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

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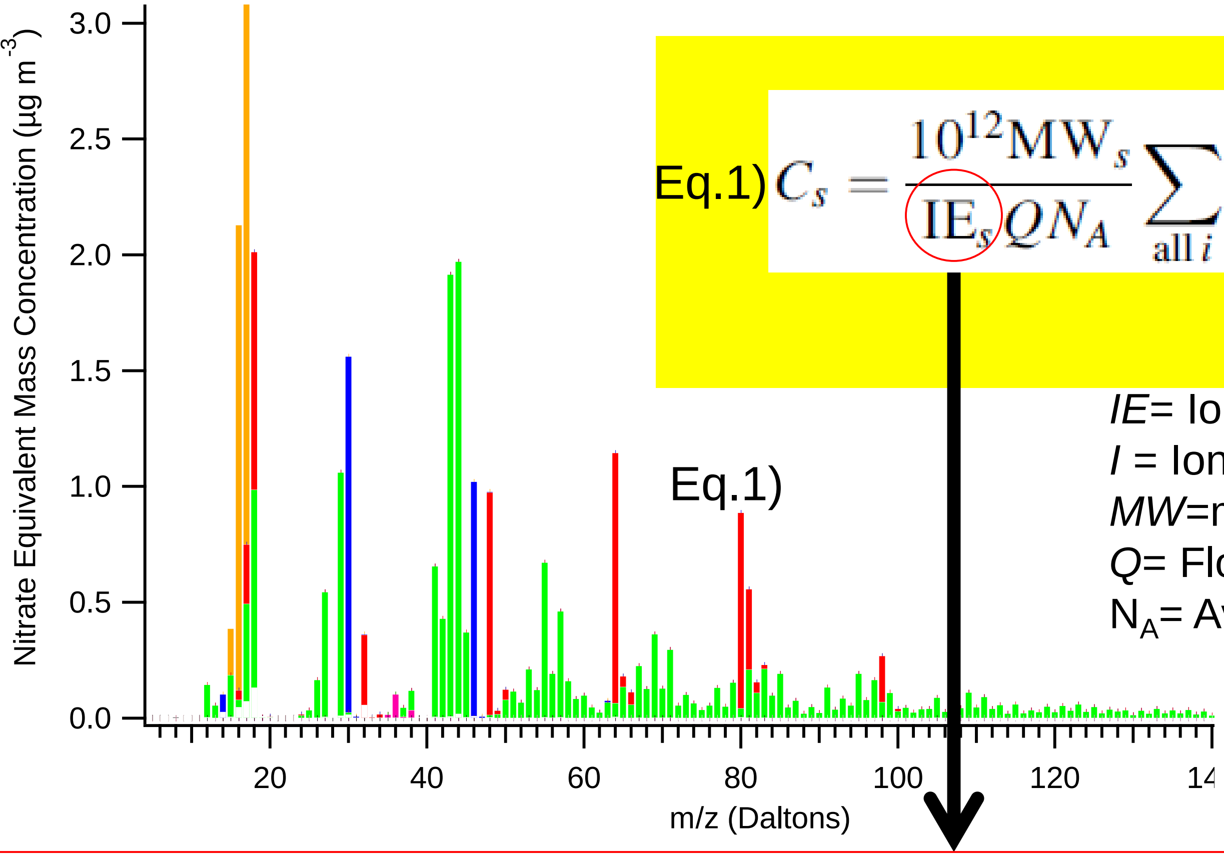
How do we get species concentrations from AMS Spectra ?



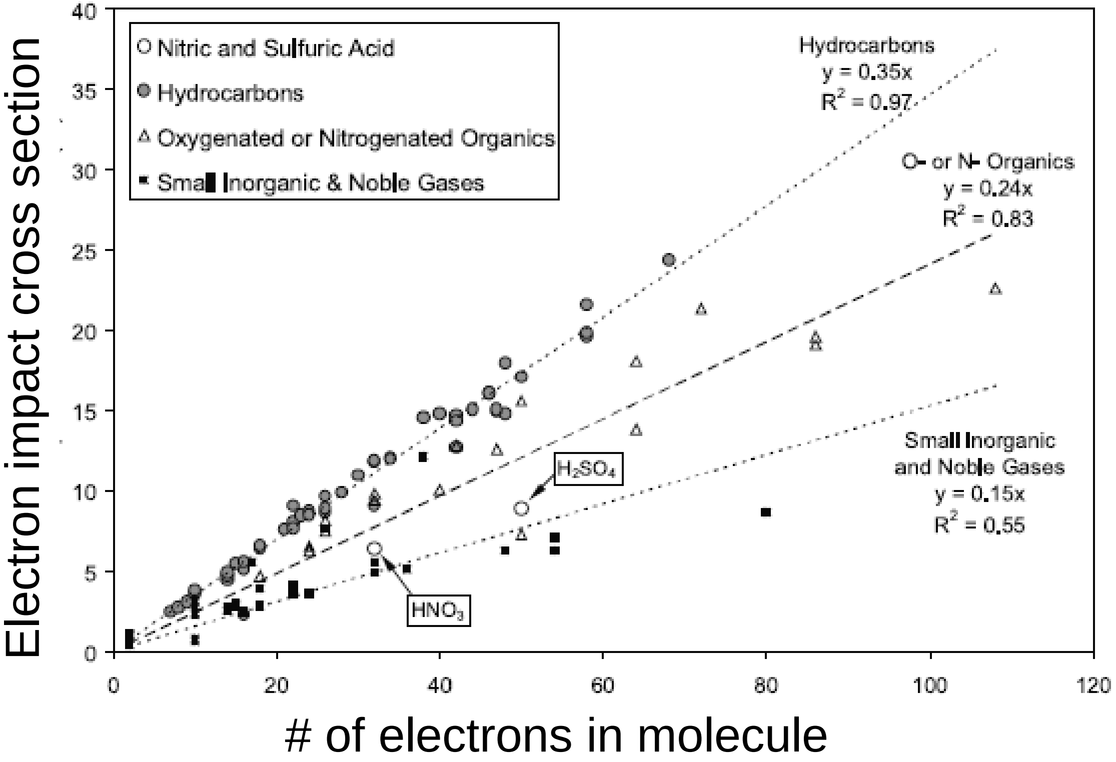
Eq.1) $$C_s = \frac{10^{12}\mathrm{MW}_s}{\mathrm{IE}_s Q N_A} \sum_{\text{all } i} I_{s,i}$$

