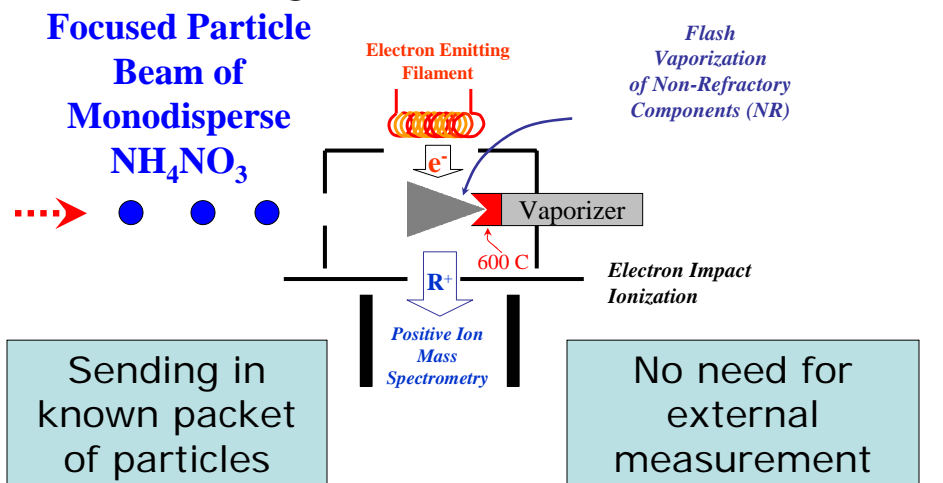
- **Ionization Efficiency = ions detected / molecules vaporized**
 - In our case done on per particle basis
 - **IPP = ions per particle; MPP = molecules per particle**
 - $IE = IPP / MPP$
 - **Based on NH_4NO_3 : $m/z\ 30 + m/z\ 46$**
- IPP calculated from AMS signals
 - MS, pToF and/or BFSP modes
- 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



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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}

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

– Means that 1 million molecules give you ~1 ion

- RIE for NH_4

- All instruments ~ 4
- Ratio of $\text{MW}(\text{NH}_4) / \text{MW}(\text{NO}_3) = 0.29$
- Expect roughly $\frac{1}{4}$ as many NH_4 ions as NO_3
- Actually see roughly equal amounts of NH_4 and NO_3 ions
- RIE is thus ~ 4

$$\text{RIE} = \frac{\text{IE}(\text{NH}_4) * \text{Cross Section}(\text{NO}_3)}{\text{IE}(\text{NO}_3) * \text{Cross Section}(\text{NH}_4)}$$

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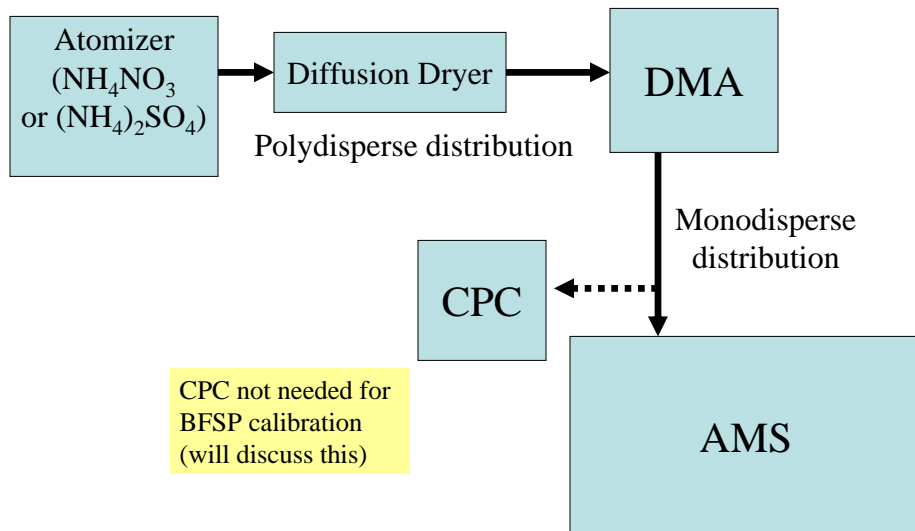
How IE and RIE Get Used

