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

Presented by Manjula Canagaratna

AMS Users Meeting, Milan

September 2015

Mass Loading Calculations

$$C = \frac{10^{12}}{IE} \frac{1}{Q} \frac{MW}{N_A} \cdot I$$

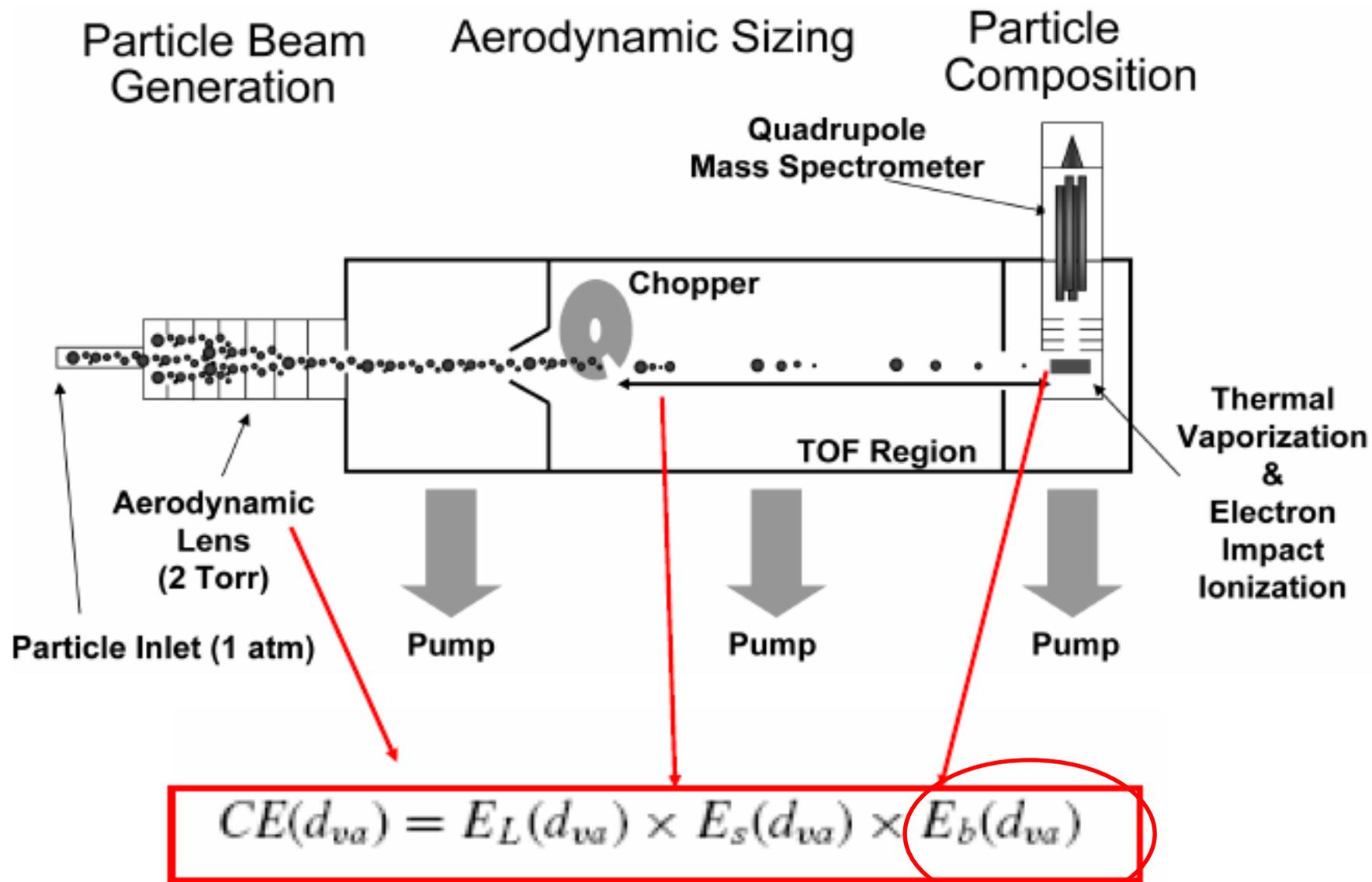$$\frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}}$$

Primary Calibration

$$C_s = \frac{10^{12} \quad MW_{NO_3}}{CE_s \, RIE_s \, IE_{NO_3} \, Q \, N_A} \sum_{all\,i} I_{s,i}$$

Nitrate Equiv.

Mass

$CE_s RIE_s$ is largest uncertainty in mass concentration calculations

Collection Efficiency Definition

Particle Beam Generation

Aerodynamic Sizing

Particle Composition

Quadrupole Mass Spectrometer

Chopper

TOF Region

Aerodynamic Lens (2 Torr)

Particle Inlet (1 atm)

Pump

Pump

Pump

Thermal Vaporization & Electron Impact Ionization

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

CE: From Lab and Field Work

E_b is dominant contribution to CE

Eb 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 NH_4NO_3 = 1

Pure $(NH_4)_2SO_4$ = 0.3

CEs for mixed NO_3 and SO_4 particles vary with 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 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)