IE= Ionization Efficiency
I = Ion count rate (Hz)
MW=molecular Weight
Q= Flow rate
N_A= Avogadro Number

- Ionization Efficiency(*IE*)$_s$ = # Detected ions / Parent molecule of species *s*
  IE_{NO3}, IE_{SO4}, *and* IE_{NH4} calibrated with lab aerosol: NH_4NO_3 and $(NH_4)_2SO_4$

- *OA made of up 1000s of molecules,* IE_{OA} can't be explicitly calibrated in lab for all
  Define IE_{OA} *in terms of* IE_{NO3} *and a relative OA response (Semi-empirical)*

Semi-Empirical Description for IE_S



Jimenez et al., *JGR* 2003

- Slopes in this plot differ according to chemical composition (Inorganic vs. organic, variation in organic)
- Use this variation to parameterize IE in terms of primary calibrant (NO_3)

Assumptions

- IE (Y-Axis) ∝ EI cross section
- # of electrons (X-Axis) ∝ MW
- Slope ∝ IE_s/MW_s

Eq.2) $$\frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}}$$

Mass Loading Calculations

Eq. 1) $$C_s = \frac{10^{12}\mathrm{MW}_s}{\mathrm{IE}_s Q N_A} \sum_{\text{all } i} I_{s,i}$$

Eq. 2) $$\frac{\mathrm{IE}_s}{\mathrm{MW}_s} = \mathrm{RIE}_s \frac{\mathrm{IE}_{\mathrm{NO_3}}}{\mathrm{MW}_{\mathrm{NO_3}}}$$

NH_4NO3 is primary calibrant

Eq. 3) $$C_s = \frac{10^{12}\,\mathrm{MW}_{\mathrm{NO_3}}}{\boxed{\mathrm{RIE}_s}\,\mathrm{IE}_{\mathrm{NO_3}} Q N_A} \sum_{\text{all } i} I_{s,i}$$