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

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

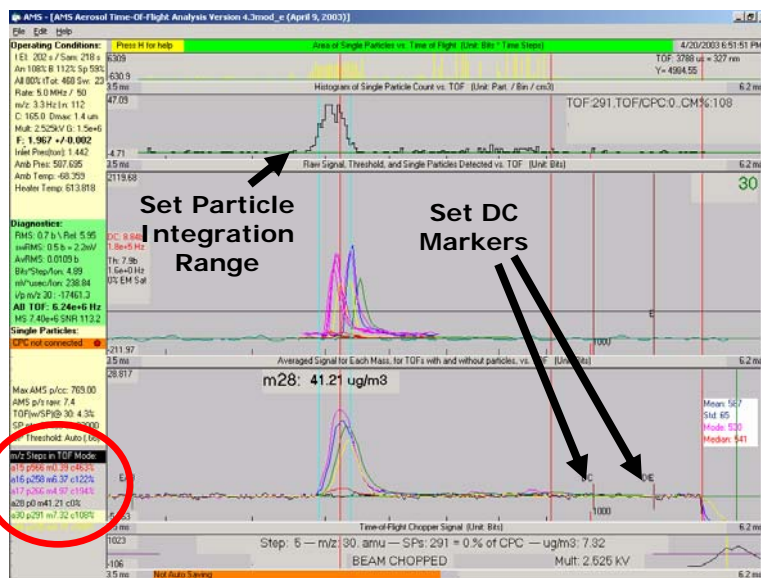
- From Squirrel (current as of v 1.33):
 - Ionization Efficiency waves
 - root:diagnostics:ionEff
 - root:diagnostics:ionEff_logged
 - Relative Ionization Efficiencies
 - IEfac_list in Batch Table
 - Within SQ MS Concentration.ipf
 - ugfac=ug_op?((aw/Navo)*1e12/(ioneff_wave[p1]*flowrate[p1]*rie*ce)):1

Typical Calibration Set Up



Q-AMS IE Calibration Procedure

Data Used are from PToF



Record several m/z : NO₃: 30, 46 Airbeam: 28
 NH₄: 15, 16, 17

MS Taken for Consistency and AB

Quad

AMS - [AMS - Mass Spectrum Window]

2048 b = 71 %Sat = 4.2e7 Hz = 4.5e2 UqPerM3

LEAD IN

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

Operating Conditions:
 4/20/2003 6:50:34 PM
 Elap: 1.48 s Samp: 124 x ToF
 Air MS: 0.97% Sp: 82% at 79 %
 1 ms/amu 20 kHz/yr (5.0MHz)
 F: 1.966 +/- 0.002 cm/s
 Oven Temp: 613.564

Diagnostic:
 RMS: 11.200 b 54.72 mV 112.1
 DC: 1.333 b +/- 6.48 mV
 Time Open: 63.7 Closed: 50.1
 Ionization Efficiency: 4.86E-6

Scanning: 0 to 330 amu

	NO ₂	SO ₄	NH ₄	Cl	NH ₄ Oba/Cal	DPMS + 60	DPMS + 80	H ₂ O	Total
MS Loading (ug/m ³)	14.990	0.007	4.674	0.043	1.115	0.605	0.689	2.218	21.295
MS Det Lim (Photo) in 1 min (ug/m ³)	0.010	0.008	0.041	0.030	0.054	0.037	0.124	0.084	

BEAM BLOCKED

IE Calibration Panel for Q-AMS

Quad

MassCal

User Inputs for Mass Calibration of the AMS

Particle Geometric Diameter (um): 0.02
 Particle Density (g/cm³): 1.720
 Shape Factor: 0.000

Species 1: NO₂ Mass Fraction: 0.775
 Species 2: NH₄ Mass Fraction: 0.225
 Species 3: Mass Fraction: 0.000
 Species 4: Mass Fraction: 0.000