Background: AMS IE and RIE

Y axis is proportional to IE

X axis is proportional to MW
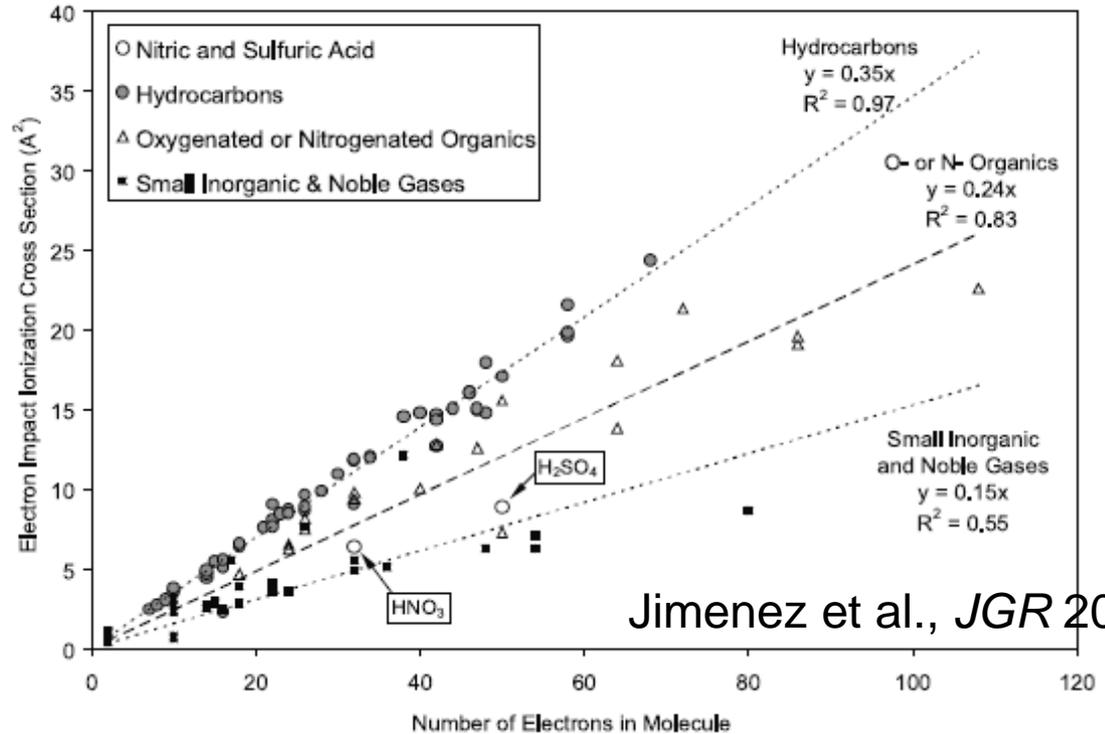
Slope is proportional to IE_s/MW_s

Figure 6. Electron impact ionization cross sections of small molecules versus number of electrons in the molecule.

Jimenez et al., *JGR* 2003

$$\frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}}$$

RIE (Relative Ionization Efficiency)

Inorganic Species

Early work on these subjects by Frank Drewnick, Ann Middlebrook

RIE_{NO3} - 1.1
(Accounts 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 CE,RIE for Organics

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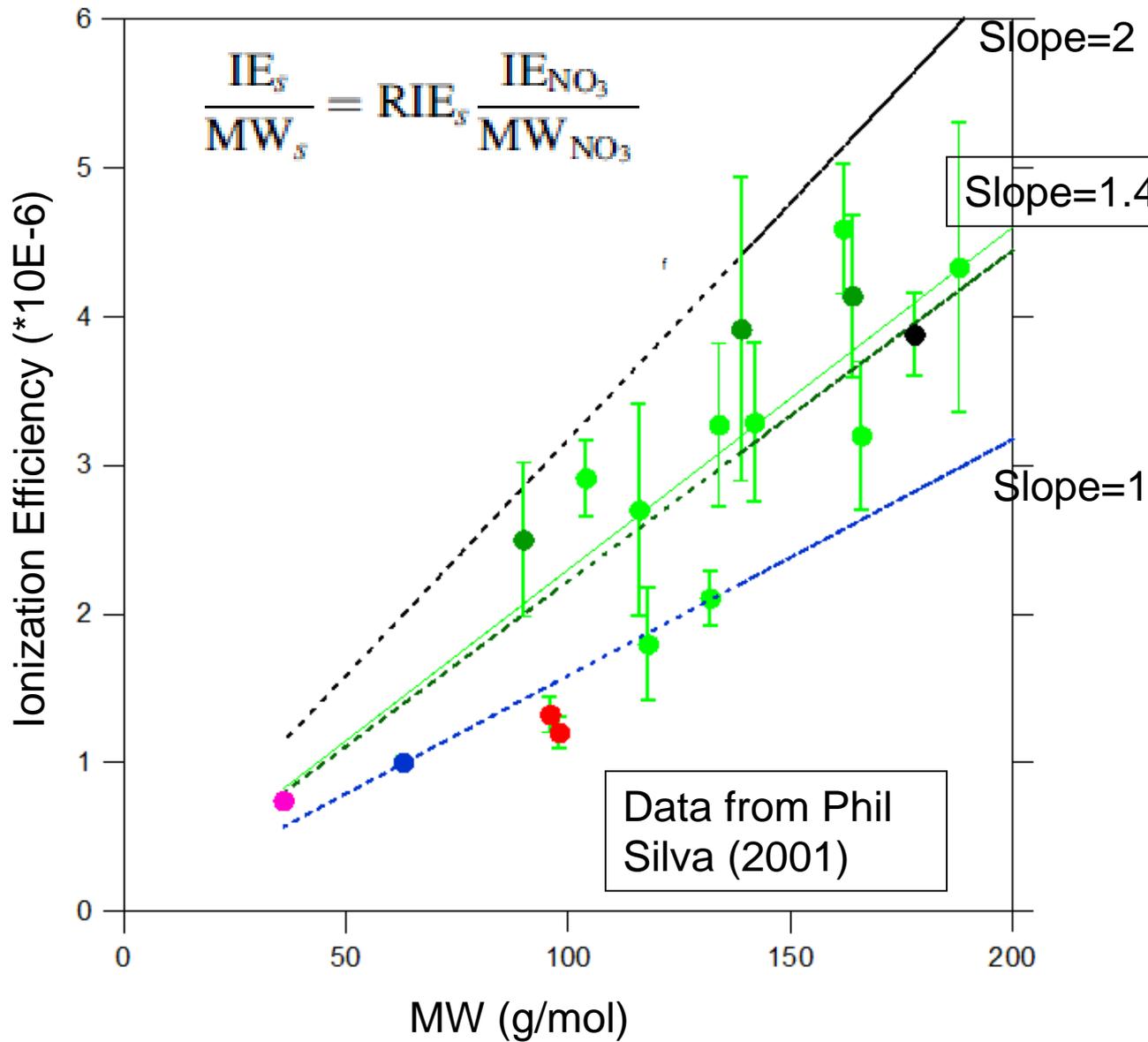
Ambient Measurements:

Usually $CE*RIE_{Org}$= (0.5*1.4)=0.7

Assume CE_{Org} same as sulfate due to internal mixture

RIE_{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 RIE$_{Org}$

$$\frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}}$$

Ionization Efficiency (*10E-6)

MW (g/mol)

Slope=2

Slope=1.4

Slope=1

Data from Phil Silva (2001)

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

Caveat
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).