→ Nitrate Equiv. Mass

Calibrated or Semi-Empirical

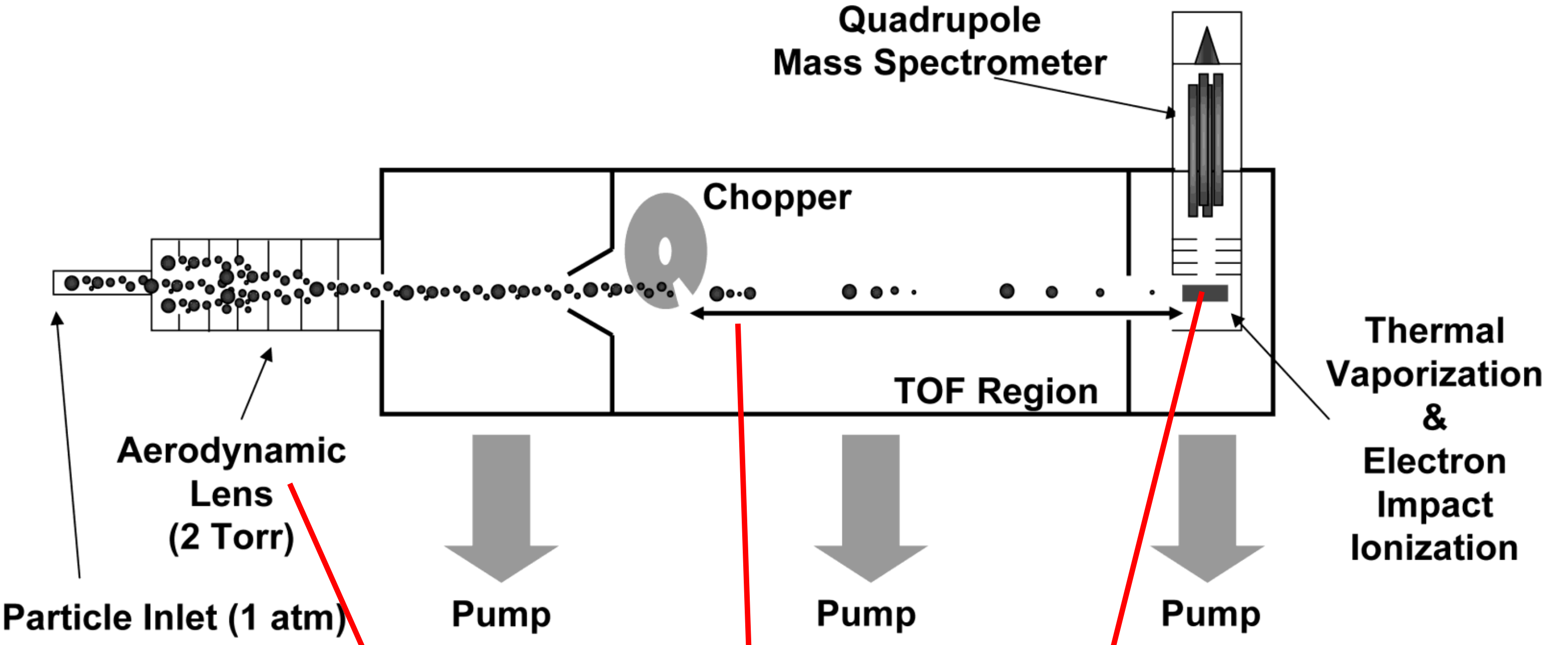
Collection Efficiency

Detection efficiency of particles that are transmitted into AMS

Particle Beam Generation

Aerodynamic Sizing

Particle Composition



Huffman et al.

$$CE(d_{va}) = E_L(d_{va}) \times E_s(d_{va}) \times E_b(d_{va})$$

Lens Transmission

Overlap between beam and vaporizer

Particle Bounce on oven

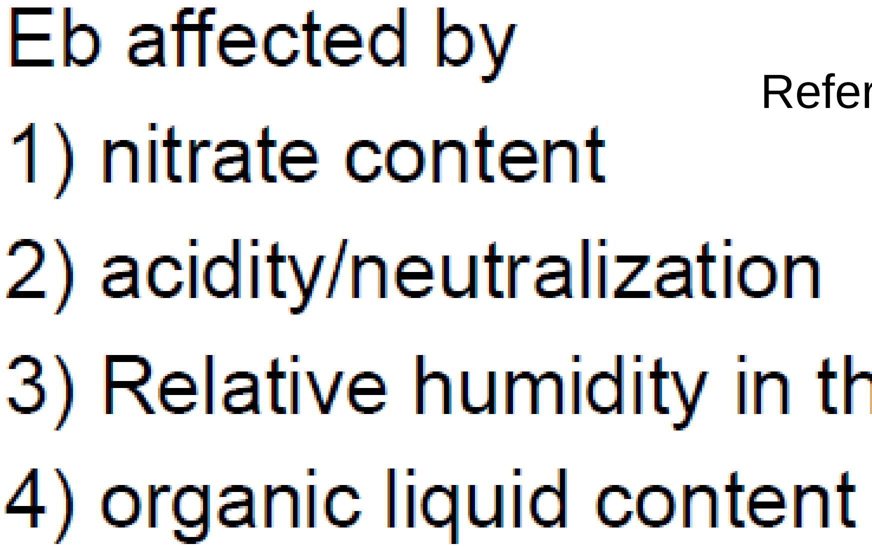
Mass Loading Calculations: Putting it all together

Eq. 4) $$C_s = \frac{10^{12}}{\boxed{\mathrm{CE}_s\,\mathrm{RIE}_s}}\,\frac{\mathrm{MW}_{\mathrm{NO}_3}}{\mathrm{IE}_{\mathrm{NO}_3}\,Q N_A}\sum_{\mathrm{all}\,i} I_{s,i}$$

- Largest Source of uncertainty for species mass concentrations

CE: Lab and Field Results

E_b is dominant contribution to CE and affected by particle bounce (depends on particle phase)



Eb affected by

1) nitrate content

2) acidity/neutralization

3) Relative humidity in the sampling line

4) organic liquid content

References: Matthews et al., Quinn et al.

Typically, ambient CE=0.5 (+/-0.15) for all species with empirical composition dependence (*Middlebrook et al.)*

Lab CE_S values are more variable since pure particles may not be identical in phase to complex, ambient particles (*Matthews et al.*, *Docherty et al.*)

RIE (Relative Ionization Efficiency)

Inorganic Species

Early lab calibrations on inorganics by Frank Drewnick, Ann Middlebrook

RIE$_{NO3}$ - 1.1 (for ions other than *m/z* 30 and 46)
RIE$_{NH4}$ - 3-5
RIE $_{SO4}$ - 1.2

IE$_{NO3,}$ RIE$_{NH4,}$ are routinely calibrated for each instrument

RIE $_{SO4}$ can be measured for each instrument.

Complicated by non-unit CE

1) Get RIE$_{NH4}$ from NO_3 cal

2) Use RIE$_{NH4}$ from step 1 to calculate input NH_4 and SO_4 masses for sulfate calibration.

Determination of 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*RIE_{Org}= (0.5*1.4)=0.7

- CE=0.5 assumes organic and inorganics internally mixed
- RIE_{Org} = 1.4 is based on unpublished laboratory work by Silva et al. (2001)

Recent Lab work : Evaluating AMS Quantification uncertainties

1) What is variability in Organic RIEs across a range of O/C values?
2) Can simple theory be used to accurately predict measured organic RIE values?
3) Is RIE of individual species significantly different when in pure or mixed aerosol

   (i.e. NO_3 in NH_4NO_3 vs NH_4NO_3/ $(NH_4)_2SO_4$ mix, Organics in mixed organic/nitrate particles)