Non-User Inputs for the Calibration

Input Flow Rate (cm³/s): 1.966 +/- 0.002
 Chopper Frequency (Hz): 166.9
 Chopper Duty Cycle: 1.10%

Electron Multiplier Volt: 2.53
 Electron Multiplier Gain: 1.43e+6
 Single Ion Signal (Hz): 4.89e+0

CPC Num. Conc. (p/m³): 0.0
 Calc. CPC Mass Conc. (at D=1) (ug/m³): 0.00
 AMS Conc. (p/m³): 395.23
 Calc. AMS Mass Conc. (at D=1) (ug/m³): 14.42

Instrument Performance

TOF Mass Spec. Num.	m/z (amu)	Parent Species	Flag	Frag. Fraction from Parent	# Particles Counted (Imp. 2)	Counted AMS Mass Fraction	AMS / CPC (%)	TOF up / MS up	TOF Det. Limit (ug/m ³) in 1 min
15	NH ₄	86.1	0.040	176.0	2.02	0.0%	30%	0.01	
16	NH ₄	971.8	0.095	167.0	1.39	0.0%	48%	0.04	
17	NH ₄	1077.6	0.05	161.0	1.54	0.0%	32%	0.04	
28	AM	0.0	0	0	0.00	0.0%	20%	0.00	
30	NO ₂	61.5	0.77	156.0	1.03	0.0%	73%	0.00	
46	NO ₃	62.5	0.23	153.0	1.00	0.0%	100%	0.00	

Calibration Results

Species Index	Species	IE (at 0.3)	IPP	AMS / CPC (%)	TOF up / MS up
1	NO ₂	1475.96	0	0	0.02
2	NH ₄	2135.43	0	0	0.50

Mass Calibration DONE!

Calculate Now Save Calibration Exit Window

If you have CPC, check transmission

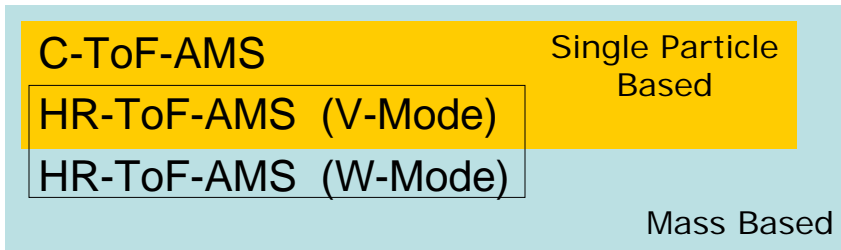
ToF / MS should be 100%

• Calculate IPP for list of m/z
 • Sum up IPPs for NH_4 & NO_3
 • Calculate MPP (not shown)
 • $\text{IE} = \text{IPP} / \text{MPP}$

Checking for H₂O in Particles



On to the ToF...



