Quantification of Aerosol Species with the AMS:
Background and Recent lab results relevant for OA

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Mass Loading Calculations

\[ C = \frac{10^{12}}{IE} \frac{1 \text{ MW}}{Q NA} \cdot I \]

\[ \frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}} \]

\[ C_s = \frac{10^{12}}{CE_s RIE_s} \frac{MW_{NO_3}}{IE_{NO_3} QNA} \sum_{all\ i} I_{s,i} \]

Primary Calibration

Nitrate Equiv.
Mass

CE_sRIE_s is largest uncertainty in mass concentration calculations
Collection Efficiency Definition

\[ CE(d_{va}) = E_L(d_{va}) \times E_s(d_{va}) \times E_b(d_{va}) \]
CE: From Lab and Field Work

$E_b$ is dominant contribution to CE

$E_b$ affected by

1) nitrate content
2) acidity/neutralization
3) Relative humidity in the sampling line
4) organic liquid content

MUCH (ALL?) OF THIS IS DRIVEN BY PHASE DEPENDENCE:

- Solids Bounce, Liquids Don’t Bounce

“Impactor 101”, same is true for ELPI (Virtanen et al. Nature 2010)

References: Matthews et al., Quinn et al., Middlebrook et al.
CE (Collection Efficiency)

Lab CEs: *(Matthews et al., Docherty et al.)*
- Pure $\text{NH}_4\text{NO}_3 = 1$
- Pure $(\text{NH}_4)_2\text{SO}_4 = 0.3$
- CEs for mixed $\text{NO}_3$ and $\text{SO}_4$ particles vary with $\text{NO}_3$ content, humidity, and liquid organic coating
- Lab SOA $> 0.2$ (Range observed, dependence on $f_{44}$)

Ambient CEs: *(Middlebrook et al.)*
- CE=$0.5$ (+/-0.15) with empirical composition dependence
- Pure lab particles are poor models for ambient mixed particles, but similar trends observed with humidity and $\text{NO}_3$
  
  *Ambient particles are solid/ mix of solid and liquid/glassy phase states*
  
  *(State of particles in ambient or in AMS after transmission through lens)*
RIE (Relative Ionization Efficiency)

$RIE_{NO_3} = 1.1$
(Accounts for ions other than $m/z$ 30 and 46)

$RIE_{NH_4} = 3.5$

$RIE_{SO_4} = 1.2$

$RIE_{SO_4}$ can be measured for each instrument.

Complicated by non-unit CE

1) Get $RIE_{NH_4}$ from NO$_3$ cal

2) Use $RIE_{NH_4}$ from step 1 to calculate input NH$_4$ mass and then input SO$_4$ for sulfate calibration.
Determination of CE, RIE for Organics

Complication: Ambient OA is made up of thousands of individual organic species. What do we use as a calibrant?

Ambient Measurements:
Usually $CE \times RIE_{\text{Org}} = (0.5 \times 1.4) = 0.7$
Assume $CE_{\text{Org}}$ same as sulfate due to internal mixture

$RIE_{\text{Org}} = 1.4$

(Value published in Canagaratna et al. (2007) and is based on unpublished laboratory work by Silva et al. (2001).)
Lab measurements of $\text{RIE}_{\text{Org}}$

Data from Phil Silva (2001)

 Calibration Species: inorganic and organic acids (oxidized species – surrogates of OOA)

 Lab particles not necessarily good models for ambient.

 In practice, ambient organic mass concentrations typically evaluated by comparing with other measurements (total mass, OM/OC ratios).

 Examples will be discussed in next talk
 By Jose
Time spent in ionization region (t) is inversely proportional to $\sqrt{MW}$. RIE is directly proportional to t

Kinetic Energy$ = \frac{1}{2} mv^2 \propto \frac{1}{2} MW \left(\frac{1}{t}\right)^2$

$\text{RIE} \propto t \propto \left(\frac{1}{\sqrt{MW}}\right)$

Expect MW dependence in RIE

How could this affect AMS mass concentration measurements?

Original AMS data from Phil Silva doesn’t show clear MW dependence within measurement uncertainties for Oxidized organic species MW <200

More on this topic later this morning
Measurement Uncertainties: RIE\textsubscript{Org}

Basic Idea: Compare measured OM with \textit{known} input OM

Producing \textit{known} input mass is hard
\begin{itemize}
\item Atomizing organics (H\textsubscript{2}O vs. other solvents)
\item Calculating mass of input particles properly even with DMA size-selected particles
  \begin{itemize}
  \item Accounting for Q>1 particles in DMA output (Used single particle from TOF)
  \item asphericity (shape factors)
  \end{itemize}
\item loss of volatiles in lens
\item Non-unit CE due to bounce
\end{itemize}

New measurements with control of input OM mass
\textcolor{red}{\textbullet} Use Centrifugal Particle Mass Analyzer (CPMA) to control of input mass/particle
**Experimental setup**

**Particle Generation**
- Particle Source (Atomizer, Nucleation)
- Mobility Diameter Selection (DMA)
- Mass/Particle Selection (CPMA)

**Measurements**
- Number Conc (CPC)
- Mass Conc
  - Q-AMS
  - HR-ToF-AMS
  - ACSM (Standard Vaporizer)
  - ACSM (Capture Vaporizer CE~1)

**Data**
Input Mass = (CPMA Mass/particle)*CPC Number
AMS Mass = (1/CE\(_S\)*RIE\(_S\))*AMS NO3 Equiv. Mass

\[ CE\(_S\)*RIE\(_S\) = NO3 Equiv. Mass/CPMA Input Mass \]
Extract RIE\(_S\) by measuring
\[ CE\(_S\) ~AMS Single Particle Counts/ CPC Counts \]

*Data obtained by*
Andy Lambe, Wen Xu, Phil Croteau, Lindsay Renbaum Wolff
Oxidized Organic standards <200 MW don’t show obvious non-linear RIE trend with MW. More work to be done with more “atmospherically relevant” standards.
Role of Thermal Decomposition

Thermal Decomposition reduces effective MW of parent molecules in vapor phase
- Acidic species lose CO2, H2O, CO
- Alcohols lose H2O
- Oligomeric species likely decompose into monomers

Sucrose, MW=342

MW dependence of RIE unlikely to be a big effect for Ambient OOA
Large MW species that thermally decomposes has similar RIE to smaller oxidized organics
MW dependence of $\text{RIE}_{\text{org}}$

Recent Results using CPMA (2015)

Expect less thermal decomposition here. More measurements in progress to see if this is unique to particular molecules or more general trend for hydrocarbons.
Work in progress

• Measuring RIEs of large MW hydrocarbons which are less likely to thermally decompose.

• Measure RIEs for more oxidized organic species that are more atmospherically relevant (PAM SOA, ambient OA)

• Compare/Analyze data from all AMS instruments (standard vs. capture vaporizer)