IE and RIE Measurement Uncertainties

Basic Idea: Compare measured mass with **known** input mass

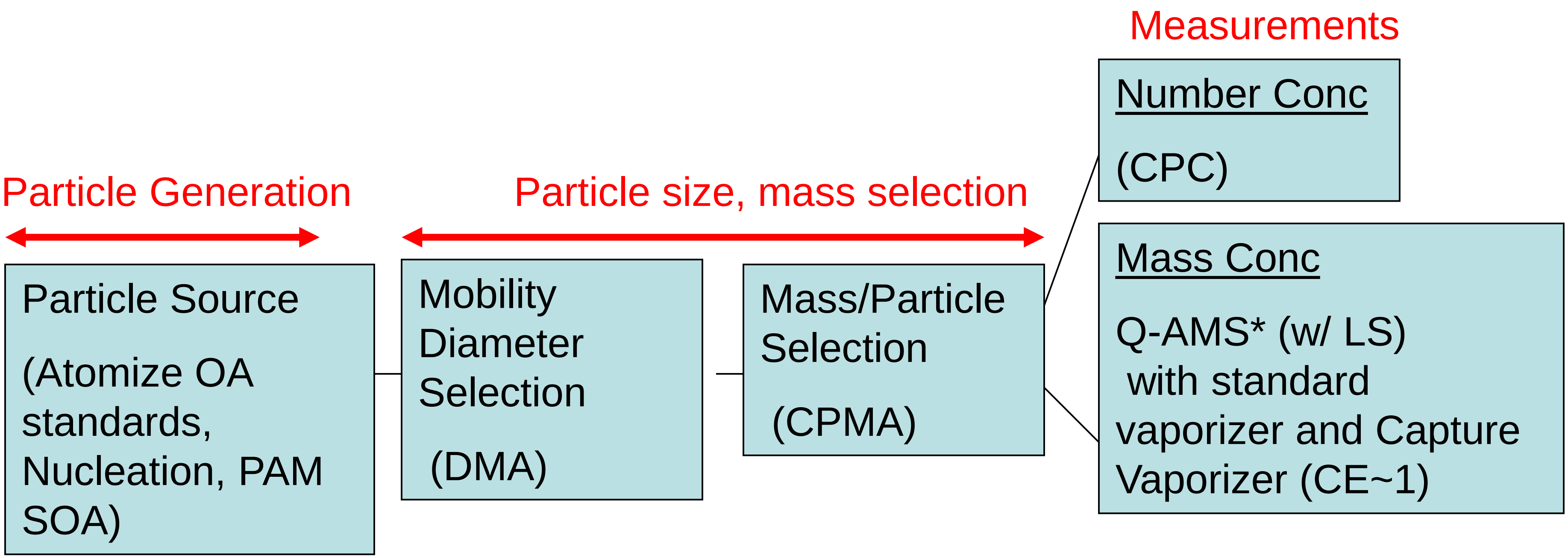
Producing **known** input mass is hard, particularly for OM

- Atomizing organics (H_2O vs. other solvents)
- Calculating mass of input particles properly even with DMA size-selected particles
  - Accounting for Q>1 particles in DMA output (Used single particle from pTOF)
  - asphericity (shape factors)
- loss of volatiles in lens
- Non-unit CE due to bounce

New measurements with control of input aerosol mass

↓ Use Centrifugal Particle Mass Analyzer (CPMA) to control of input mass/particle, remove DMA Q>1 ambiguity

Improved Calibration Protocol for RIE_{OA}



Measurements

Particle Generation

Particle size, mass selection

Particle Source

(Atomize OA standards, Nucleation, PAM SOA)

Mobility Diameter Selection

(DMA)

Mass/Particle Selection

(CPMA)

Number Conc

(CPC)

Mass Conc

Q-AMS* (w/ LS) with standard vaporizer and Capture Vaporizer (CE~1)

Data Processing

Input Mass= (CPMA Mass/particle)*CPC Number

AMS Mass = $(1/CE_S RIE_S)$*AMS NO3 Equiv. Mass

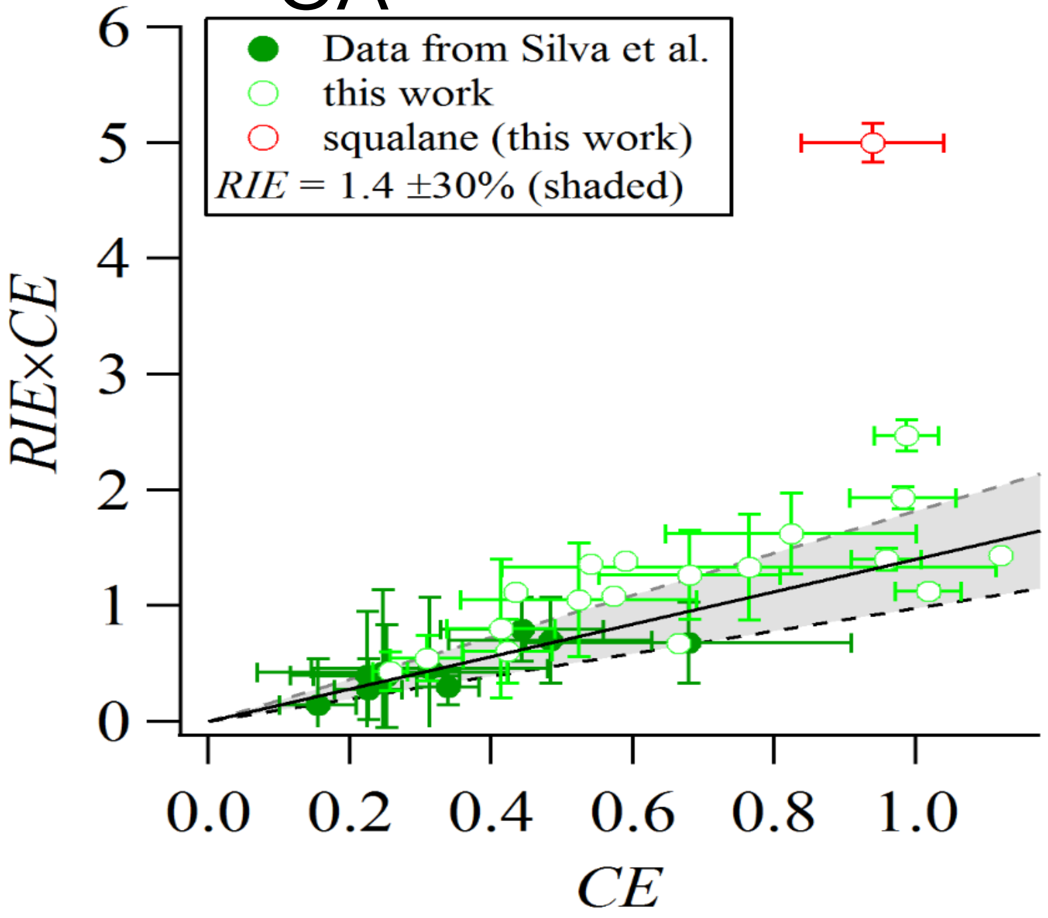
$CE_S*RIE_S = NO_3$ Equiv. Mass/CPMA Input Mass