Recent Lab work : Evaluating AMS Quantification uncertainties

1) RIE of an individual species isn't significantly different when pure or mixed aerosol

   (i.e. NO_3 in NH_4NO_3 vs NH_4NO_3/ $(NH_4)_2SO_4$ mix)

   Are there matrix effects on inorganic RIEs?

2) Single RIE for multitude of organic species

   What is variability in Organic RIEs?

MW dependence of RIE_{org}

Time spent in ionization region (t) is inversely proportional to sqrt(MW). RIE is directly proportional to t

Kinetic Energy= ½ mv² $\propto$ ½ MW(1/t)²

RIE $\propto$ t $\propto$ (1/sqrt(MW))

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

IE and RIE Measurement Uncertainties

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

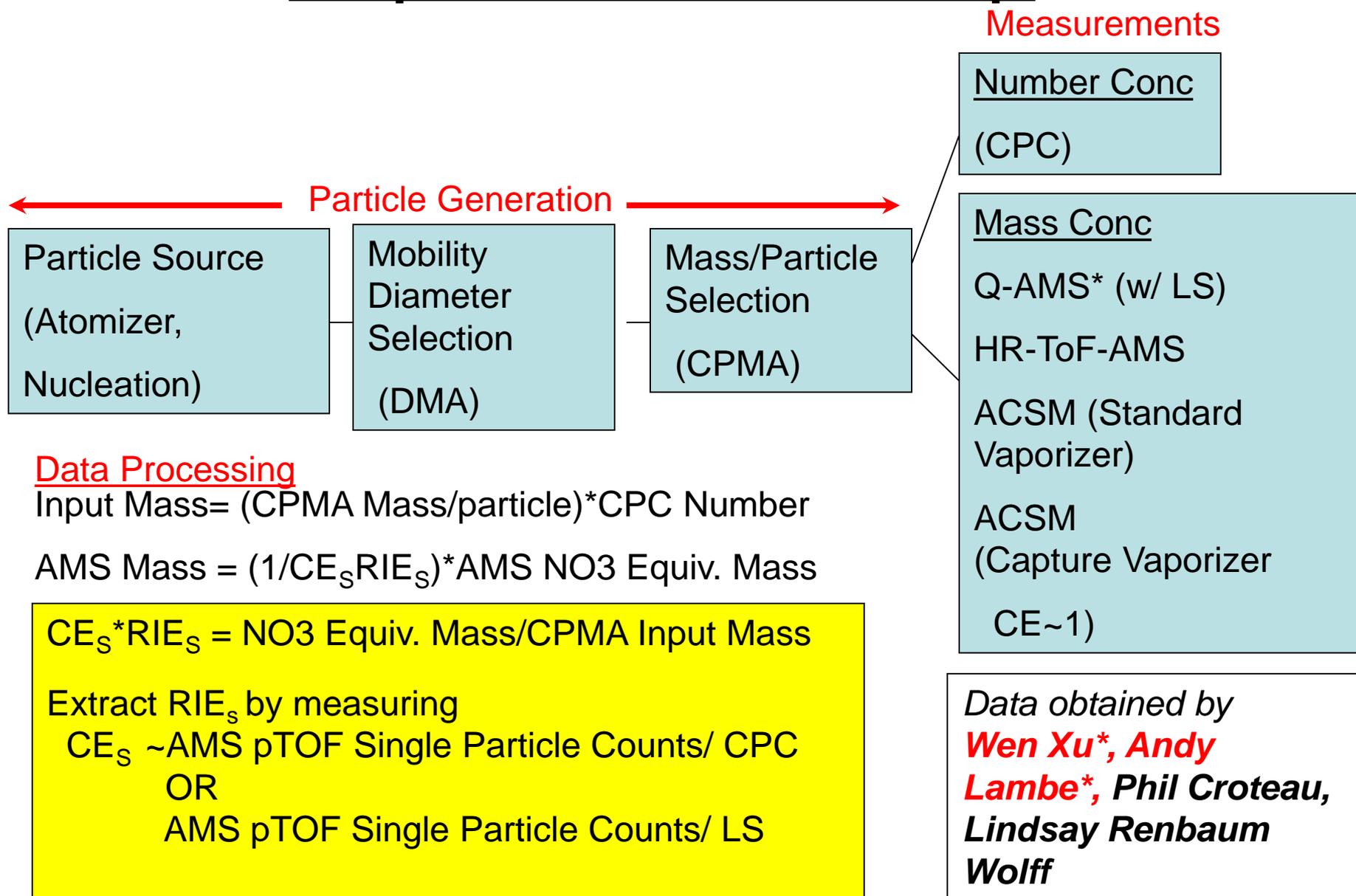Producing **known** input mass is hard, particularly for OM

