Calibrations

13:15-13:50
There are 3 fundamental calibrations

- Flow rate
- Ionization efficiency
- Particle size calibration

**Particle Mass Loading**

*From Mass Spectrometer*
*Ionization Efficiency calibration*

\[
\frac{\text{mass}}{\text{volume}} \rightarrow \frac{\mu g}{m^3}
\]

*From volumetric flow rate*

**Particle Size**

*pTOF to $D_{va}$*
Flow Rate Calibration
AMS Flow Rate Calibration Setup

Poiseuille equation relates volumetric laminar flow ($F$) to a pressure drop ($\Delta P$) across the tube:

$$F = \Delta P \pi r^4 / 8 \eta l.$$
Flow Calibration
Depends on Pressure and Temperature

Always document ambient pressure and temperature
Flow Rate Calibration Summary

• In principal you only need to do this once as long as you document ambient pressure and temperature condition when you do the calibration (also assumes you are always sampling air).
• What you are measuring/calibrating here is a property of the aerodynamic.
• When reporting $\mu g \, m^{-3}$, always reference the T&P conditions.
Velocity Calibration
Particle Velocity Calibration

Sample known size particles and calculate a velocity…

Velocity = flight path / TOF

PSLs and NH$_4$NO$_3$
What’s wrong with this calibration?
Velocity calibration data should span maximum measurable range

Extrapolation of fit beyond data points can introduce errors
Do not “over-interpret” small and large sizes.

Extrapolation of size calibration curve fit

Slow vaporization and bounce
Size Calibration Summary

- Work hard at getting data at the small and large sizes.
- Use caution extrapolating velocity curve.
- Document lens pressure (flow) during a calibration.
- Watch for a lens pressure change when connecting the AMS inlet to a sampling system.
- Our calibration is based around determining velocity but we don’t use velocity for anything…
- Recommend using peak of mass distribution to find pToF.

*Advanced discussion topic*
IE Calibration

• We have two approaches
  – Single particle (requires DMA)
  – Total mass based method (requires DMA and CPC)

• In principal the SP method is probably better.

• In practice there are problems with both approaches so it is **recommended to do both.**
Single Particle Based IE Calibration

Ionization Efficiency = IPP/Molecules per Particle
Setup for CPC-Mass Based IE Determination

Input Mass = \( \rho \times \text{Volume(size)} \times \text{Number} \)

Plot Instrument Response vs Input Mass

Very Important!!
**NH₄NO₃ Ionization Efficiency Calibration**

\[ \text{NO}_3 = \text{NO}^+ + \text{NO}_2^+ \]

\[ \text{NH}_4 = \text{NH}^+ + \text{NH}_2^+ + \text{NH}_3^+ \]

- Multi-point calibration, tests linearity of system
- Ratio of slopes directly measures RIE NH₄
IE Calibration

• Issues with mass based method:
  – DMA-multiple charged diameters.
    • Use pTOF to determine contribution of larger diameters.
  – Lens transmission limitations.
  – Requires a CPC.
  – Accuracy limited by CPC.
CPC-Mass Based IE Determination

Multiple charged diameters

Lens transmission limitation

Calculated Mass

Let's discuss the units on this plot...
Minimizing multiple charged mobility diameters by decreasing NH$_4$NO$_3$ atomizer concentration

5 mM solution recommended
BFSP - IE Calibration

• Issues with single particle approach:
  – IPP can be low, not much bigger than a single ion, *use larger diameter particles (>400 nm).*
  – Need faster acquisition to time resolve entire vaporization event, *increase TOF extraction rate.*
  – Its only a single point calibration.
    *Could look at different sizes, but limited by DMA*
  – Selection of threshold is critical.
    *We use a default of 10, should be ok...*
Last year we proposed the CPC-mass based method to be integrated with ToF DAQ

Now in V4.x ToF AMS DAQ

This will help simplify and standardize IE calibrations.
“Ionization Efficiency” - Units

the AMS detects \textbf{ions} which we want to relate to particle \textbf{mass}
New proposed units for a “mass based Ionization Efficiency”

$mIE$

Ions / pg

- Has a more intuitive meaning.
- Can be more easily related to other instrument.
Order of magnitude relationship between $IE$ and $mIE$ for different mass spec systems.

<table>
<thead>
<tr>
<th>Typical Values</th>
<th>$IE_{NO3}$ (ions/molec.)</th>
<th>$mIE_{NO3}$ (ions/pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-AMS C-TOF-AMS</td>
<td>$10^{-6}$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>V-mode (HR-AMS)</td>
<td>$10^{-7}$</td>
<td>1000</td>
</tr>
<tr>
<td>W-mode (HR-AMS)</td>
<td>$10^{-8}$</td>
<td>100</td>
</tr>
<tr>
<td>ACSM</td>
<td>$10^{-7}$</td>
<td>1000</td>
</tr>
<tr>
<td>ccTOF AMS</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>
Lens Alignment

• This is often not checked.
• Generally, this does not need to be adjusted but if its off and not checked your data will likely be invalid.
• Recommend checking this after shipping the AMS.
END PRESENTATION