Overview of collection efficiency (CE):

Standard vaporizer vs Capture vaporizer

Weiwei Hu

2018-04-20

AMS user's meeting @ Nanjing

Collection efficiency definition

Mass loading based:

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

$$\frac{\mathrm{IE}_s}{\mathrm{MW}_s} = \mathrm{RIE}_s \frac{\mathrm{IE}_{\mathrm{NO_3}}}{\mathrm{MW}_{\mathrm{NO_3}}}$$

Primary Calibration

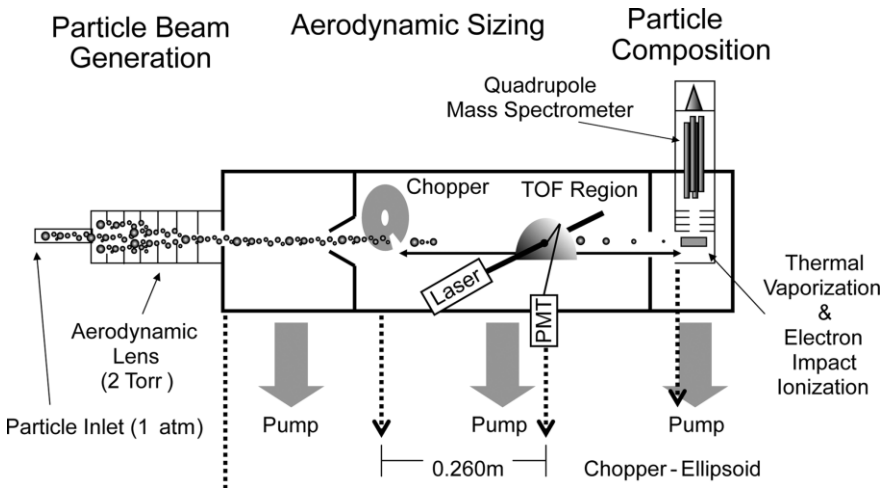
$$C_s = \frac{10^{12}}{\mathrm{CE}_s\,\mathrm{RIE}_s\,\mathrm{IE}_{\mathrm{NO_3}}\,Q N_A} \frac{\mathrm{MW}_{\mathrm{NO_3}}}{\sum_{\mathrm{all}\,i} I_{s,i}}$$

→ Nitrate Equiv. Mass

CE_sRIE_s is largest uncertainty in mass concentration calculations

Number counting based:

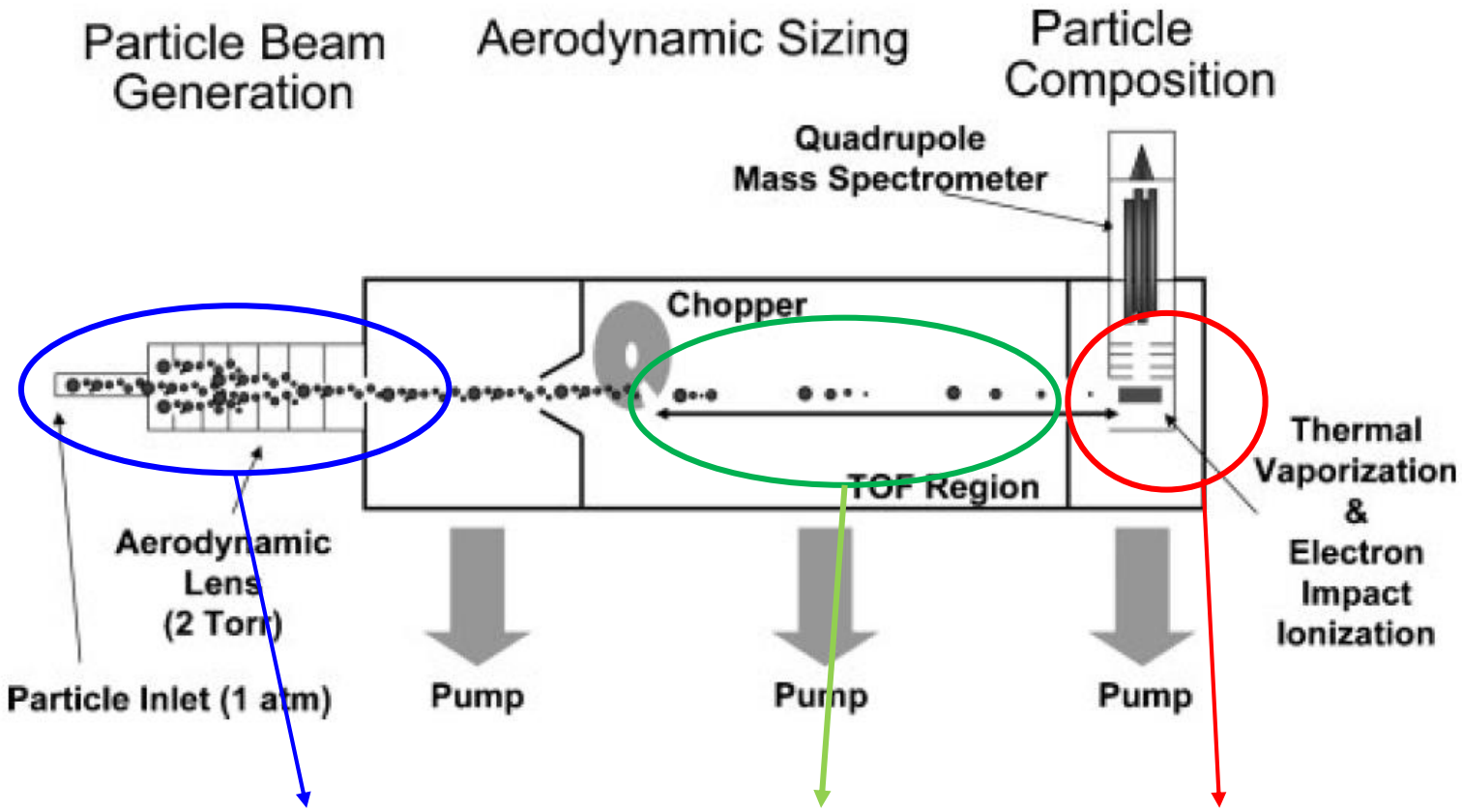
$$\mathrm{CE_p} = \frac{\text{Particles with ion signal above threshold}}{\text{All particles detected by LS}}.$$



$CE_{number} \geq CE_{mass}$

Canagaratna et al. AMS clinic meeting, 2015; Cross et al. 2007;

Collection efficiency definition

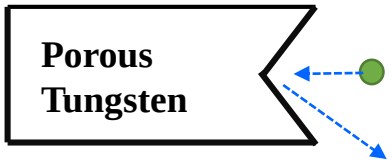


CE=E_L (lens) × E_s (scattering) × E_b (Bounce)

minor **minor** **Major**

Canagaratna et al. 2007; Huffman et al. 2005

CE from field and laboratory work



SV

Species: Organic aerosol, Sulfate

Collection efficiency (CE) depends on :