- 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

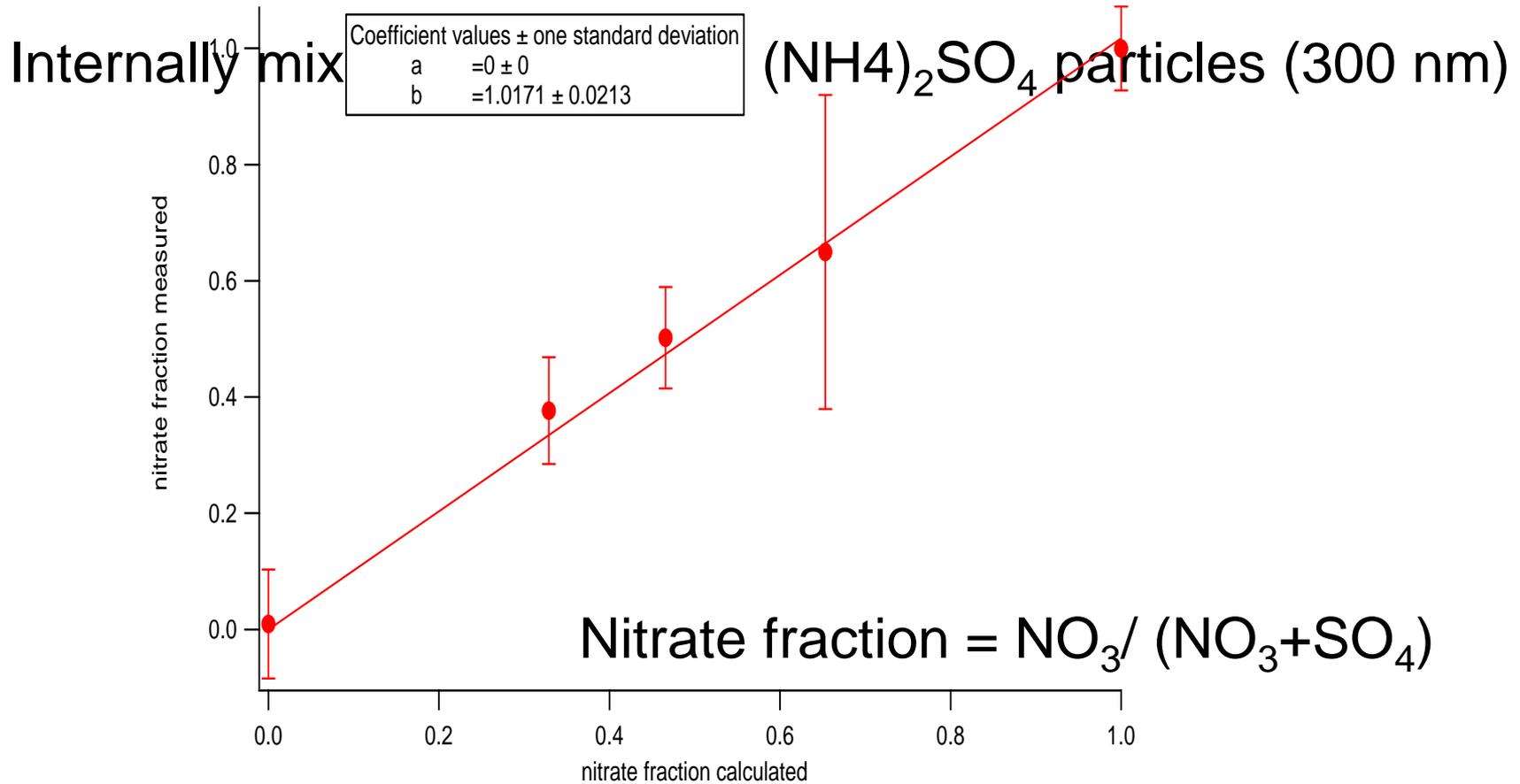New measurements with control of input aerosol mass

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

Experimental setup

Particle Generation

Number Conc

(CPC)

Mass Conc

Q-AMS* (w/ LS)

HR-ToF-AMS

ACSM (Standard Vaporizer)

ACSM (Capture Vaporizer

CE~1)

Particle Source

(Atomizer,

Nucleation)

Mobility Diameter Selection

(DMA)

Mass/Particle Selection

(CPMA)

Data Processing

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

Data obtained by Wen Xu, Andy Lambe*, Phil Croteau, Lindsay Renbaum Wolff*

Lab Results: Mixed Inorganics

Internally mix

(NH4)$_2$SO$_4$ particles (300 nm)

Coefficient values ± one standard deviation	
a	=0 ± 0
b	=1.0171 ± 0.0213

Nitrate fraction = NO$_3$/ (NO$_3$+SO$_4$)

nitrate fraction measured (y-axis)
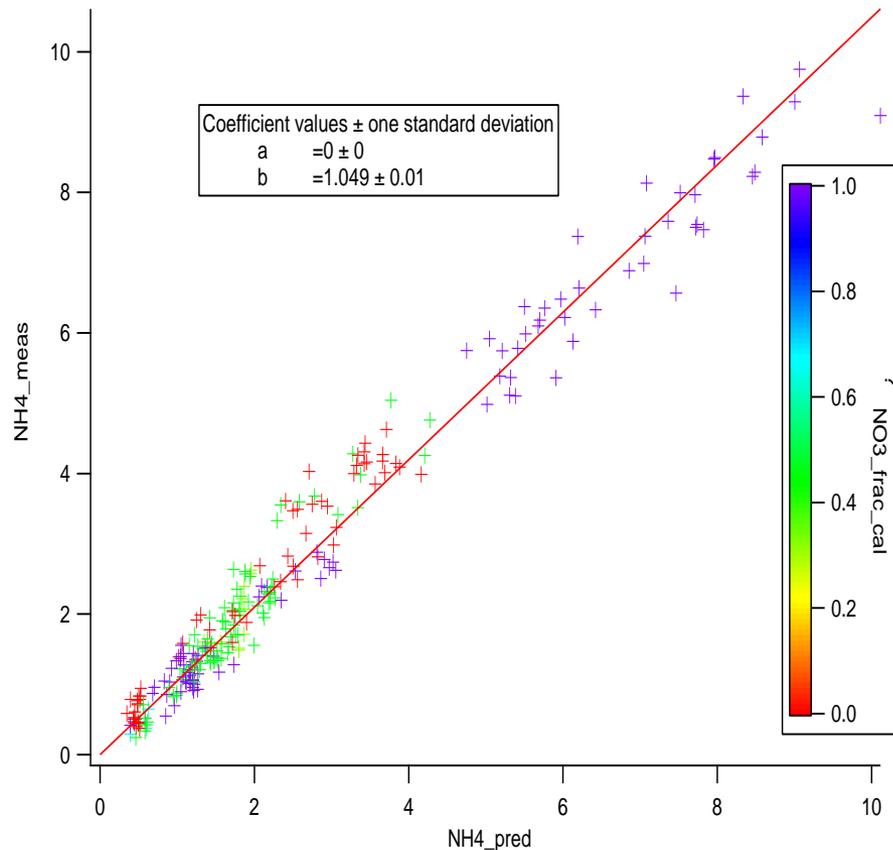
nitrate fraction calculated (x-axis)