CE_S ~AMS pTOF Single Particle Counts/ CPC
OR
AMS pTOF Single Particle Counts/ LS

Data obtained by ***Wen Xu*, Andy Lambe* et al.***

Manuscript in preparation, Xu et al.

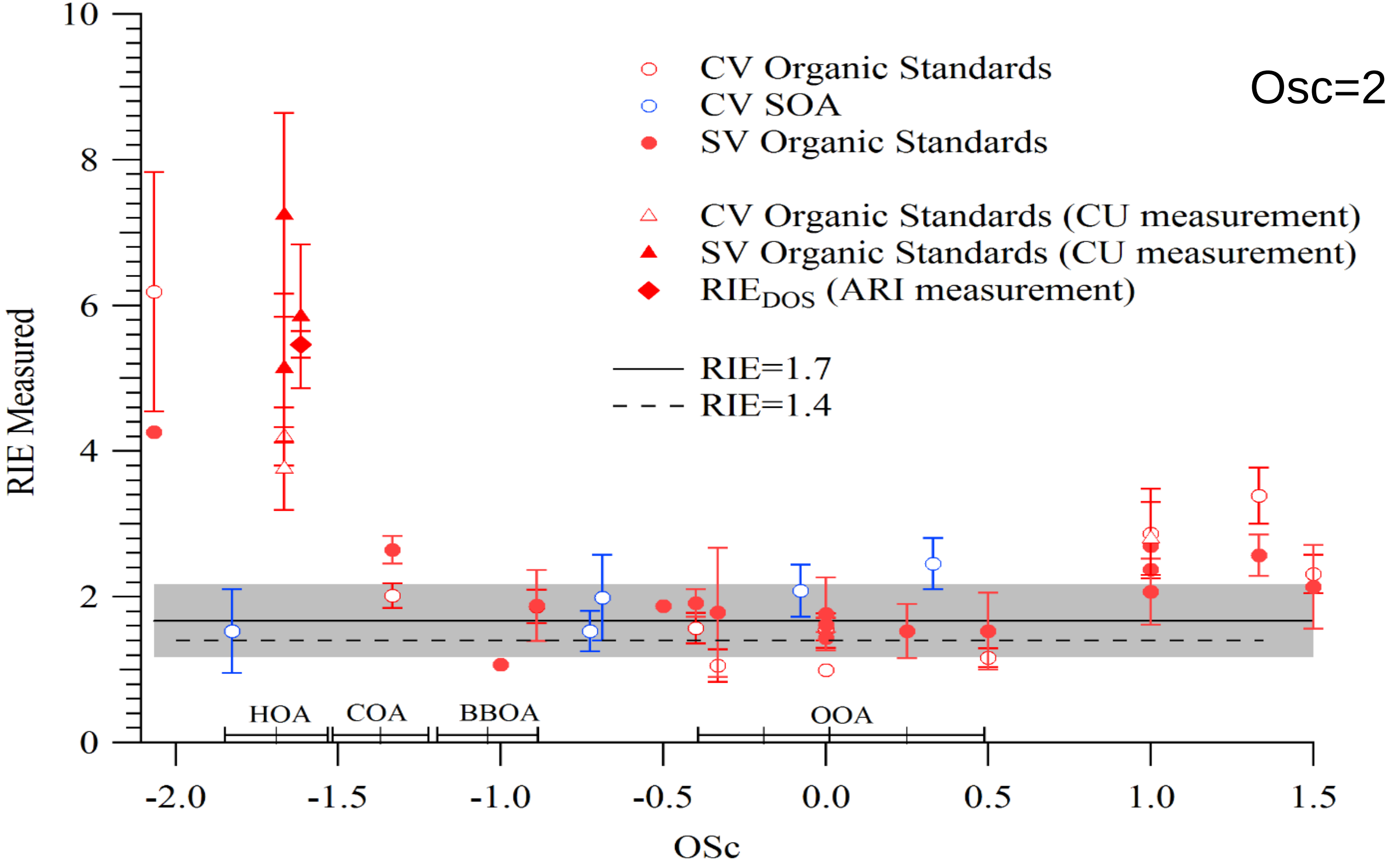
RIE_{OA} :Lab Measurements



Standard Vaporizer

- Uncertainty in CE introduces uncertainty in extracted RIEs
- Some species have RIE values that are much higher than 1.4
- Use capture vaporizer to help reduce uncertainty and examine trends