1) Nitrate content
2) Acidity/neutralization
3) Relative humidity in the sampling line
4) Organic liquid content

Much of this driven by aerosol phase: Solid/semisolid/liquid particle

Solids bounce ***Liquids do not bounce***

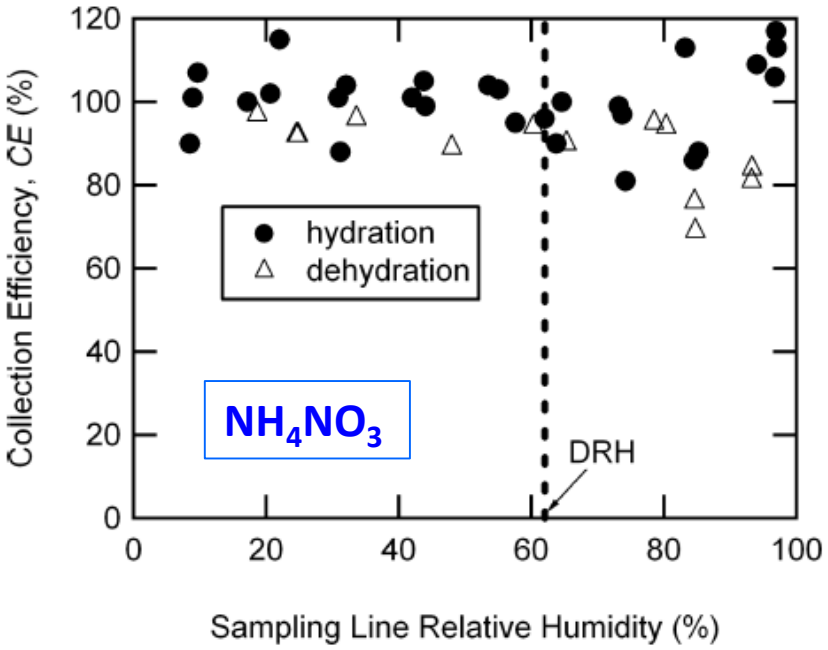
Typically contribute the most uncertainty for ambient aerosol measurement

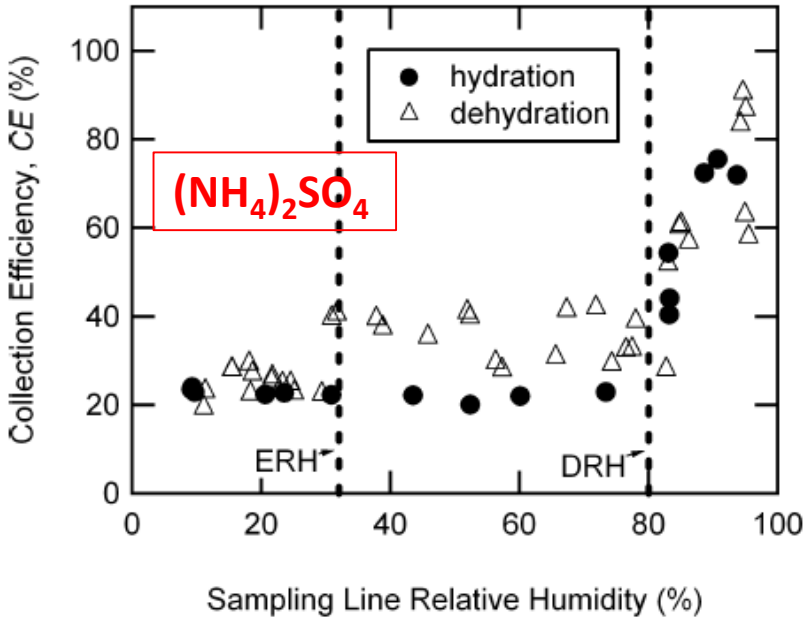
Middlebrook et al., AST, 2012;
Canagaratna et al. AMS clinic meeting, 2015

Values of CE: Laboratory work

Pure inorganic chemical compounds:

- NH_4NO_3 = 1
- $(NH4)_2SO_4$ = 0.2-0.5 (dry condition)
- NH_4Cl = 0.2-0.4

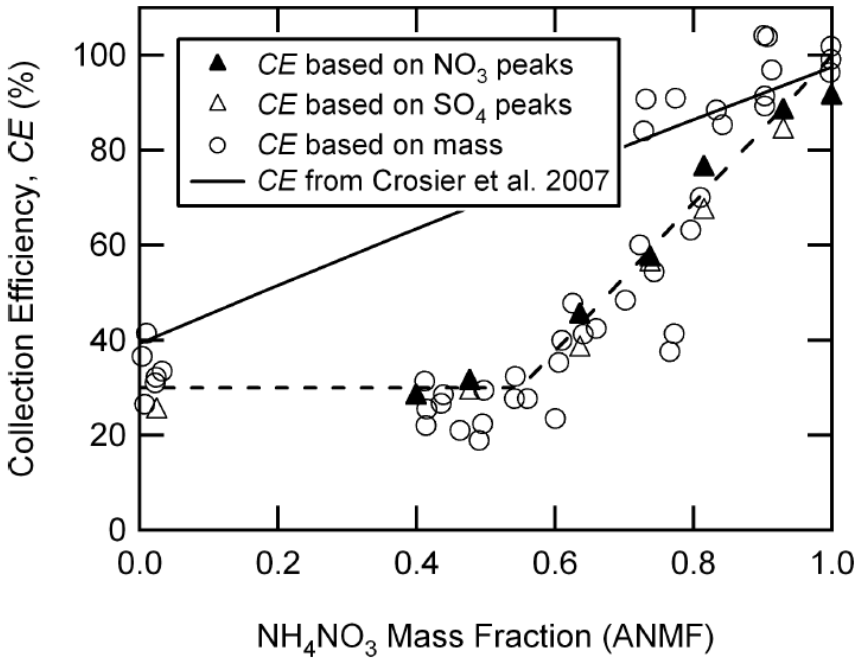


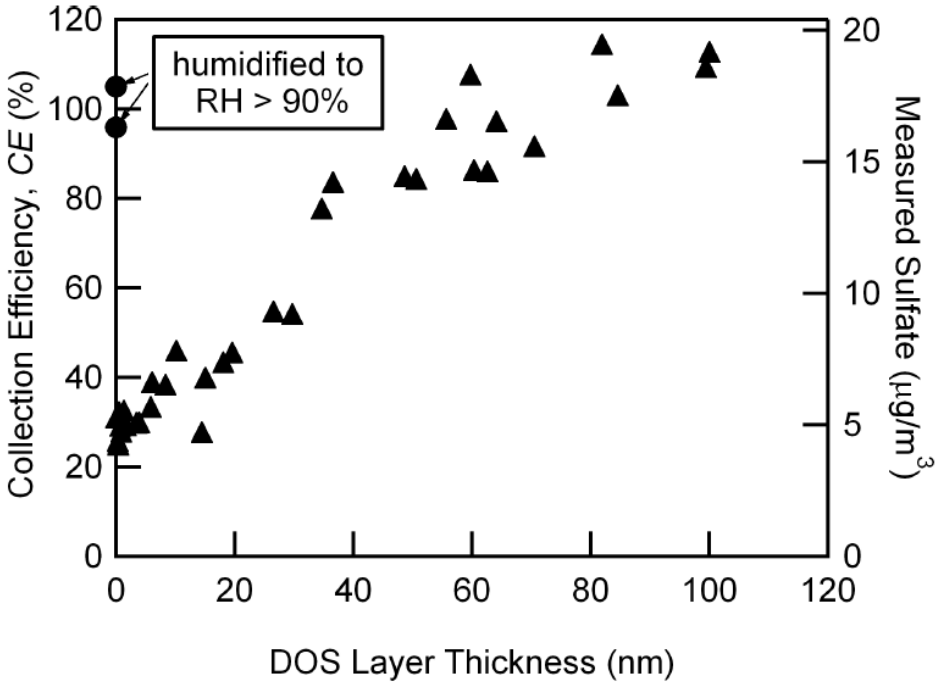


Matthew et al. 2008; Hu et al. 2017

Values of CE: Laboratory work

- **CEs for Mixed of nitrate and sulfate vary with NO_3 content, humidity, and liquid organic coating.**

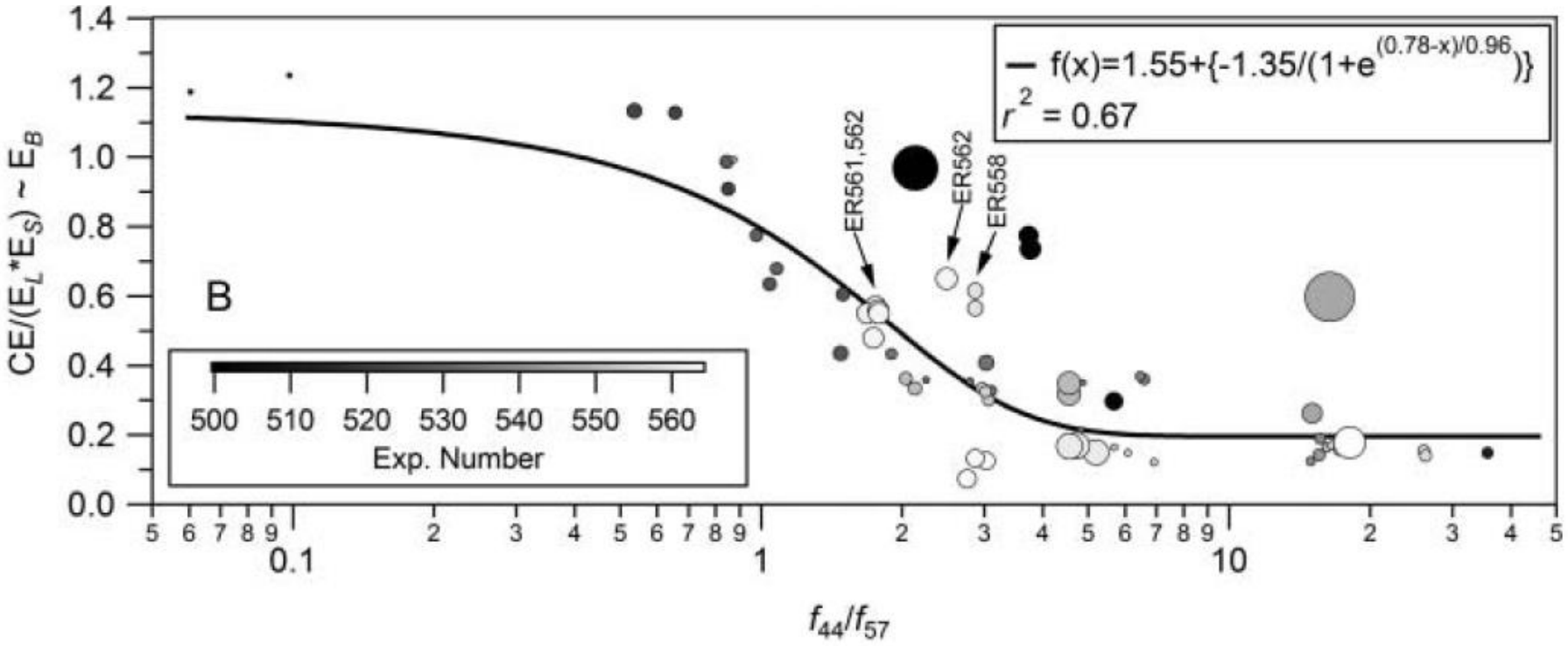




Matthew et al. 2008

Values of CE: Laboratory work

Laboratory SOA usually> 0.2 (Range observed, dependence on f_{44})



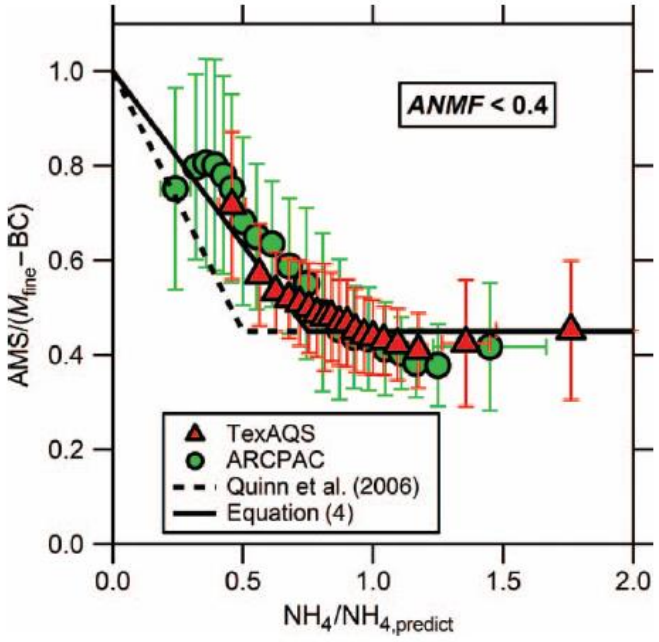
Docherty et al. 2012

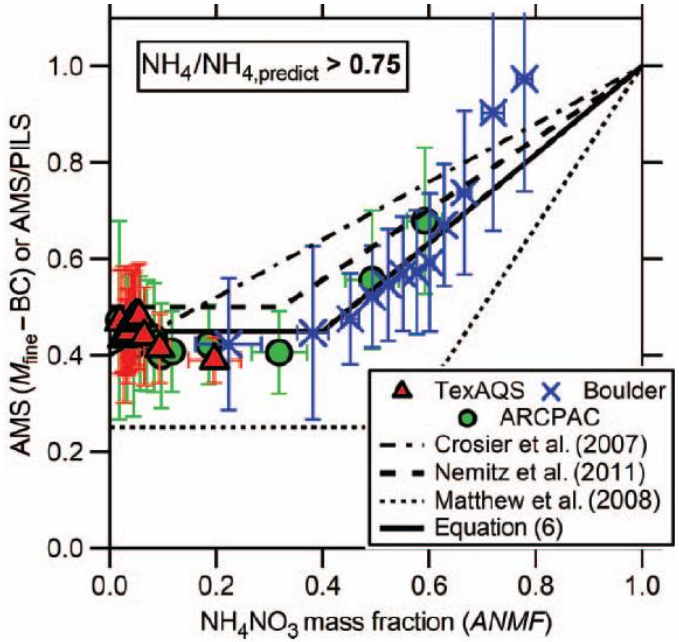
Values of CE : ambient aerosol

- CE=0.5 (±0.15) in average: empirical composition dependence (Middlebrooks et al. AS&T 2012)
- Pure laboratory particles are poor models for ambient mixed particles, but similar trend with humidify and NO_3 (*State of particles in ambient or in AMS after transmission through lens*)

$$CE_{\mathrm{dry}} = \max\left(0.45,\ 1.0 - 0.73 \times \left({}^{\mathrm{NH_4}}/_{\mathrm{NH_{4,predict}}}\right)\right)$$