Accuracy of nitrate fraction measurement not affected by matrix

→ NO$_3$ RIE similar in different mixed inorganic particles

Lab Results: Mixed Inorganics

Coefficient values ± one standard deviation
a   =0 ± 0
b   =1.049 ± 0.01

Internally mixed NH_4NO_3 and $(NH4)_2SO_4$ particles (300 nm)

NH_4 meas calculated using single RIE from NH_4NO_3 calibration

$NH_4NO_3 \xrightarrow{\triangle} NH_3 + HNO_3$

$(NH4)_2SO_4 \xrightarrow{\triangle} NH_3 + H_2SO_4$
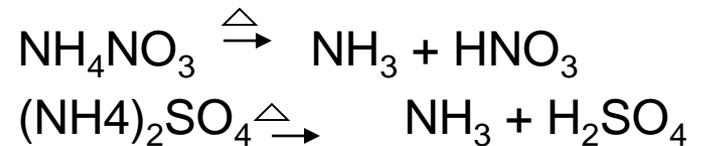
Quantification of NH_4 not affected by matrix

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

Lab Results: Mixed Inorganics
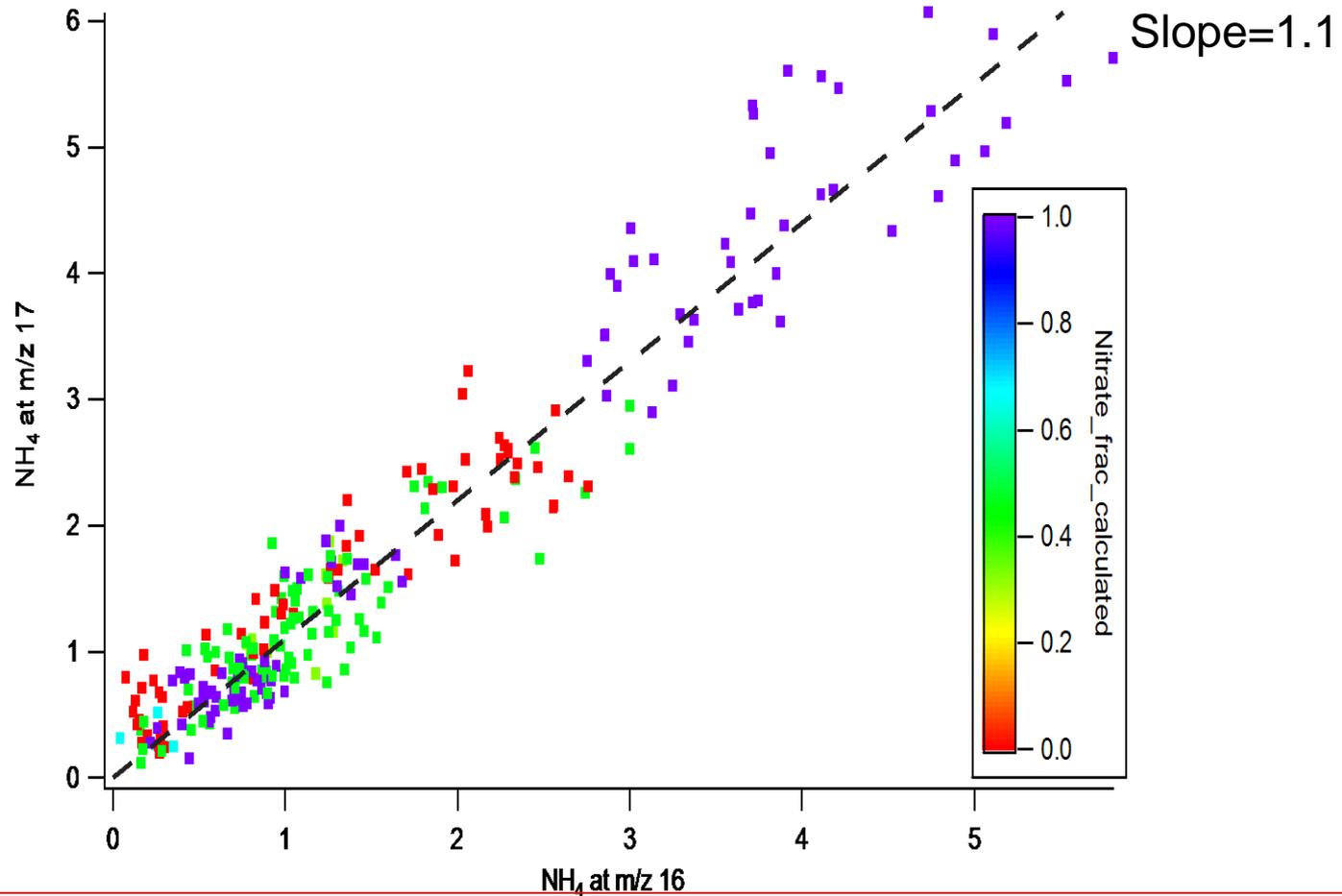
Measured NH$_4$ fragmentation pattern not affected by matrix

→ (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and mix all decompose on oven to produce NH$_3$ which yields the detected NH$_2^+$ and NH fragments

