AMS/ACSM
Ionization Efficiency Introduction

Tuesday May 9, 2017
14:00
Calibrations

How to convert mass spectrometric ion signals into meaningful quantities?

- Particle velocity-aerodynamic size
- Volumetric flow rate
- Ionization efficiency

AMS Reported quantity is particle mass loading
Particle Mass Loadings Reported by the AMS requires an Ionization Efficiency

From Mass Spectrometer Ionization Efficiency calibration

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

From volumetric flow rate
EI Ionization Cross Sections

$$A + e^- (70 \text{ eV}) \rightarrow A^+$$

Mass Loading $A \propto \left( \frac{MW_A}{IE_A} \right) \sum (\text{all Ion Signals})$

Calibration Factor $\star \left( \frac{MW_{NO3}}{IE_{NO3}} \right)$

![Graph showing EI Cross Section vs Molecular Mass](image-url)
Determination of “Ionization Efficiency”
IE Calibration

There are two methods:

1. DMA/CPC mass based method.
2. Single particle based method
   I. BFSP mode in V4 DAQ
   II. Event Trigger mode in V5 DAQ

- ACSM systems are calibrated using the mass based method
- AMS systems can be calibrated using either method
Typical Calibration Set Up

Requires:
- Atomizer/dryer
- DMA
- CPC
Single Particle Based IE Calibration

Particle threshold set above single ion level

Average single particle pulse
Average single ion pulse = Ions per particle (IPP)

Ionization Efficiency = IPP / Molecules per Particle
Average Single Particle Signals

- NO$_2^+$ Ion Signal vs. Time (µs)
- Average No. of Ions Particle$^{-1}$ vs. Molecules Particle$^{-1}$

Graphs showing the time dependence of NO$_2^+$ ion signal for different particle sizes (200 nm, 320 nm, 440 nm) and the average number of ions per particle for NH$_4$NO$_3$ and DOP (Dissolved Organic Phosphates) in the wavelength range of ~250 – 850 nm.
For Details on SP Based IE Calibration See Presentation from 2006 AMS Users Meeting

Ionization Efficiency Calibration Tutorial for the ToF-AMS

AMS Users Meeting
September 17, 2006
Edward Dunlea, University of Colorado

Thanks to: Roya, Ann, Pete, Ken, Ingrid, Dara, Qi, Shane, John, Jose, Tim, Doug...

The purpose → Quantification!!!

In DAQ 5 we now use Event Trigger Mode for Single Particle based IE cal.

Donna and Joel will mention this later in this meeting.

http://cires1.colorado.edu/jimenez-group/wiki/index.php/AMSUsrMtgs#7th_AMS_Users.27_Meeting
Setup for Mass Based IE Determination

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

Reported Mass

*Plot Measured Mass vs Input Mass*
Mass Based IE Determination

Mass reported by V1.5 ToF DAQ (ug/m³)

Calculated/Input AN mass (based on CPC, ug/m³)

Dmob
- 300 nm
- 250 nm

intercept = 0.068 ± 0.041
slope = 0.493 ± 0.003

Fast_IE_Cal.pxp

Mass Spec Signal Response for selected Ions

Slope of this line is the response factor which is proportional to IE

Calculated mass based on DMA+CPC
ACSM Mass Based Calibration

The ACSM response is calibrated using the mass based method.

There are two practical concerns:

1) the primary DMA size selected should not be larger than 350 nm, 300 nm is suggested. This is to avoid particle loss due to limited transmission in the aerosol (standard) lens system.

2) One must be careful about the atomizer solution concentration. Too high a concentration can result in a significant mass at the higher charged diameters (Q2, Q3 etc.) NH4NO3 solution concentration of 0.005M (molar) is recommended.
Minimize multiple charged mobility diameters by decreasing \( \text{NH}_4\text{NO}_3 \) atomizer concentration.

AN Solution Concentration
- 0.030 M
- 0.018 M
- 0.005 M

5 mM solution 300 nm recommended
Mass Based IE Determination

In practice we measure AN and AS.

Need to consider fragmentation pattern for $NH_4NO_3$
Mass Based IE Determination

Multiple charged diameters

Lens transmission limitation

Mass Spec Signal Response for selected ions

Calculated mass based on DMA+CPC

Dmob
- 200 nm
- 250 nm
- 300 nm
- 400 nm

intercept = 0.068 ± 0.041
slope = 0.493 ± 0.003
## Comparison of Mass and CPC Based Ionization Efficiency Determination

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>CPC/Mass</td>
<td>Multiple point calibration</td>
<td>Requires a CPC and a DMA</td>
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<tr>
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<td>Better precision</td>
<td>Lens transmission consideration</td>
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<tr>
<td></td>
<td></td>
<td>Multiple charged DMA diameters</td>
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<tr>
<td>Single Particle</td>
<td>Does not require a CPC</td>
<td>Single point calibration</td>
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<td>Not dependent on lens transmission properties</td>
<td>Breaks down in the limit of low IPP</td>
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<td>Not dependent of multiple charged diameters exiting DMA</td>
<td>Difficult for species that produces many ions (ie, organics)</td>
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<td>Could be performed without a DMA</td>
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END
IEs Measured by Harvard Group wTOF AMS

J. Shilling, Qi Chen - Ver2.2.0 May 2006

Partilce mobility diameter (nm) vs. IE

- BFSP method
- Mass method
- fit_BFSPBased
Aerosol transmission tests were performed using this plumbing arrangement.
QAMS, standard lens, 215 series chamber.
BFSP Analysis Panel for IE Determination

Edward Dunlea
Slide of SP signals from Igor plot
D:\Igor\SP_Data
D:\IgoDOS_Single.pxp
NO3_051298.pxp AN data
NO3_980617_sp.pxp use this