IE Calibration Bias from Hygroscopicity and DMA Multiple Charge

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DMA – CPC
IE Calibration Setup

IE: Ionization Efficiency

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

Important Settings:
- 0.015M NH$_4$NO$_3$ solution
- Dry efficiency: Depends on different driers
- DMA: 250nm ~ 350nm

IE Calibration Setup Schematics
**Atomizer Generated**

![Graph showing particle size distribution](image)

**Drier**

NOT completely dry
STILL contain water!

**DMA Multiple Charge**

![Graph showing DMA selection](image)

**Assumptions:**
- Spherical particle → Shape Factor (~ 0.8 for NH₄NO₃)
- CPC and ACSM/AMS test the same NH₄NO₃ burden
- Dry particle
- Uniform distribution at mode diameter

**Reality:**
- Actual distribution has multiple charges (495nm, 685nm etc. while they are considered to be 300nm)
- Incompletely dry NH₄NO₃ particles

**RF Fitting (ions/pg)**

\[ RF = \frac{\text{Nitrate Ions}}{\text{CPC Mass}} \]

\[ IE \propto RF \]

**IE Bias**

**Drier Type** | RH after drying
--- | ---
Silica Drier(tested here) | ~ 35%
PD-Series Nafion Drier | ~ 15%
MD-700 Nafion Drier | ~ 10%

**CPC**

**ACSM/AMS**

**RF**

Mass of nitrate (pg)

Total measured nitrate ions

0 200 400 600 800 1000 1200 1400
0 5 10 15 20 25
DMA Multiple Charge

Atomizer size distribution

Log-normal Curve fitting

Determined by

Real mass tested in TOF-ACSM

Bias = \frac{\text{Real Mass}}{\text{Assumed Mass}} - 1

Assume that they are all dry and spherical particles

Assumed Mass

\begin{align*}
\text{Assumed Mass} & = \text{CPC Number Concentration} \times \frac{1}{6} \\
& \times 300^3
\end{align*}

\[ \frac{dN}{d\ln D_p} = \frac{N_t}{\sqrt{2\pi} \cdot \ln \sigma_g} \cdot \exp \left( - \frac{(\ln D_p - \ln \overline{D}_{pg})^2}{2\ln^2 \sigma_g} \right) \]

- Use \( N_t, \sigma_g, \overline{D}_{pg} \) to describe a log-normal distribution
  - \( \sigma_g \) — geometric standard deviation (gsd) of \( D_p \)
  - \( N_t \) — total particle number
  - \( \overline{D}_{pg} \) — Median number of \( D_p \)

- Generate a series of distributions
DMA Multiple Charge Bias on IE

IE Bias at 300nm (Dry)

- If the size distribution generated by your atomizer has larger $D_{pg}$ or $\sigma_g$, the bias might be high.
- While TSI 3076 atomizer is often used for AMS/ACSM calibration, the bias from the assumption of uniform 300nm is small.

0.015mM NH$_4$NO$_3$
35 psi SynAir
$D_{pg} = 98$nm
$\sigma_g = 1.49$
**NH₄NO₃ Hygroscopicity**

- **Growth Factor**
  
  $$GF = \frac{D'}{D_0}$$

- **Bias**
  
  $$Bias = \frac{\text{Real Mass}}{\text{Assumed Mass}} - 1$$

  - There contains water in the NH₄NO₃ particle, they are all dry and assume that they are spherical particles.
  - Assumed Mass
    
    $$= CPC \text{ Number Concentration} \times 300^3$$

- **Graphs**
  
  - *Growth Factor for NH₄NO₃ at different RH* (Dawei. Hu, et al. 2011)
  - *Water Mass vs. NH₄NO₃ Mass*
Multiple Charge & Hygroscopicity combined Bias on IE

Dry

RH=20%

RH=30%

RH=40%
A real example

- **IE Calibration Setup Parameters**
  - Atomizer 3076: \(\text{NH}_4\text{NO}_3\) Concentration of 0.015 M
  - DMA Selected Diameter: 300nm
  - CPC Type: TSI 3775
  - SMPS Type: TSI 3080

- **Total Bias on IE**

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>0</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE Bias</td>
<td>-1.64%</td>
<td>-19.76%</td>
<td>-25.98%</td>
<td>-29.13%</td>
</tr>
</tbody>
</table>

- **Importance for Capture Vaporizer**
  - CE = 1
  - IE bias directly influence the quantification

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

**MWs: Molecular Weight**

**Q: Flowrate**

**NA: Avogadros number**

**I: Ions intensity**

**Drier Type** | **RH after drying**
---|---
Silica Drier(tested here) | ~ 35%
PD-Series Nafion Drier | ~ 15%
MD-700 Nafion Drier | ~ 10%
Conclusion

- **Bias factors of IE calibration**
  - Polydisperse distribution from Atomizer -- Size distribution
  - Drier efficiency – Hygroscopicity of NH$_4$NO$_3$

The influences on IE by the actual size distribution and hygroscopic growth can be **negative or positive**, depending on these two factors.

**Be more careful when doing your IE calibration!**
**Check the size distribution from the atomizer and check the RH after the drier!**

- **May the bias of IE explain some of the discrepancies of the CE?**
  - For example, large CE at urban locations...

![TSI Atomizer 3079](image)
Thanks for your attention!

Q & A