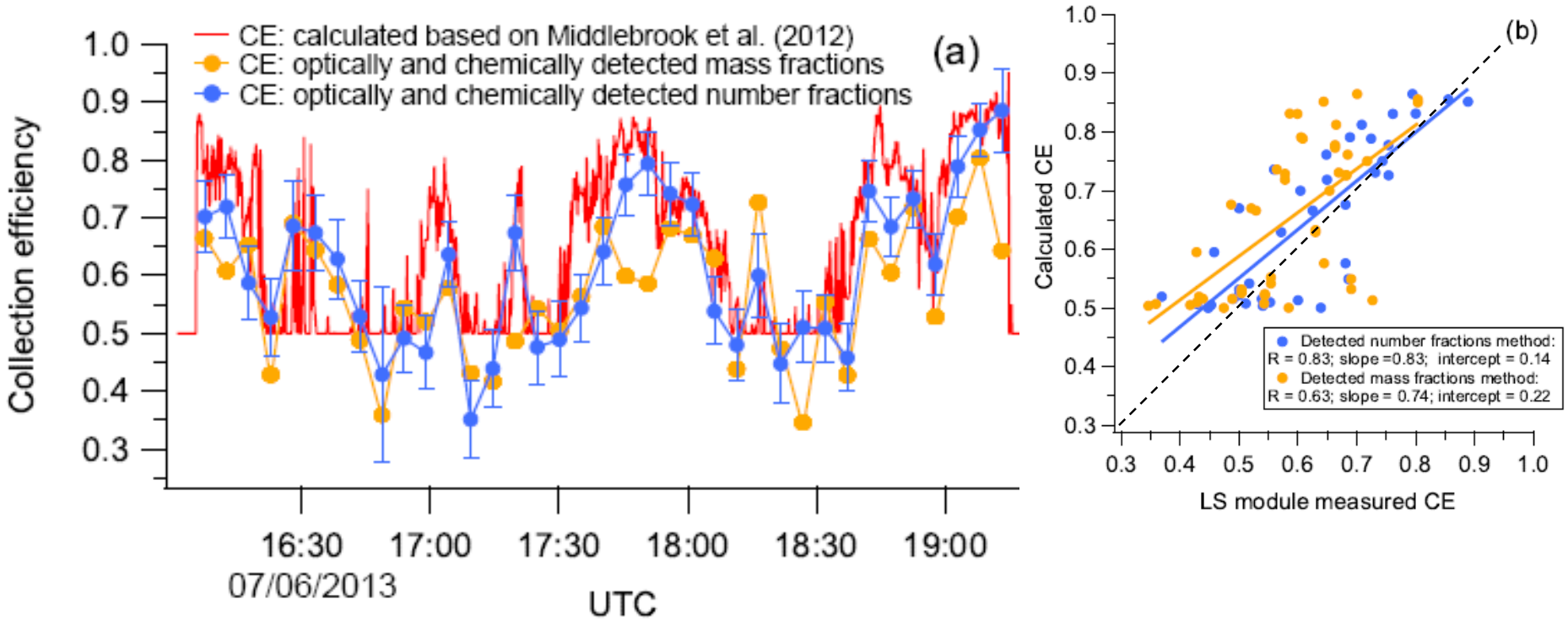
$$CE_{\mathrm{dry}} = \max(0.45,\ 0.0833 + 0.9167 \times ANMF)$$





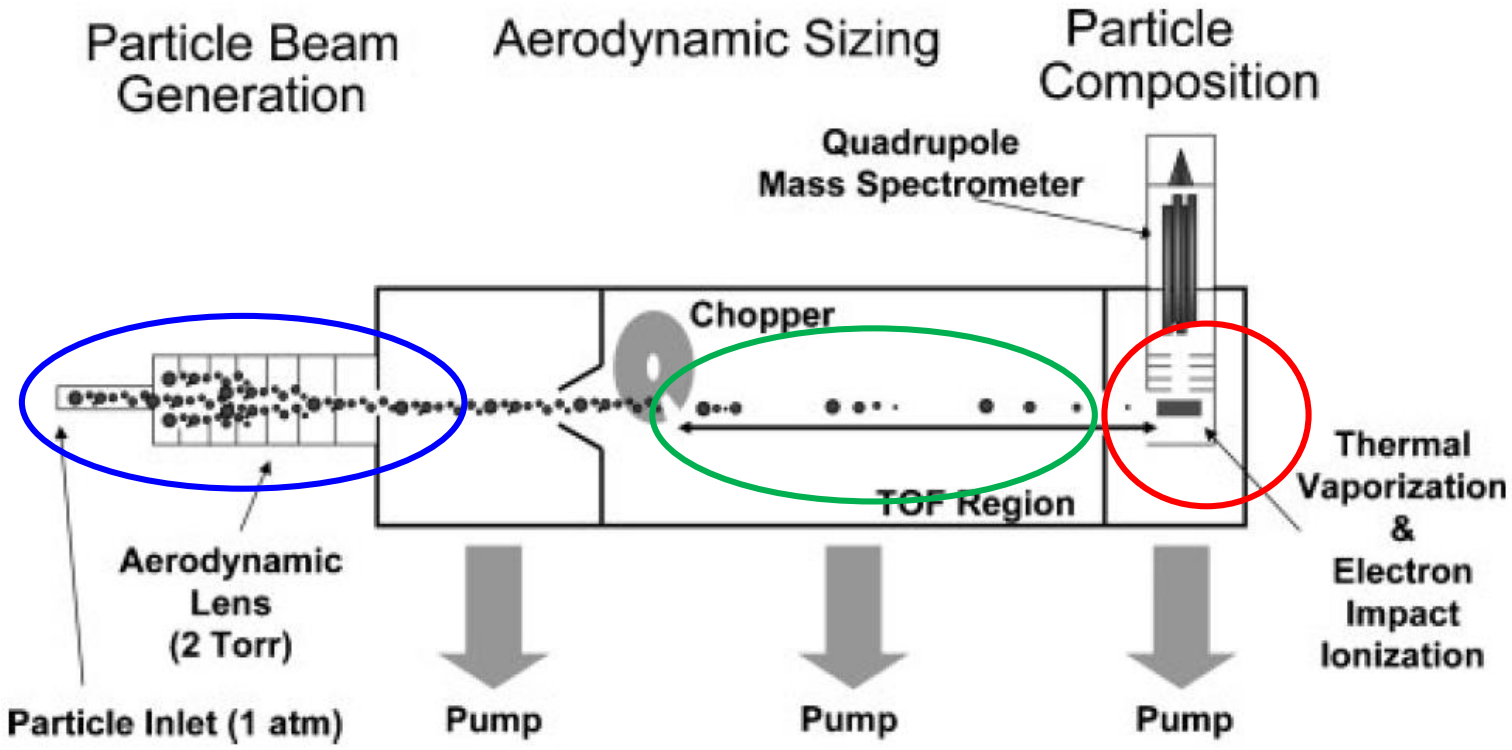
Uncertainty of AMS quantification 30%-40% for ambient organic and inorganic quantification based on comparison with other independent measurement-Bahreini et al. 2009

