Relative Ionization Efficiency Calibrations

Aerodyne Mass Spectrometers Users’ Meeting
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Ionization Efficiency

- Ionization efficiency (IE) is the number of ions generated per molecule.

\[ C_s = \frac{10^{12} MW_s}{IE_s Q N_A} \sum_{alli} I_{s,i} \]

- \( C = \text{conc. (µg/m}^3\text{)}, MW=\text{molecular weight}, Q=\text{volumetric flow (cm}^3/\text{s}), N_A = \text{Avagadro’s #}, I=\text{ion signal (Hz)} \)

This equation is true for any species, but in practice we use NO3 to calibrate. Everything else is relative to that via a relative ionization efficiency.
Relative Ionization Efficiency

- Relative Ionization Efficiency (RIE) is the ratio of the ionization efficiency of one molecule to another scaled by molecular weight.

\[
\frac{IE_s}{MW_s} = \frac{IE_{NO}}{MW_{NO}} = RIE_s
\]

\[
RF_{NO_3} = \left( \frac{IE_{NO_3}}{MW_{NO_3}} \right) \times \frac{N_A}{Q_{cal} G_{cal}}
\]

\[
RIE_s = RF_s / RF_{NO_3}
\]
Measuring Ammonium Sulfate RIE in ACSM

\[ RIE_{NH_4/NO_3} = \frac{RF_{NH_4}}{RF_{NO_3}} \]

From NH\textsubscript{4}NO\textsubscript{3} RF Calibration

\[ RIE_{NH_4/SO_4} = \frac{RF_{NH_4}}{RF_{SO_4}} \]

Same procedure, but using (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}

Doesn’t matter that (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} bounces because we only care about the ratio.

\[ RIE_{SO_4/NO_3} = \frac{RIE_{NH_4/NO_3}}{RIE_{NH_4/SO_4}} \]

So we can measure the SO\textsubscript{4} RIE
RF and RIE Calibration panel for ACSM
RF and RIE Calibration Results

- NO$_3$ RF = 3.48e-11
- NH$_4$ RIE = 5.64
- SO$_4$ RIE = 0.91
- Ref. P / Torr = 1.299
- Ref. N$_2$ = 1.00e-07
- Ref. O$_2$ = 2.34e-08
- Ref. Nap. = 9.53e-12
- Ref. Ch. T = 31.3
- Vap. T = 599

**Graph:**
- **NO$_3$** (Blue)
- **SO$_4$** (Red)
- **NH$_4$ from (NH$_4$)$_2$SO$_4$** (Orange)
- **NH$_4$ from NH$_4$NO$_3$** (Yellow)

**Axes:**
- Y-axis: NH$_3$ Signal / amps
- Y-axis: SO$_4$ Signal / amps
- X-axis: Mass Loading / $\mu$g/m$^3$
But – it is more complicated than this.

<table>
<thead>
<tr>
<th>mz</th>
<th>frag_SO3</th>
</tr>
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<tbody>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.04*frag_SO3[18]</td>
</tr>
<tr>
<td>17</td>
<td>0.25*frag_SO3[18]</td>
</tr>
<tr>
<td>18</td>
<td>0.67<em>frag_SO3[64], 0.67</em>frag_SO3[48]</td>
</tr>
<tr>
<td>19</td>
<td>0.000691<em>frag_SO3[18], 0.002</em>frag_SO3[17]</td>
</tr>
<tr>
<td>20</td>
<td>0.002*frag_SO3[18]</td>
</tr>
<tr>
<td>21</td>
<td></td>
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<td>22</td>
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<tr>
<td>23</td>
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</tr>
<tr>
<td>24</td>
<td>0.005*frag_SO3[48]</td>
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<td>25</td>
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<tr>
<td>31</td>
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<tr>
<td>32</td>
<td>0.21<em>frag_SO3[48], 0.21</em>frag_SO3[64]</td>
</tr>
<tr>
<td>33</td>
<td>0.0079*frag_SO3[32]</td>
</tr>
<tr>
<td>34</td>
<td>0.044*frag_SO3[32]</td>
</tr>
</tbody>
</table>

When we measure SO4 in this calibration, we don’t measure some key fragments, specifically m/z’s 18 and 32.

The ACSM procedure pushes the data through the frag table to calculate the total SO4 signal based on the fragments we do measure (48, 64, 80, 81, 98).
Ammonium Sulfate

- $m/z$ 18 = 0.47*($m/z$ 48 + $m/z$ 64)
- $m/z$ 18 = 1.2*($m/z$ 48 + $m/z$ 64)
- FragTable is $m/z$ 18 = 0.67*($m/z$ 48 + $m/z$ 64)