RIE_{OA} vs OSc



Osc=2*O/C-H/C

- Capture vaporizer and Standard vaporizer show similar trends with OSc
- Lab RIE_{OA} =4-8 for Osc < -1.5 (Ambient HOA doesn’t seem to show such an obvious effect potentially since it is offset by poor lens transmission for small particles (Jimenez et al., *AS&T*, 2017))
- Lab RIE_{OA} = 1.7 for Osc > -1.5 (within 20% uncertainty of 1.4 used for ambient calcs and supports use of constant RIE value for organics in this range)

RIE_{OA} (Measurements vs. Model)

Model: $IE_S = \sigma \times J_e \times t_m$

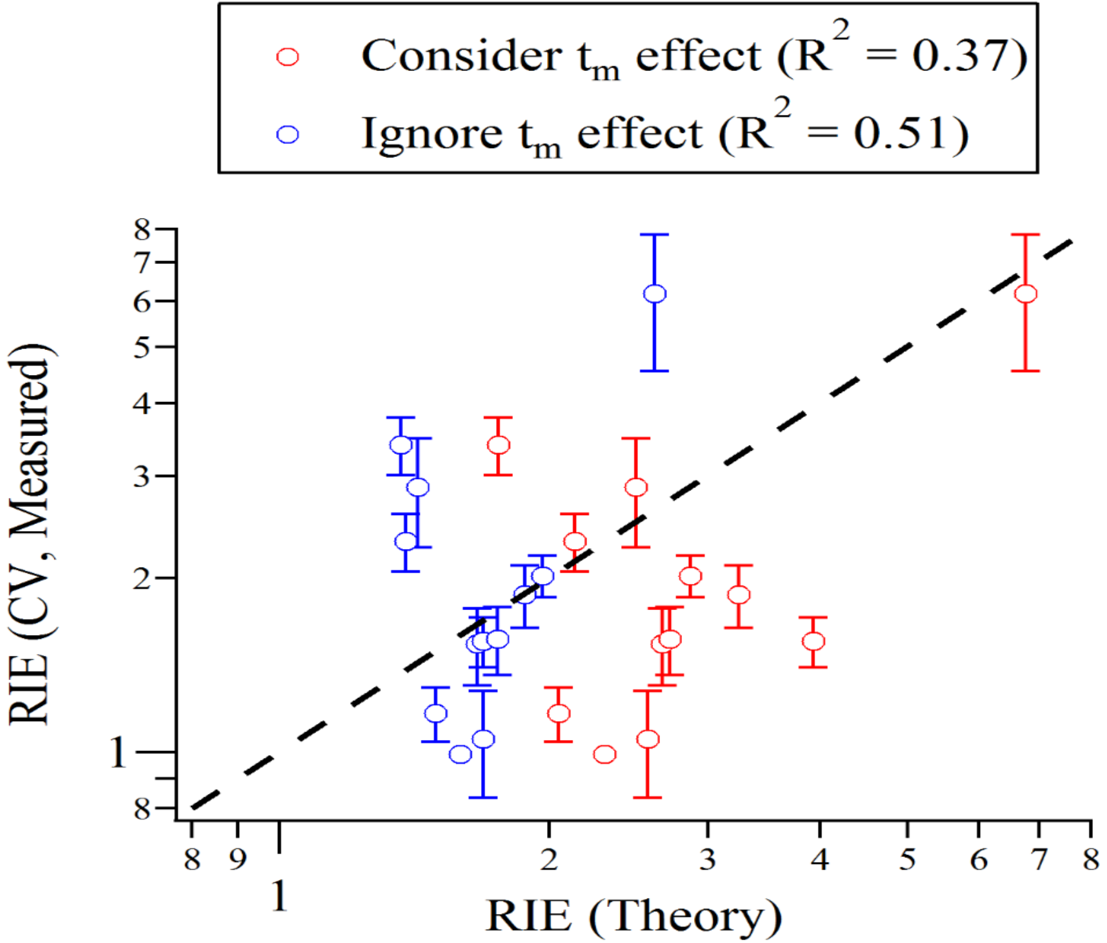
$$RIE_S = IE_S / IE_{HNO3}$$

σ = Ionization cross section

J_e = Electron flux

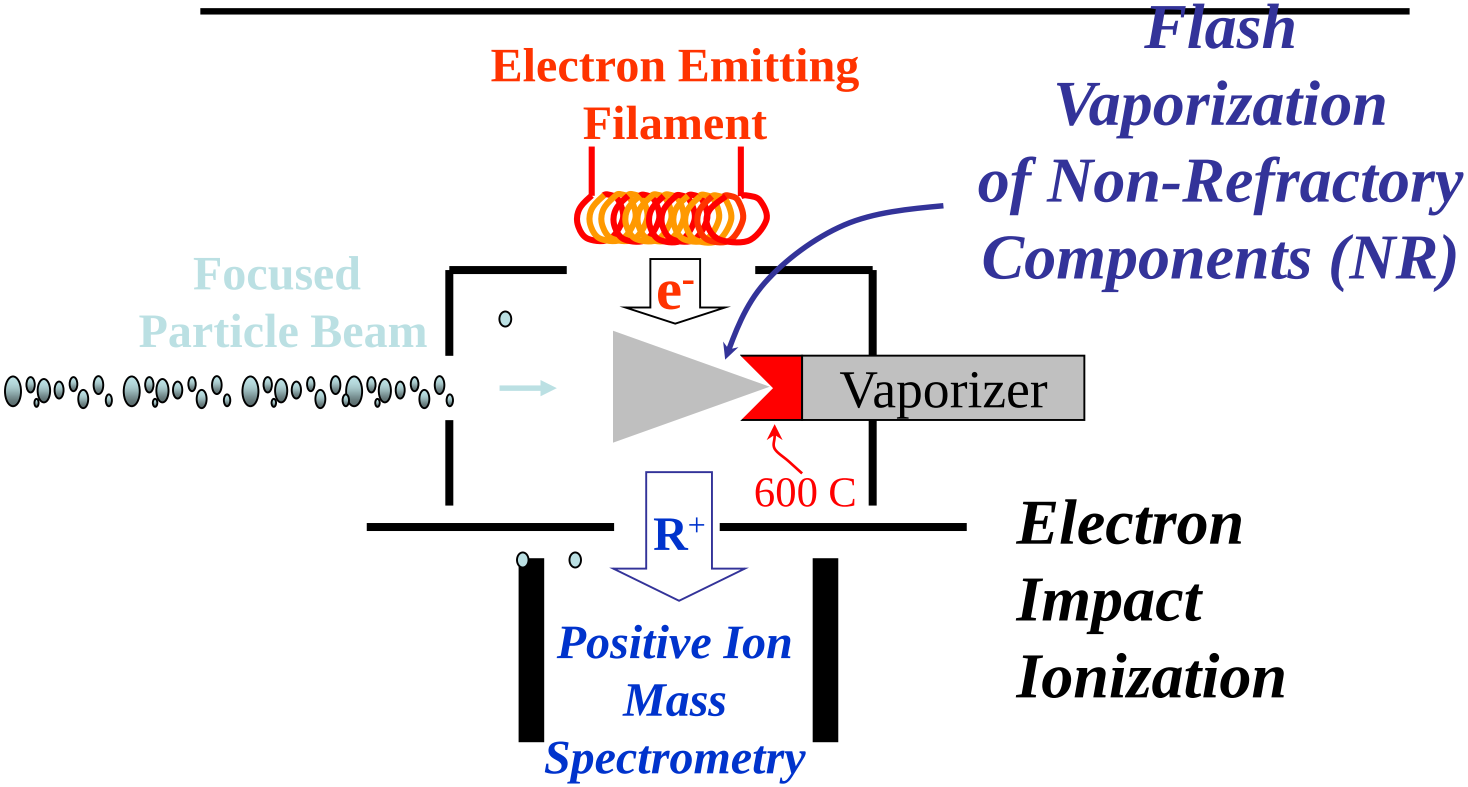
t_m = transit time of molecule through ionizer region ∝ (1/sqrt(MW))