Mass based CE vs counting based CE



Liao et al., 2017

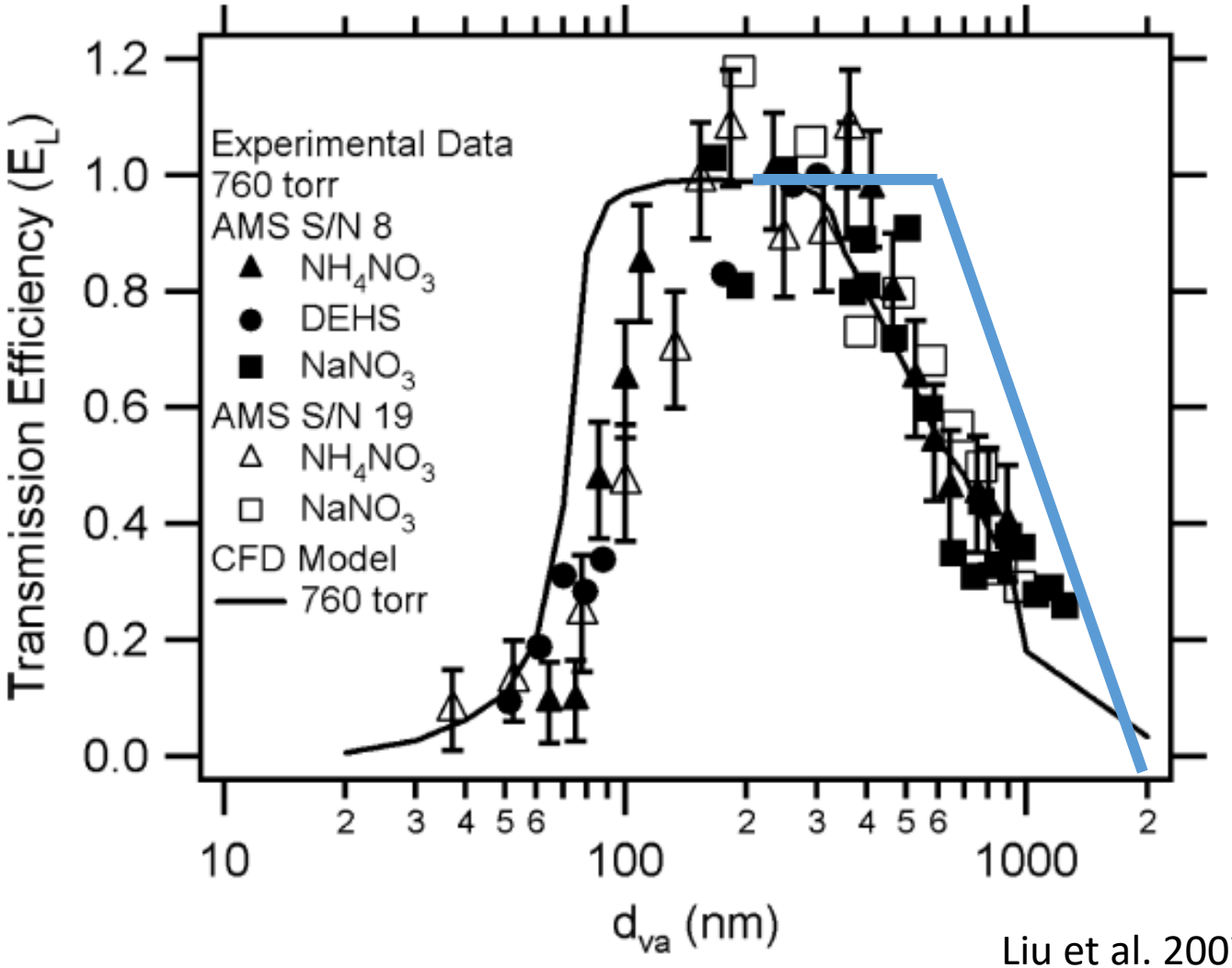
Collection efficiency definition



CE=E_L (lens) × E_s (scattering) × E_b (Bounce)