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

Set timing to include MS and BFSP data

Menu switching off

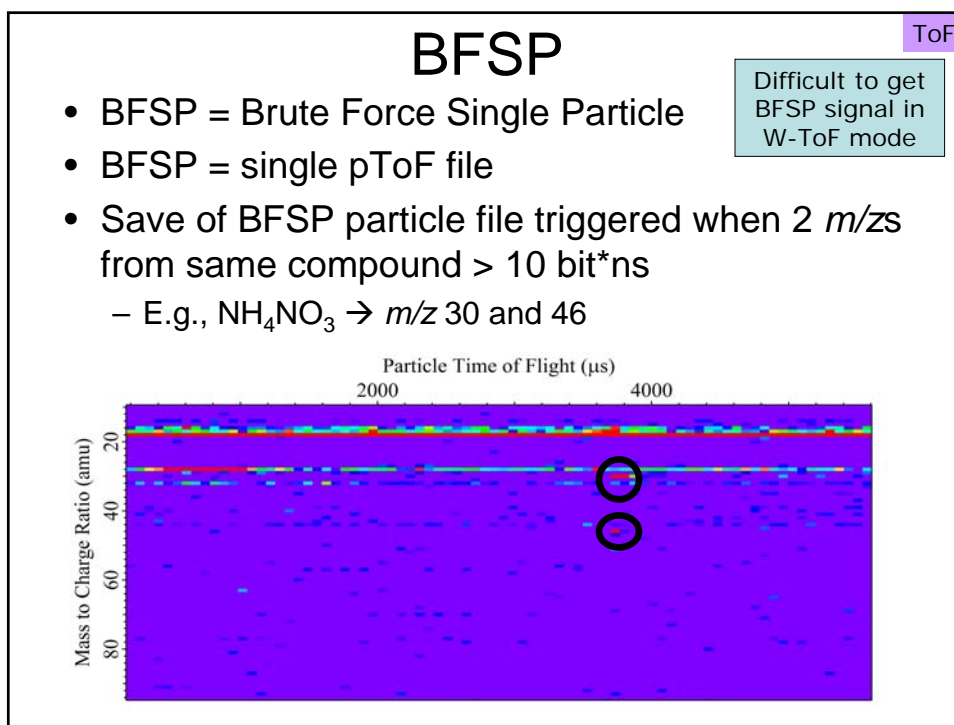
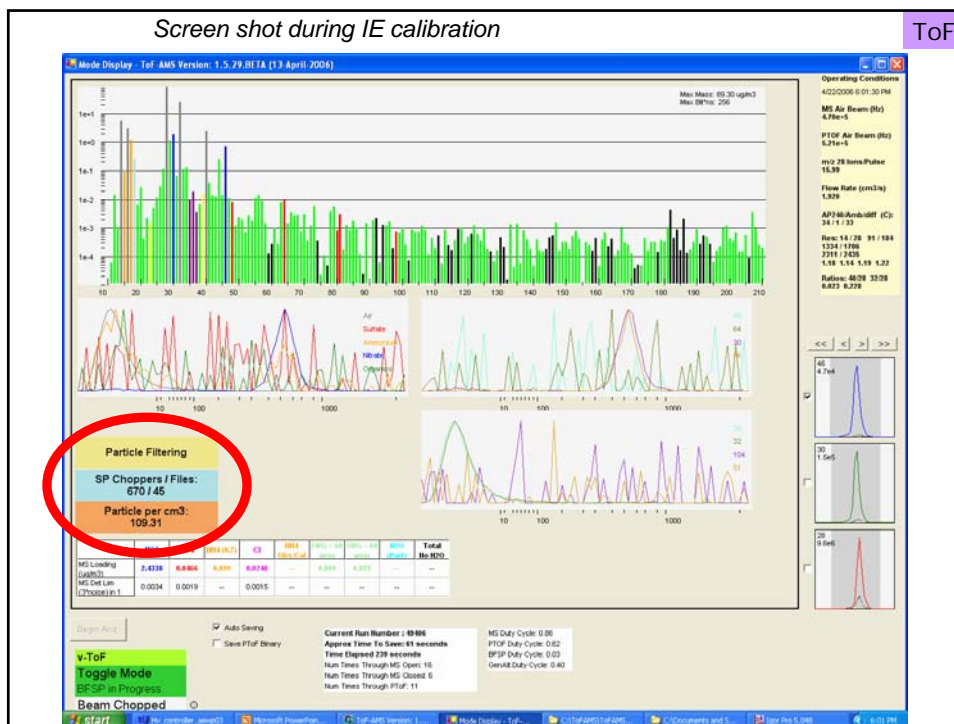
Set BFSP filters

- Filter for particles
- Chemical species filtering

Means that MS and BFSP data will have same run number

```

9/17/2006 10:43:17 AM: Software Started
9/17/2006 10:43:17 AM: Menu 1 Loaded
9/17/2006 10:43:17 AM: Menu 2 Loaded
9/17/2006 10:43:17 AM: Menu 3 Loaded
9/17/2006 10:43:17 AM: Menu 4 Loaded
9/17/2006 10:43:17 AM: Menu 1 to TPS-RC
9/17/2006 10:43:17 AM: Exact mass file loaded.
9/17/2006 10:43:17 AM: Heater Bias set to 5.60 V
9/17/2006 10:45:14 AM: Menu 1 to TPS-RC
    
```

