Sulfate RIE for Batch File

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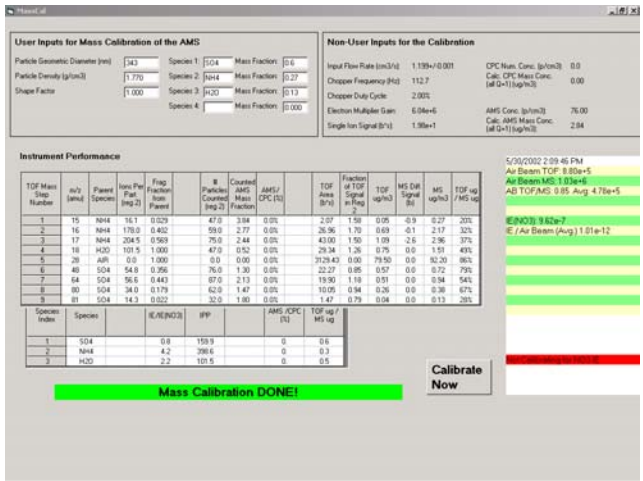
- Want IE sulfate/IE nitrate to use in Batch file, based on measured IE.
- In May, discussed with Aerodyne how to calculate IE sulfate using ammonium sulfate calibration data and Frank's sulfate fragmentation pattern (reference data).
- Step 1: account for all sulfate ions
- Step 2: include S34 isotopes
- Step 3: account for all water ions
- Step 4: sum sulfate and water ions
- Step 5: use shift-M IE sulfate/IE nitrate value and mass fractions to calculate actual IE sulfate/IE nitrate

Ammonium Sulfate Calibrations

- Several ammonium sulfate calibrations have been performed to determine the relative ionization efficiency of sulfate to nitrate.
- These include:
- 5/30/02 (dry, 343 nm with Worsnop) using AMS software v.3.83
- 2/28/03 (wet and dry 199 nm particles) using AMS software v.3.90
- 6/10/03 (199 and 343 nm dry particles) using AMS software v.4.3mod
- And more!

Example: Dry (NH4)2SO4 Calibration on 5/30/02



Sulfate Fragmentation Patterns

m/z	Reference (Batch File or Frank's)	Calibration Spectrum
18/(48+64)	0.67	0.90
32/(48+64)	0.21	Not needed
48/(48+64)	0.5	0.49
64/(48+64)	0.5	0.51
80/(48+64)	0.3	0.30
81/(48+64)	0.15	0.12
98/(48+64)	0.08	Not needed

Step 1: account for all sulfate ions

- IPP(48) = 54.8
- IPP(64) = 56.6
- IPP(80) = 34.0
- IPP(81) = 14.3
- Sum all sulfate ions = IPP(48+64+80+81)*Reference Sulfate Fragmentation Pattern (includes m/z=32, 48, 64, 80, 81, and 98)/Spectrum Fragmentation Pattern (only m/z=48, 64, 80, and 81)
- Sum all sulfate ions = 159.7 * (0.21+0.5+0.5+0.3+0.15+0.08)/(0.49+0.51+0.30+0.12)
- Sum all sulfate ions = 159.7*(1.74/1.42) = 195.7

Step 2: include S34 isotopes

- All sulfate ions + isotopes = sum all ions *1.044 (isotopic contribution)
- All sulfate ions + isotopes = 195.7*1.044
- All sulfate ions + isotopes = 204.3

Step 3: account for all water ions

- IPP(18) = 101.5
- Water Fragmentation Pattern:
  All water ions = sum ions at m/z=18, 17, and 16
  (m/z=17) = 0.27*(m/z=18)
  (m/z=16) = 0.03*(m/z=18)
  So, all water ions = (ions at m/z=18)*(1+0.27+0.03)
- Sum all water ions =
  IPP(18)*Water Fragmentation Pattern
  *Reference 18 from Sulfate/Spectrum 18 from Sulfate
- Sum all water ions = 101.5*(1.30)*(0.67/0.90)
- Sum all water ions = 98.2

Step 4: sum sulfate and water ions

- Total ions per particle = sum of all sulfate and water ions due to sulfate
- Total IPP = 204.3 + 98.2
- Total IPP = 302.5

Step 5: calculate IE sulfate/IE nitrate

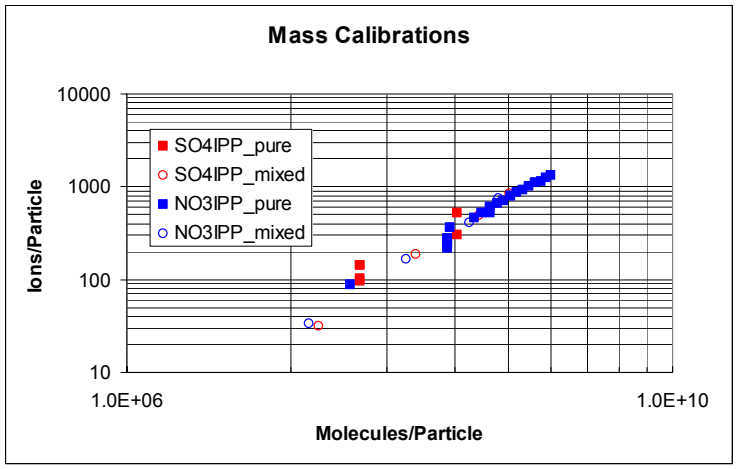
- Shift-M IE sulfate/IE nitrate = 0.8
  - IE is proportional to IPP/(mass fraction)
  - The shift-M value used the IPP from only m/z=48, 64, 80, and 81 (underestimates the actual number of ions)
  - The shift-M value used a sulfate mass fraction of 0.60 (water was 0.13), whereas the actual sulfate mass fraction in ammonium sulfate is 0.73 (underestimates the number of molecules per particle).
- Adjust the shift-M value for the real IPP and the actual mass fractions:

  IE sulfate/IE nitrate = 0.8*(302.5/159.7)*(0.60/0.73)

  IE sulfate/IE nitrate = 1.25

  Using shift-M RIE with more sig figs (0.76), IE sulfate/IE nitrate = 1.27

Summary of Nitrate and Sulfate Cals



Status

- Still working out what the RIEs are.
- Still wondering what the implications of different fragmentation patterns are. After Doug's comment, we probably need to include the fragmentation in the frag waves that was used to derive the RIE for the batch file.
- Will work on this offline and report back next time.