Reinvestigating Nitrate Relative Ionization Efficiency

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7/1/07
Standard IE Calibrations with Monodisperse Particles

1) Calibrate the SMPS for the mobility diameter, $d_m$.

2) Generate monodisperse ammonium nitrate particles and perform standard calibration and select m/z 30 and 46 for nitrate.

3) Record the ions per particle (IPP) values for each m/z generated by the calibration program.

4) The total IPP for 30 + 46 divided by the number of molecules per particle is $IE_{NO_3}(30+46)$:

$$IE_{NO_3}(30 + 46) = (IPP_{30} + IPP_{46}) \times \frac{6MW_{NH_4NO_3}}{\pi N_a S \rho_{NH_4NO_3}} \times d_m^3$$
Obtaining $RIE_{NO3}$

1) $RIE_{NO3}$ accounts for ions that aren’t measured during calibration:

$$RIE_{NO3} = \frac{\sum I_{NO3,i}}{(I_{30} + I_{46})} = \frac{(I_{30} + I_{46}) + (all\ other\ NO_3\ ions)}{(I_{30} + I_{46})}$$

2) Traditionally, we have used $RIE_{NO3} = 1.1$, implying that 10% of the nitrate ions are not accounted for with only 30 and 46.

3) Look at the fragmentation table (Allan et al. 2004)

- $\text{frag}_{NO3}[14] = 0.04 \times (\text{frag}_{NO3}[30] + \text{frag}_{NO3}[46])$
- $\text{frag}_{NO3}[31] = 0.00405 \times (\text{frag}_{NO3}[30])$
- $\text{frag}_{NO3}[32] = 0.002 \times (\text{frag}_{NO3}[30])$
- $\text{frag}_{NO3}[47] = 0.0443 \times (\text{frag}_{NO3}[46])$
- $\text{frag}_{NO3}[48] = 0.004 \times (\text{frag}_{NO3}[46])$
- $\text{frag}_{NO3}[63] = 0.003 \times (\text{frag}_{NO3}[30]) + 0.002 \times (\text{frag}_{NO3}[46])$

Putting it all together with $30/46 = 1.3-2.5$,

$$\sum (all\ other\ NO_3\ ions) = 0.049 \times (I_{30} + I_{46})$$
Obtaining $RIE_{NO3}$

1) Also, used the standard frag table to see what value for $RIE_{NO3}$ will provide consistency:
   1) Calculated NO$_3$, NO$_3$-30, and NO$_3$-46 (all with same RIE in batch file).
   2) $RIE_{NO3} = NO_3/(NO_3-30 + NO_3-46) = 1.049 +/- 0.00008$

$$\sum_{i} I_{NO_3,i} = 1.05 * (I_{30} + I_{46})$$

➢ To be consistent with the current standard frag table, need to use $RIE_{NO3} = 1.05$ in the program instead of 1.1.