BFSP Files

Name	Size	Type	Date Modified
000425_52390_1_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_2_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_3_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_4_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_5_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_6_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_7_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_8_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_9_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_10_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_11_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_12_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_13_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_14_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_15_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_16_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_17_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_18_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_19_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_20_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_21_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_22_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_23_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_24_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_25_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_26_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_27_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:38 PM
000425_52390_28_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_29_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_30_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_31_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_32_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_33_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_34_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_35_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_36_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_37_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_38_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_39_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_40_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_41_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_42_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM
000425_52390_43_BFSP.itx	72 KB	IGOR Text Data	4/25/2006 1:40 PM

- 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

BFSP Software Versions

- ~~Version 1 – Created by Roya Behneini~~
- ~~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 measurement 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

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

Sum for m/z s
in molecule

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

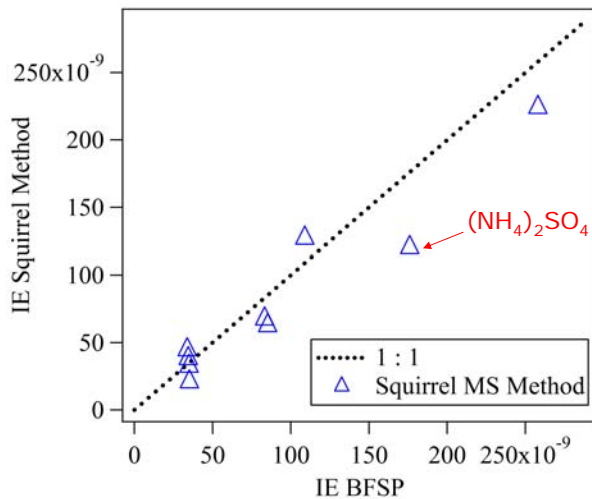
$$\text{Molecules Per Particle} = \frac{\rho(\text{g} \cdot \text{cm}^{-3}) * S * \text{ParticleVol}(\text{cm}^3) * N_A(\text{molecule} \cdot \text{mol}^{-1})}{MW_{\text{NH}_4\text{NO}_3}(\text{g} \cdot \text{mol}^{-1})}$$

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

Mass Based Method

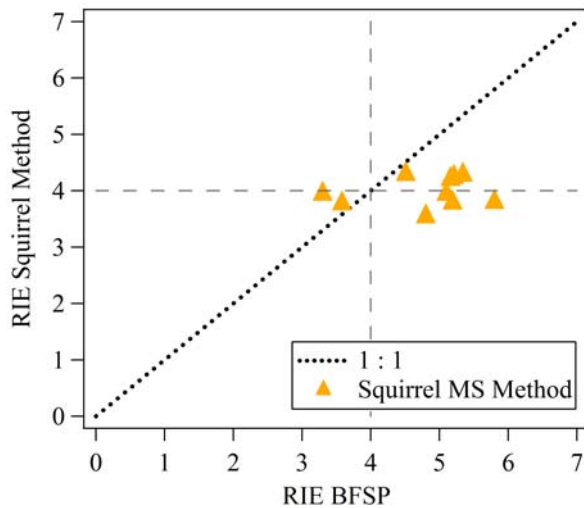
- We're working on writing up method for a web site
 - Not that hard, just haven't gotten to it
- Comparisons shown below from mass based method:
 - Use Squirrel to calculate mass loadings with assumed IE
 - Calculate mass loadings from CPC numbers
 - Use ratio to calculate real IE

IE Comparisons



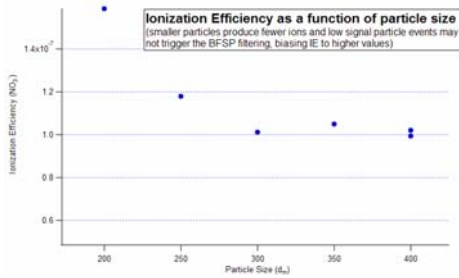
- Comparisons generally pretty good
 - Within 30% or so
 - This plot for 300 – 400 nm NH_4NO_3
- We currently believe BFSP IE calibrations are valid
 - More data points welcomed
 - For now, send to Ed