minor **minor** **Major**

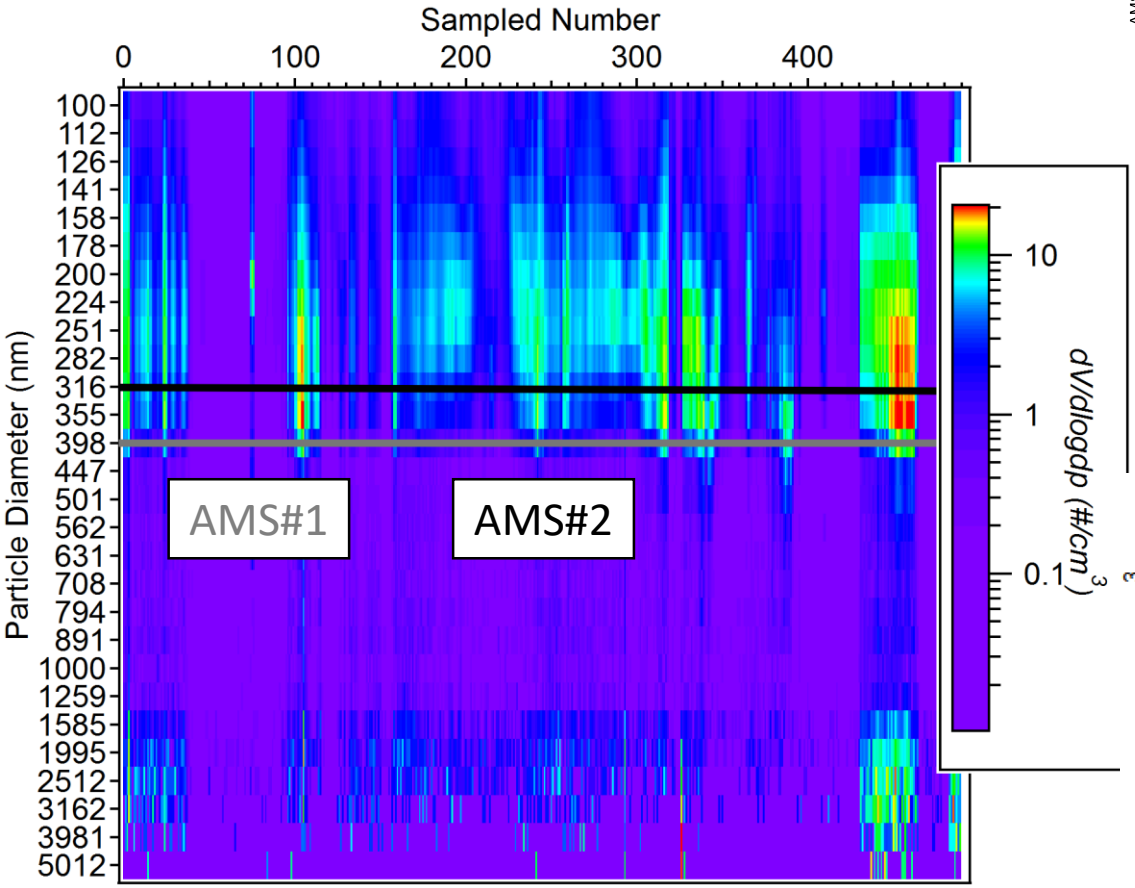
Lens transmission

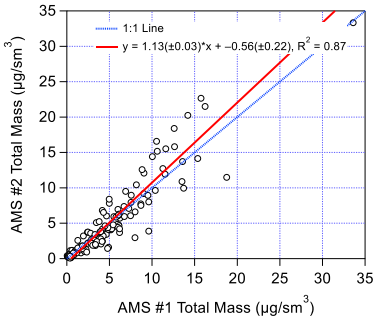


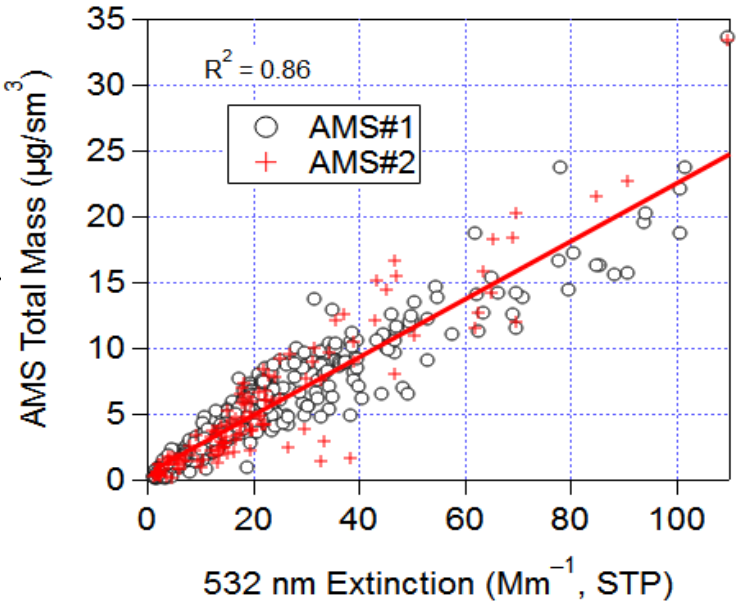
Liu et al. 2007

University of Colorado Boulder

Aerosol conc.: low

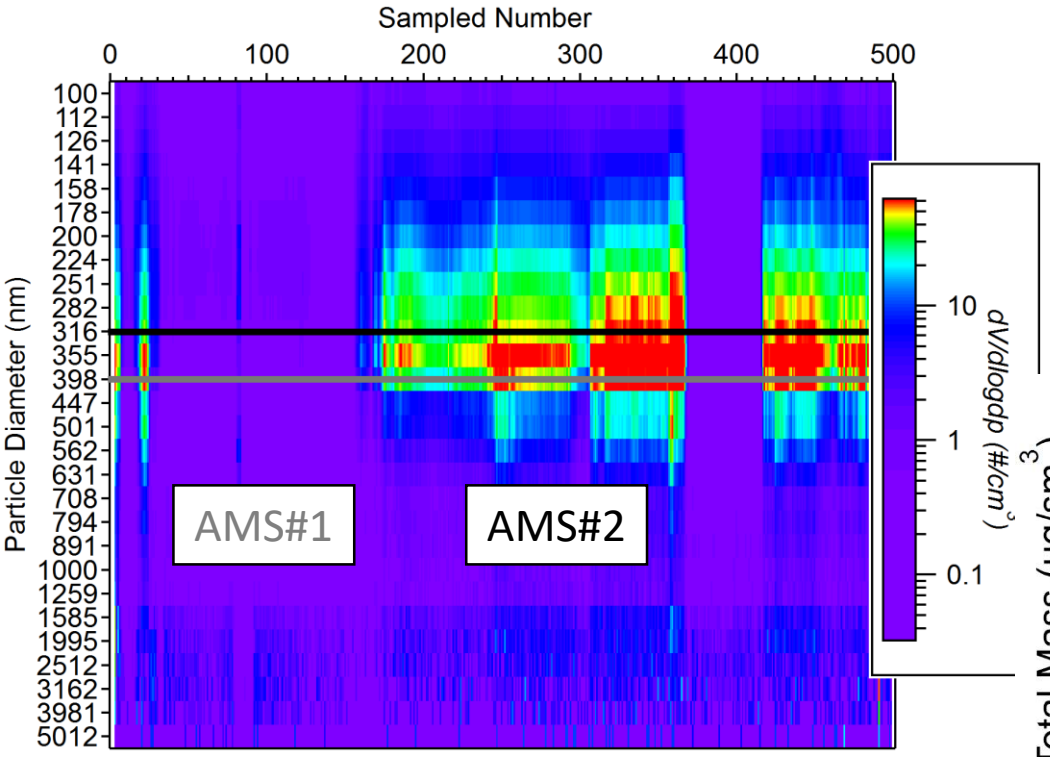


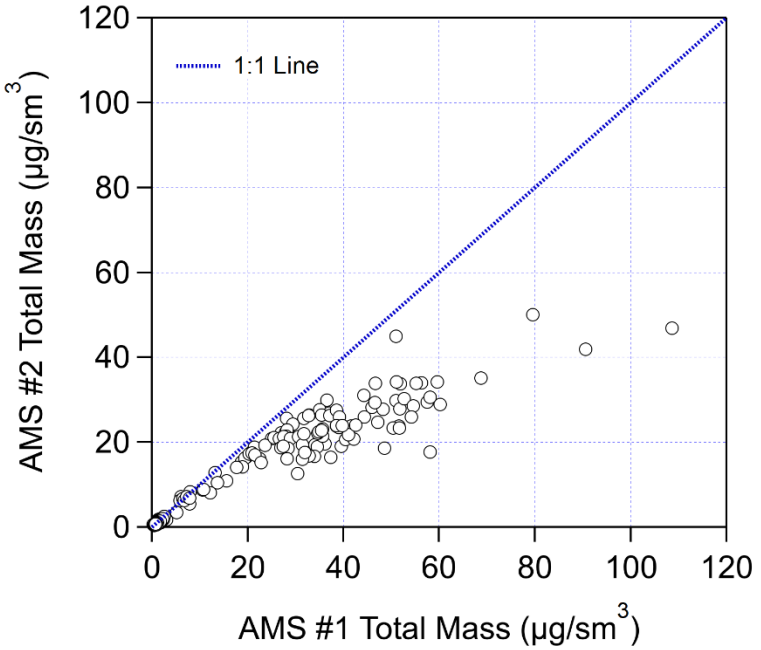