Lab measurements of RIE_Org
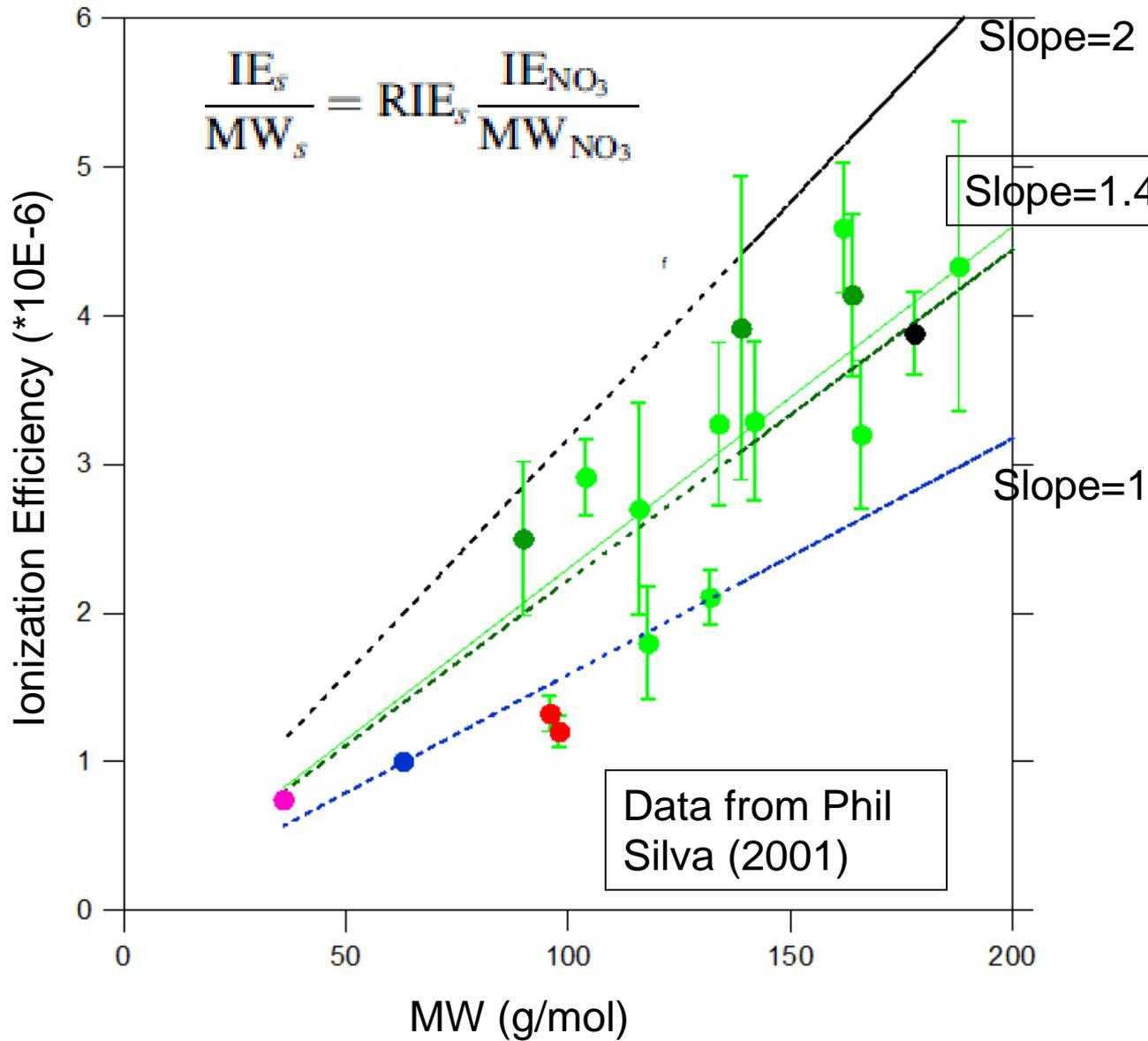
$$\frac{IE_s}{MW_s} = RIE_s \frac{IE_{NO_3}}{MW_{NO_3}}$$

Slope=2

Slope=1.4

Slope=1

Ionization Efficiency (*10E-6)

MW (g/mol)

Data from Phil Silva (2001)

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

Caveat
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).
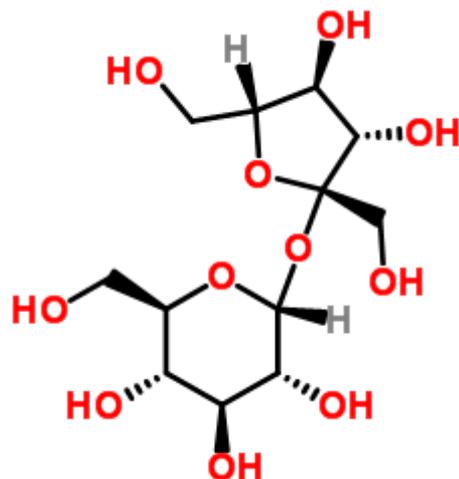
Lab Results: MW dependence of RIE_{org}