Results for OA Standards Measured in this study



Poor correlation between measured and modeled RIE_{OA} values

AMS Particle Detection Process



Electron Emitting Filament

Flash Vaporization of Non-Refractory Components (NR)

Focused Particle Beam

e^-

Vaporizer

600 C

R^+

Positive Ion Mass Spectrometry

Electron Impact Ionization

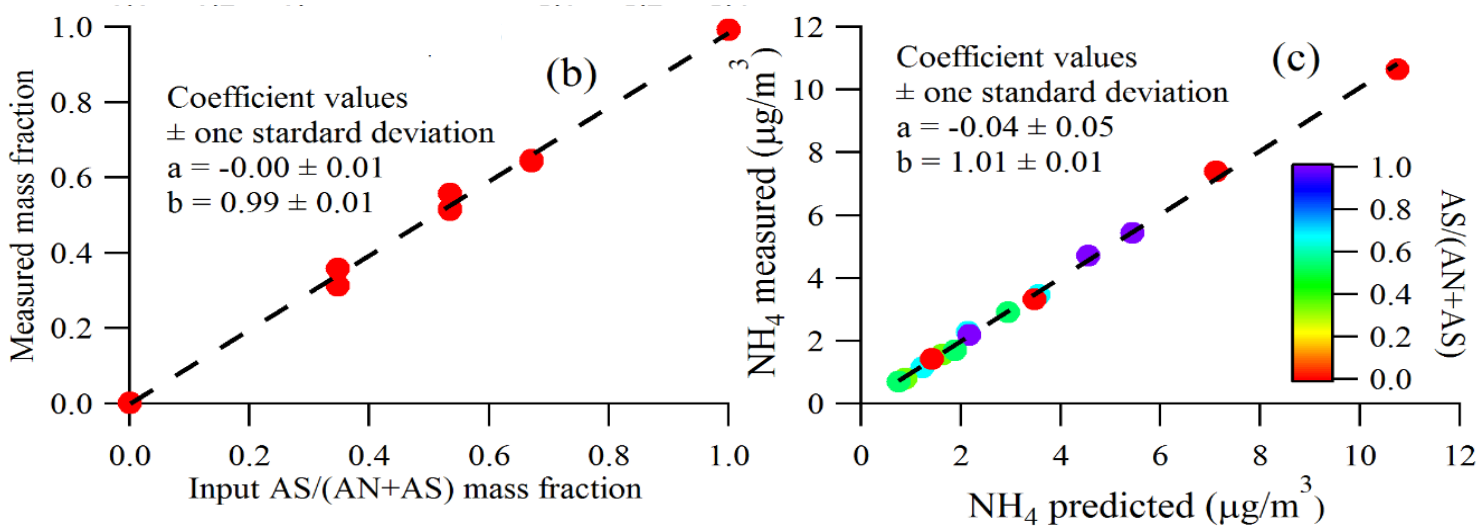
IE_S (i.e. Ions measured/input molecules) measurements reflect

- -efficiency of ionizing gas phase molecules → Included in model
- - thermal decomposition on vaporizer
- - bounced particle vaporization off cooler surfaces
- - interaction of vapors with ionizer surfaces

} processes not accounted for in simple model

Measured ionization efficiency reflects multiple processes
Cannot use simple model to predict RIE. Need to calibrate.