RIE Comparisons

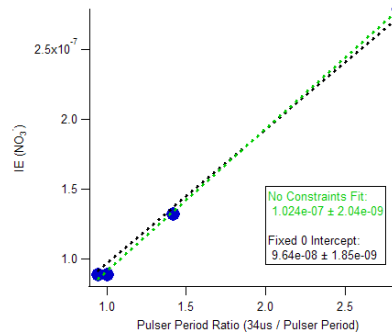
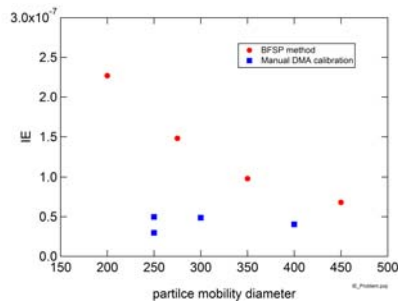


- RIE from Squirrel ~ 4 consistently
- RIE from BFSP ~ 5 for many calibrations
 - BFSP “threshold” too high

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

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

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

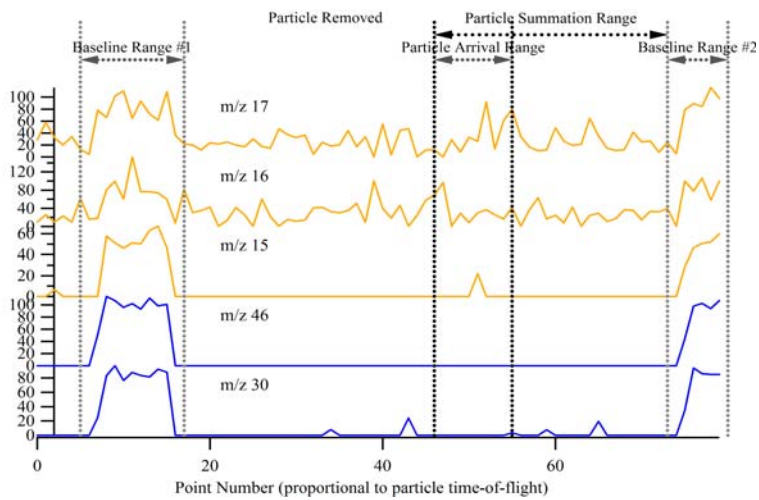
Coding To Do

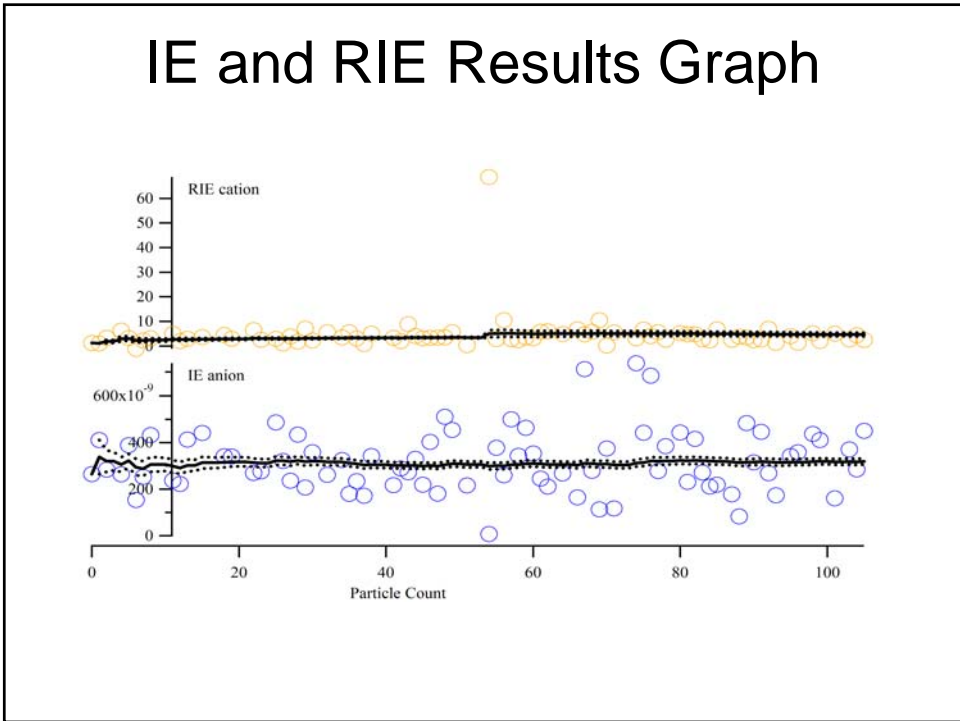
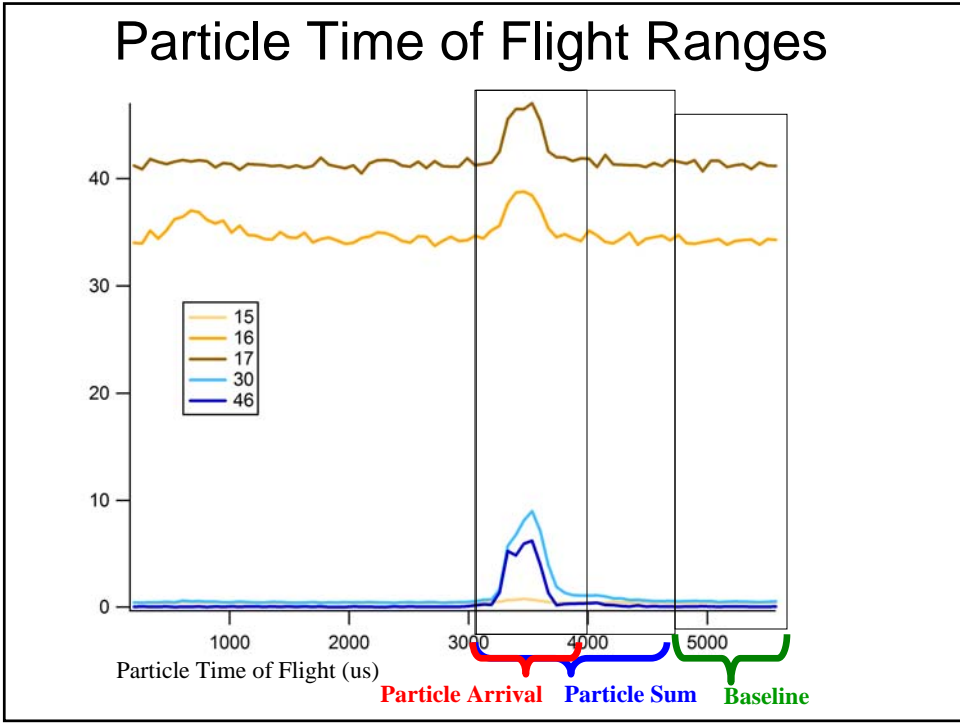
- Improve blacklisting
 - Will interact with Dolt button instead of load step
 - Add blacklist button to IE / RIE window
- Include dateTime as one of the parameters saved in the info waves
- Add ability to use different run number for MS data??

Extra Slides

Screen Shots and Further
Explanation Slides

Particle Time of Flight Graph





“MS Method” – Used in This Tutorial

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

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

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

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

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

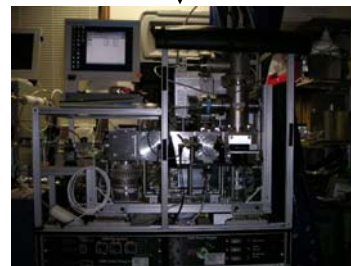
Typical Calibration Set Up



Atomizer and DMA



CPC



AMS