Recent Results using CPMA (2015)
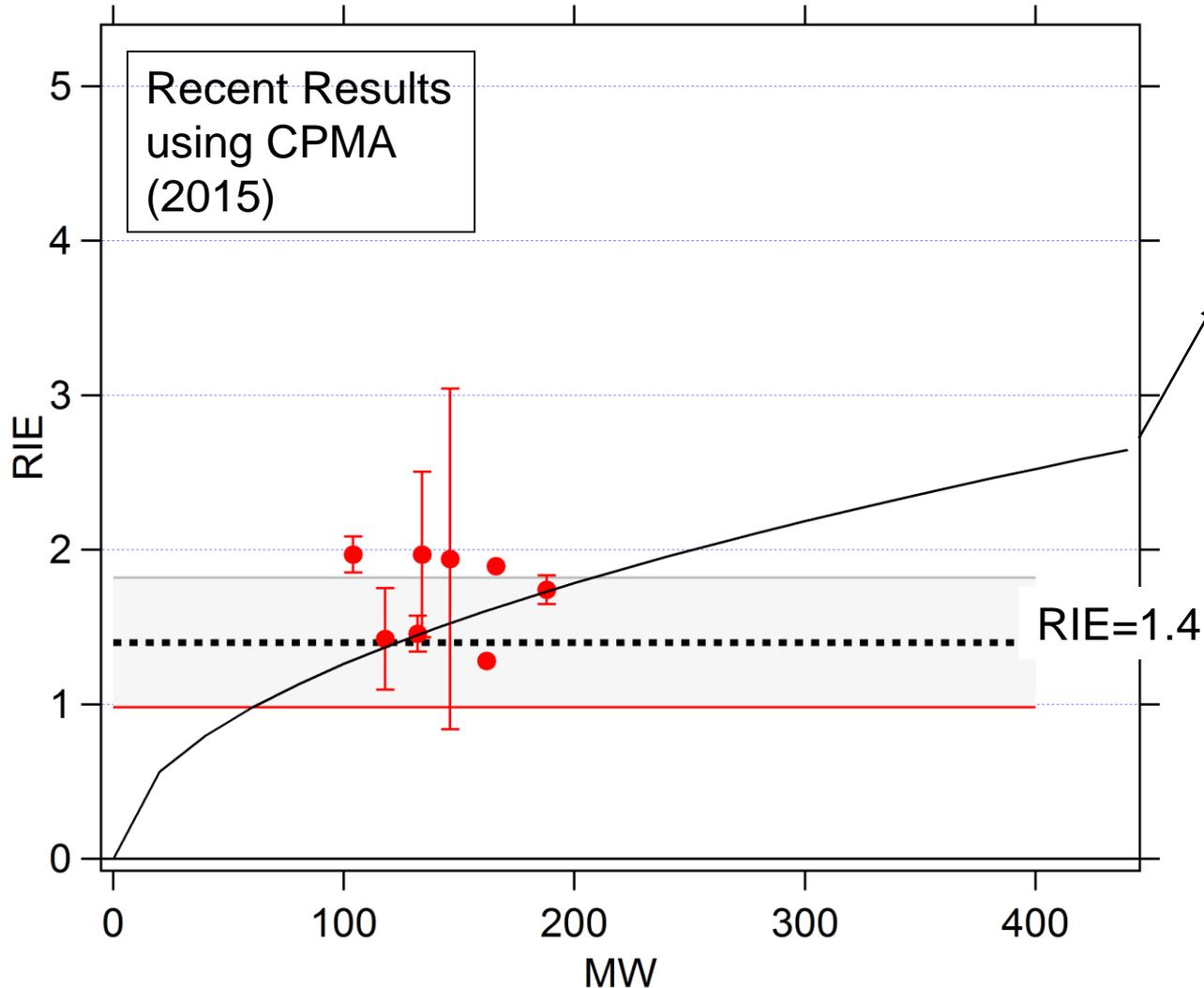
Curve shows RIE proportional to Sqrt(MW). Here MW132 is arbitrarily set at a reference RIE value of 1.4

RIE=1.4

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

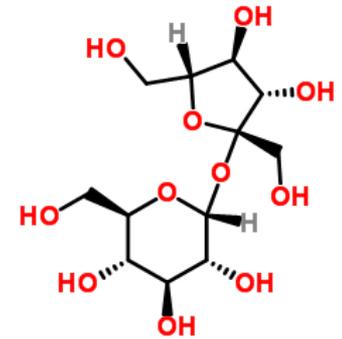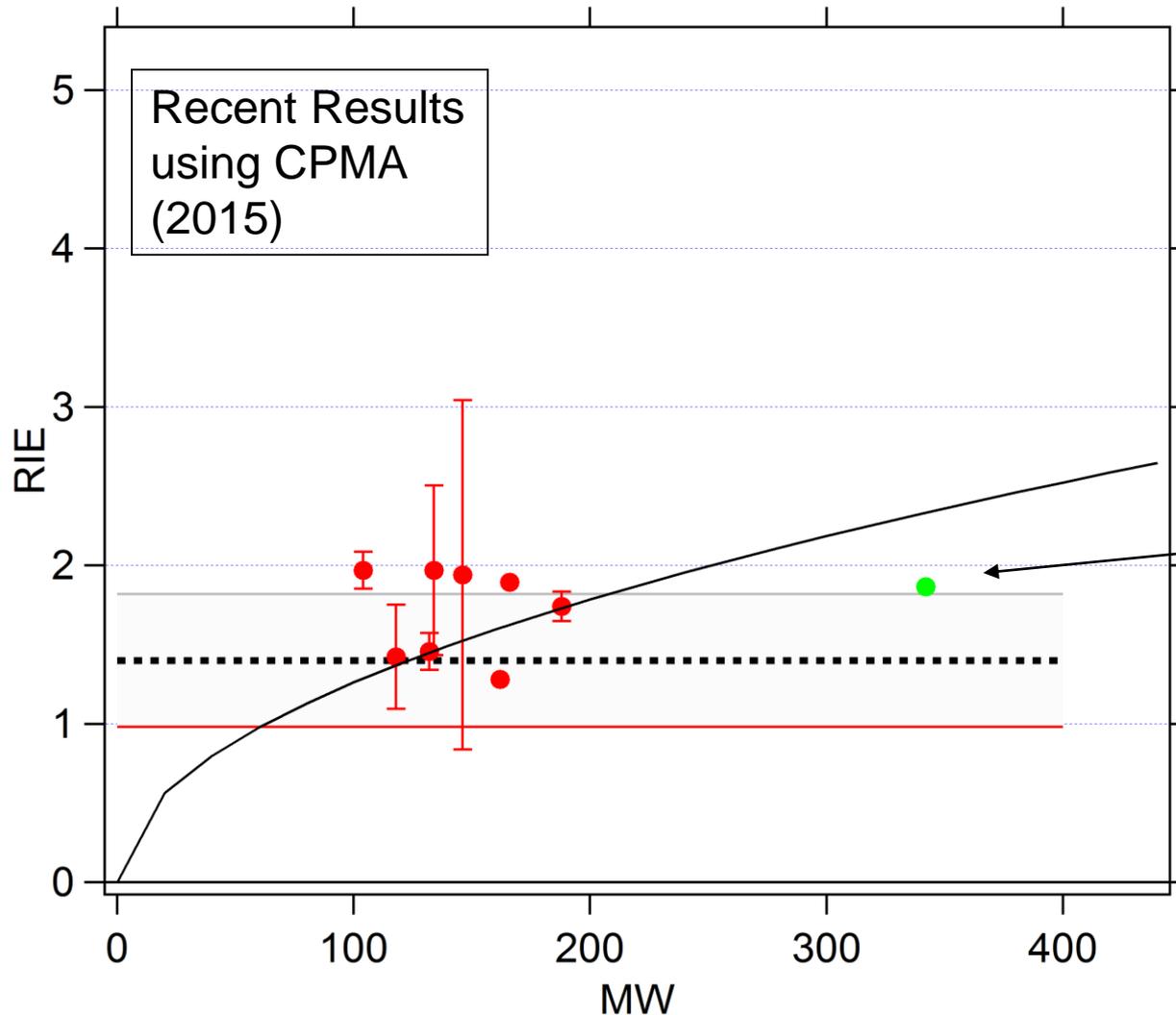Thermal Decomposition reduces effective MW of parent molecules in vapor phase

