DETERMINING THE RIE OF MSA

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SOME BASICS

- MSA has been measured by AMS many times before
- Most studies use calibrated ratio of the very specific marker ion CH$_3$SO$_2^+$ to total ion counts to quantify MSA
- This ratio is pretty variable in the literature
- Importantly, the RIE of MSA was often not determined, just inferred
- MSA is semivolatile ($P_{vap} = 6 \times 10^{-4}$ Torr at 25°C), NH$_4$MSA is as semivolatile as ammonium nitrate ($T_{vap} = 200°C$)

\[
[MSA] = \frac{C}{CE} \sum \frac{MW_{MSA}}{IE_{MSA}} I_{MSA} = \frac{C}{CE} \frac{MW_{NO3}}{RIE_{MSA} IE_{NO3}} I_{CH3SO2} f(CH3SO2)
\]

Needed:
1. Total ion response for MSA (including sulfur, CO$_2$ and water)
2. Fraction of the marker ion, $f(CH_3SO_2)$
3. RIE of MSA

I. TOTAL MSA ION INTENSITY

Add up families with no background

Special cases:

- Sulfur from fitting $^{34}\text{S}$ (or $^{32}\text{S}$ for $>1$ mg sm$^{-3}$)
- Water and CO$_2$ from unconstrained regressions

- Sulfur and Water account for $1+3\sim4\%$ (Sulfate: $8+31\sim39\%$)
- CO$_2$ is negligible (CO likely as well)
II. FRACTION OF CH$_3$SO$_2^+$

Ambient data PMF (OA + SO$_x$, ATom-1) to the rescue!!

- Low concentration calibration of AMSA agrees with PMF
- No evidence for $f$(CH$_3$SO$_2$) being a function of particle acidity

Zorn et al, 2008
III. RIE OF MSA

1. RIE from Ammonium Balance

![Ammonium Balance Graph]

RIE of NH₄ = 3.57
RIE of MSA = 1.72

2. Monodispersity and Density from ePToF

![Monodispersity Graph]

3. CE of 1 determined from ET

4. Sanity Check

![Sanity Check Graph]

Calibration 8/2/2017
- 350 nm
- 300 nm (not used)

Slope 0.94, $r^2 = 0.98$

Calibration 6/29/2018
- 400 nm (1:1 Line)

RIE(MSA) = 1.70 ± 0.08

- Despite the very different water and sulfur contributions, RIE is very similar to sulfate
- On the high end of previous values
RIE OF MSA FROM ET

ET experiments with 400 nm AMSA particles (triggering on CH$_3$ and CH$_3$SO$_2$) showed CE=1

An RIE can be calculated from the ratio of Ions Per Particle for MSA vs Nitrate in back-to-back ET Calibrations:

$$RIE_{MSA} = \frac{IE_{MSA} \cdot MW_{NO3}}{IE_{NO3} \cdot MW_{MSA}} = \frac{IPP_{CH3SO2}/f(CH3SO2)}{\rho_{ANO3} \cdot MW_{MSA} (D_{ANO3})^3 \cdot MW_{NO3}}$$

However, the results were less than impressive (RIE in previous experiments was 1.70!)

<table>
<thead>
<tr>
<th>Ion</th>
<th>IPP</th>
<th>f(Ion) [%]</th>
<th>Calc RIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$SO$_2$</td>
<td>13.05</td>
<td>7.8</td>
<td>1.42</td>
</tr>
<tr>
<td>CH$_3$O</td>
<td>8.5</td>
<td>5.0</td>
<td>1.45</td>
</tr>
<tr>
<td>HSO$_2$</td>
<td>5.5</td>
<td>3.3</td>
<td>1.36</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>31.05</td>
<td>23.2</td>
<td>1.02</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>5.71</td>
<td>5.2</td>
<td>0.87</td>
</tr>
<tr>
<td>Sum(NH$_x$)</td>
<td>72.4</td>
<td>100</td>
<td>1.7</td>
</tr>
</tbody>
</table>

RIEs calculated this way are 25% to 60% too low!

However, using:

$$RIE_{MSA} = \frac{RIE_{NH4} \cdot IPP_{NH4} \cdot MW_{MSA}}{RIE_{NO3} \cdot IPP_{MSA} \cdot MW_{NH4}}$$

works IF we use the $RIE_{NH4}$ from ET (not squirrel)
1. SO WHY ARE THE RIES FOR SOME IONS SO LOW?

- About 30% of the total MSA mass is not present in the ET Spectrum, especially in $SO_x$.
- This is NOT PARTICLE BOUNCE (CE=1!!), but slow evaporation from vaporizer (PTOF looks like ET).
- Using the fractional contributions in the ET spectrum lines all MSA ions up.
- But they are still low by ~20%.
LET'S LOOK AT ANOTHER SV AEROSOL WITH CE=1: AMMONIUM NITRATE

- Signal from NO$^+$ is missing in ET (vs squirrel) due to slow evaporation
- Hence the IE of NO$_3$ needs to be corrected for the missing mass
- For ATom-3, that would suggest an RIE of NO$_3$ of 1.19 (+0.05 or +0.1 to account for N and HNO$_3$)
- With this correction, RIE of NH$_4$ (and of MSA) matches up!
ADDITIONAL SLIDES
SOME AN DATA

300 nm AN, RIE NH₄ = 4.47

400 nm AN, RIE NH₄ = 4.35

750 nm AN, RIE NH₄ = 4.30