Lab Results: Mixed Inorganics



Quantification of Inorganic species not affected by matrix

NH_4 from $(NH_4)_2 SO_4$, NH_4NO_3 detected with same RIE

SO_4 RIE constant across solutions

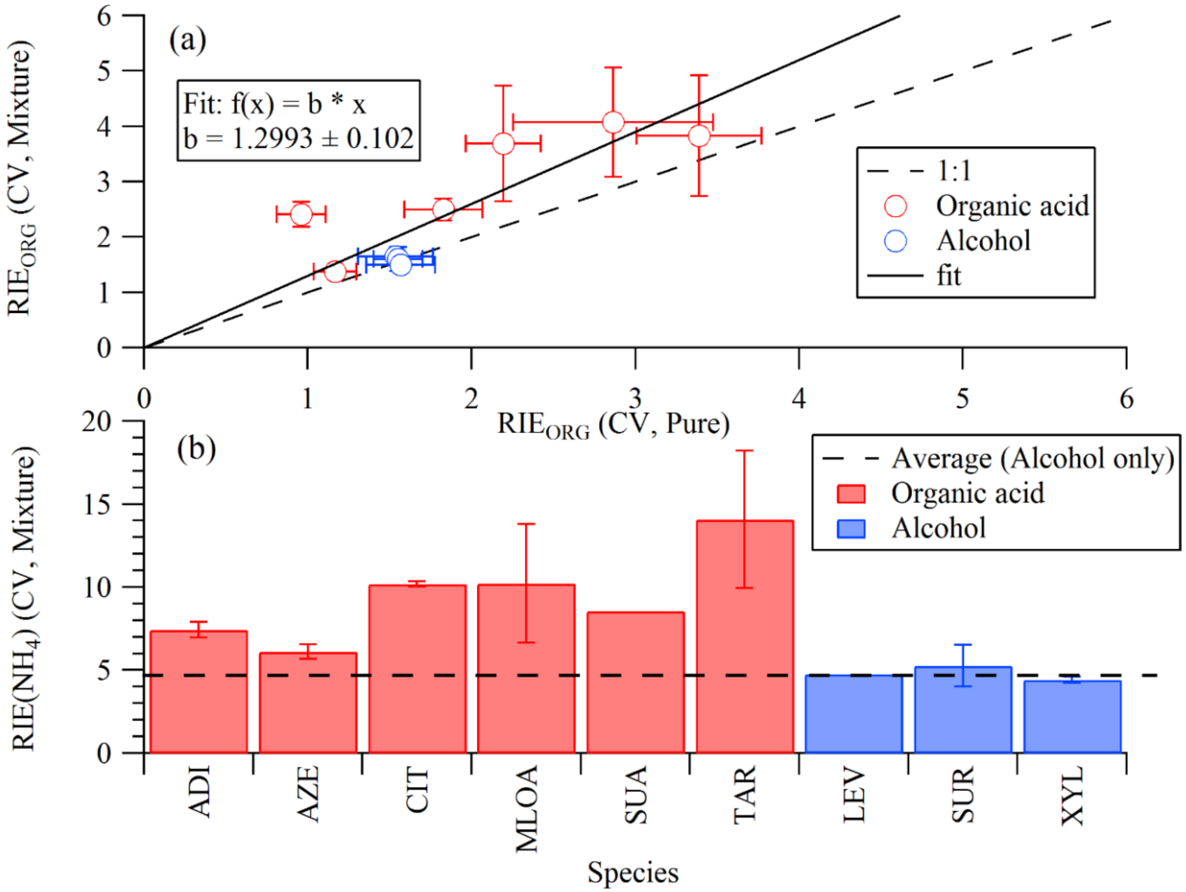
Lab: Binary Organic/NO3 Particles

Can we obtain RIEs of organics by mixing with NH_4NO_3 and directly measuring org/NO_3 ratio compared to known value from DMA&CPMA size and mass selection?

Advantage:

Direct ratio to NO_3 for internally mixed particles offsets need to measure CE_B which is variable for lab particles.

Lab: Binary Organic/NO3 Particles



Mixed Alcohol particles

- RIE$_{Org}$ and RIE$_{NH4}$ agree well with measurements from pure particles

Mixed Acid particles

- RIE$_{Org}$ and RIE$_{NH4}$ higher than measurements from pure particles

- Mixed Acid and nitrate particles may lose NO$_3$ through displacement reaction and volatilization of HNO$_3$
- Mixed alcohol and nitrate particles may provide an easier method of calibrating reference RIE$_{Org}$ values

Conclusions

- Product of RIE and CE biggest source of uncertainty for calculating OA mass
- New calibration protocol allows for more accurate RIE_{OA} measurements
- RIE_{OA} vs. OSC trend examined
    - Plateau in RIE_{OA} for Osc>-1.5 supports use of single value. Average RIE_{OA} for this Osc range = 1.7 (within 20% uncertainty of 1.4)
    - High RIE_{OA} observed for hydrocarbons
    - Need careful evaluations of ambient OA mass closure to look for these effects
- RIE_{OA} cannot be predicted with simple models. Calibration necessary
- Mixed binary alcohol/nitrate particles may be useful method for calibrating reference RIE_{OA} values.

Acknowledgements

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