- Acidic species lose CO_2, H_2O, CO
- Alcohols lose H_2O
- Oligomeric species likely decompose into monomers

Sucrose, MW=342

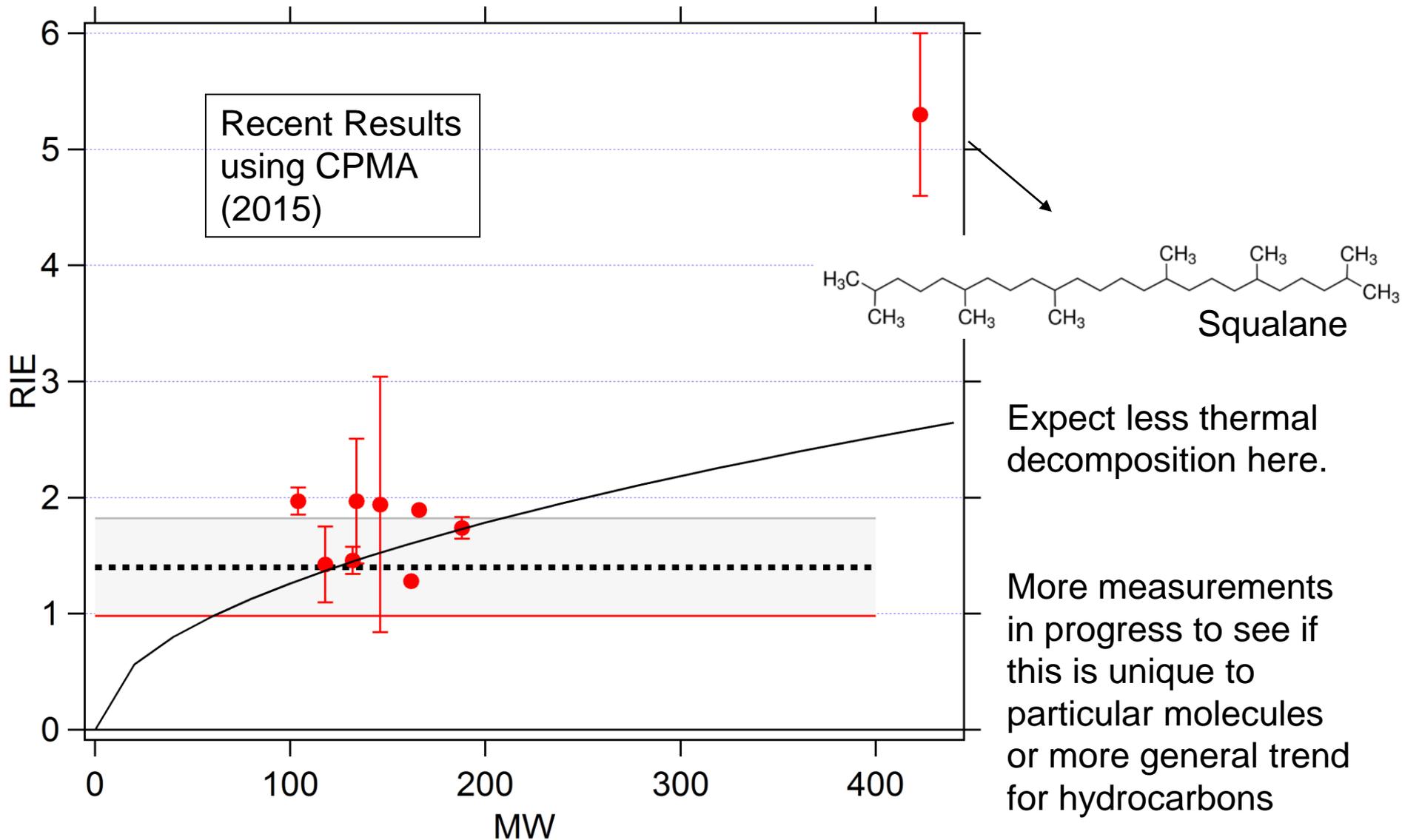MW dependence of RIE unlikely to be a big effect for Ambient OOA

MW dependence of RIE~org~

Sucrose

Large MW species that thermally decomposes has similar RIE to smaller oxidized organics

MW dependence of RIE_{org}

Recent Results using CPMA (2015)

Squalane

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 for measurements of RIE$_{org}$

- Measuring RIEs of large MW hydrocarbons which are less likely the 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 Q,ToF,ACSMs (standard vs. capture vaporizer)