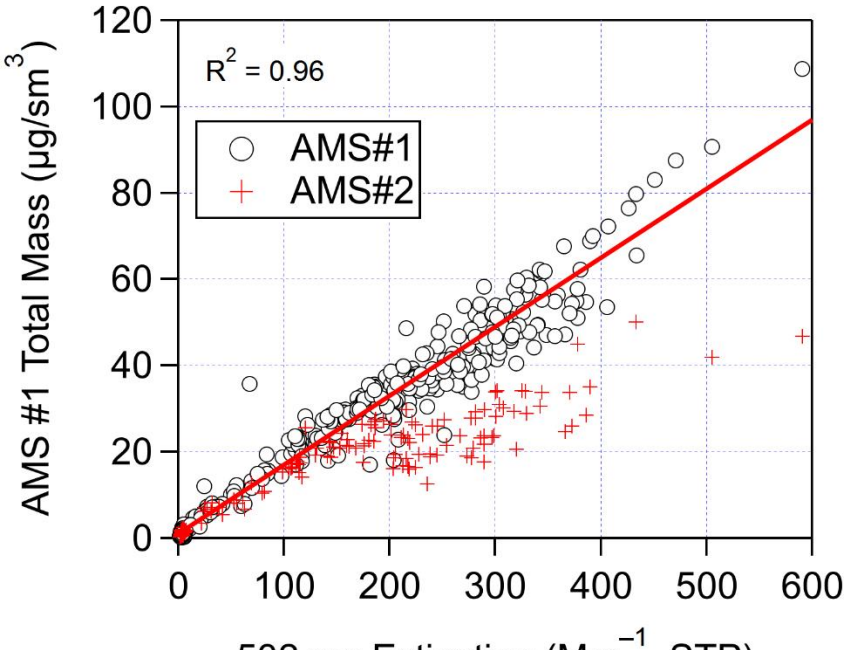


University of Colorado Boulder

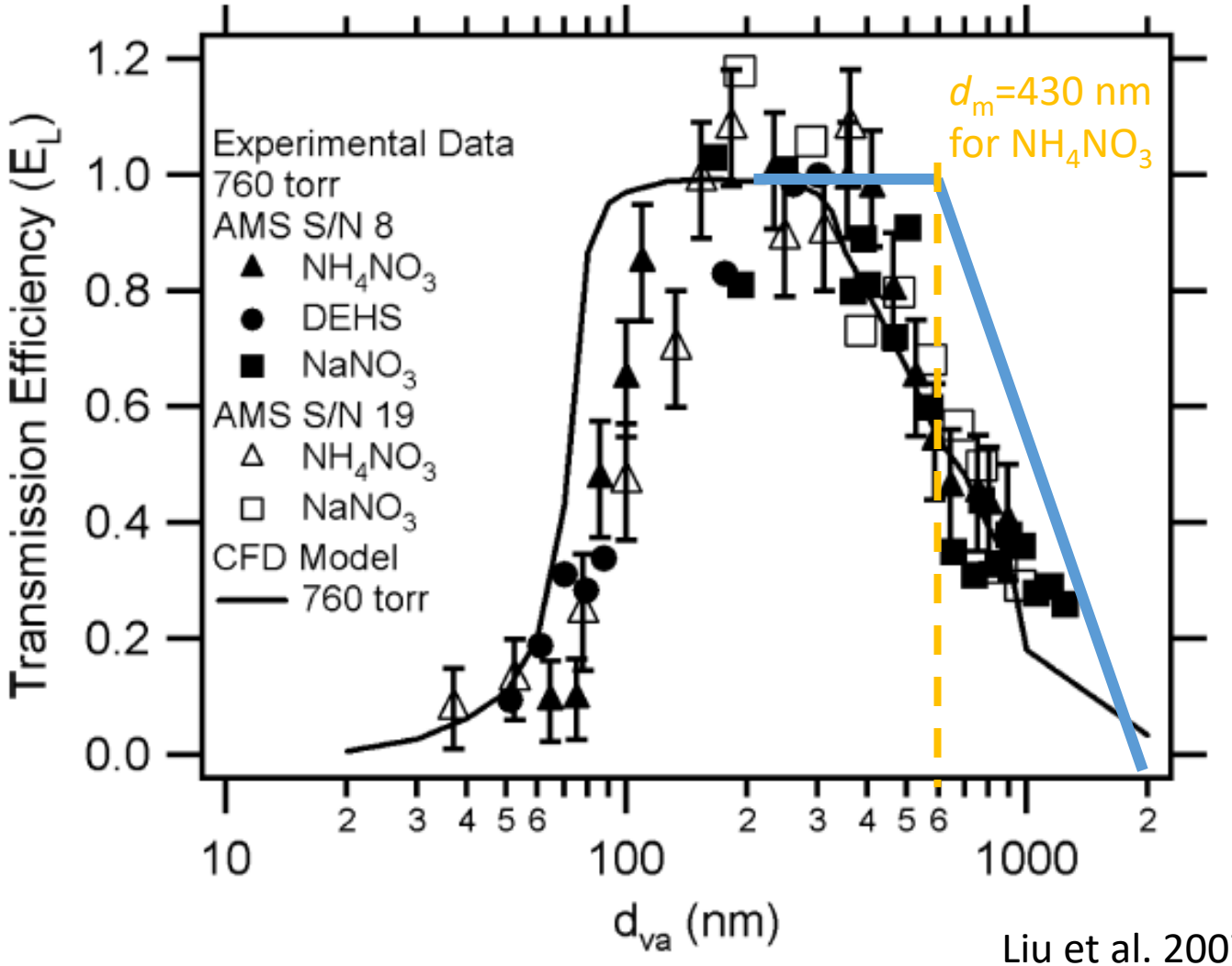
Aerosol conc.: High







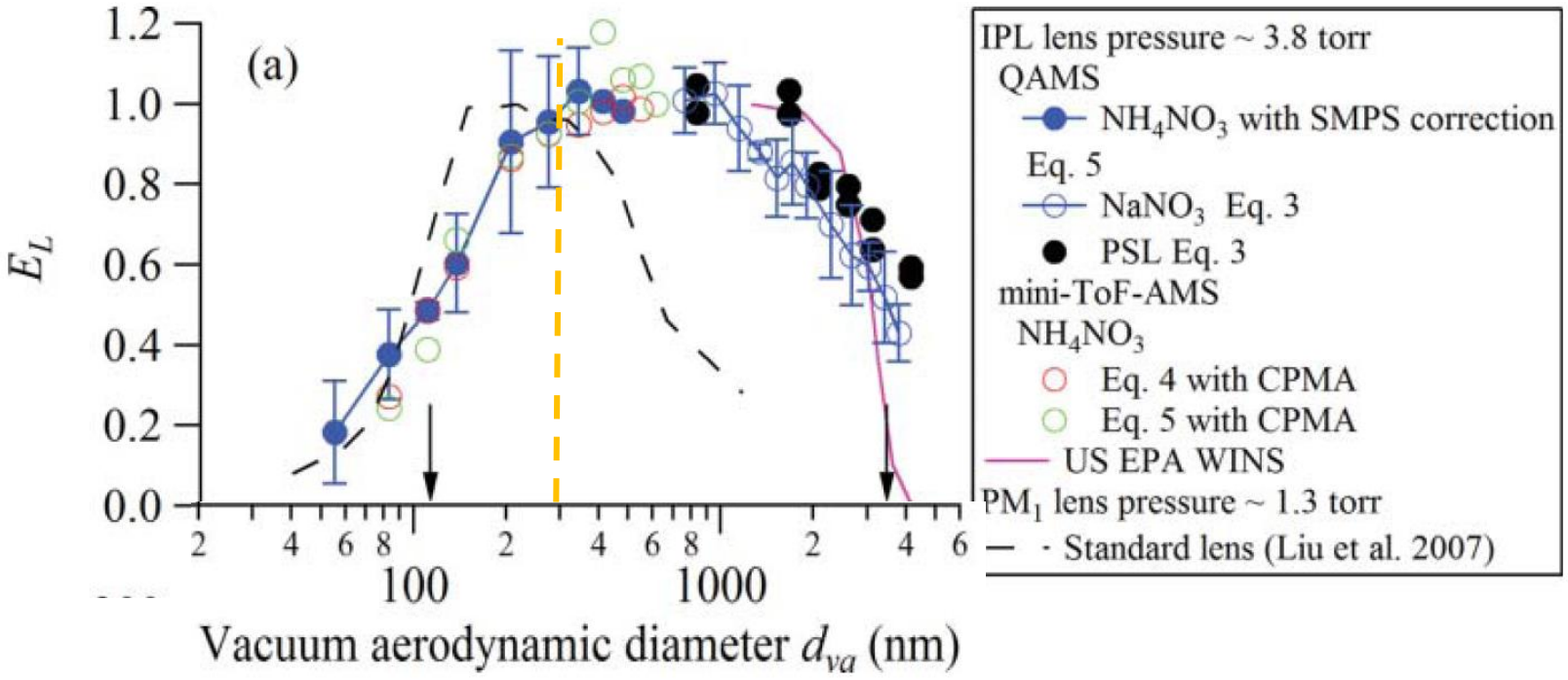
Lens transmission curve for PM_1



Liu et al. 2007

Lens transmission curve for $PM_{2.5}$

d_m=213 nm for NH_4NO_3



How to calibrate your lens

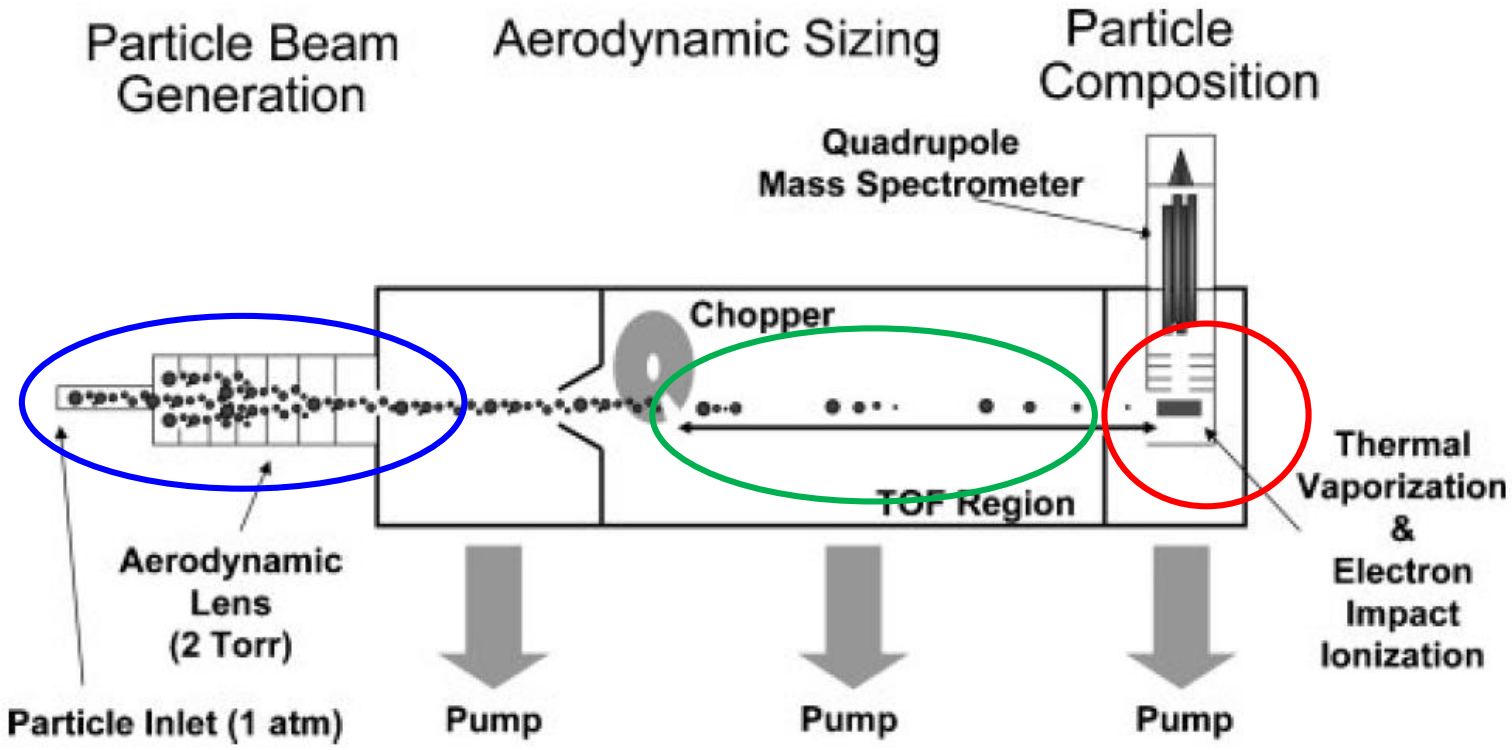
- Particle counts based: Event trigger and BFSP:
  - ✓faster
  - ✓Do not need to worry about double charge particles.

- Mass based: different size-resolved particles
  - Pay attention to the double charge particles; impactor should be used !

➢200-500 nm $(NH_4)_2SO_4$, NH_4NO_3 at 600 ^oC

➢Or other species $NaNO_3$ and KNO_3 at 800 ^oC

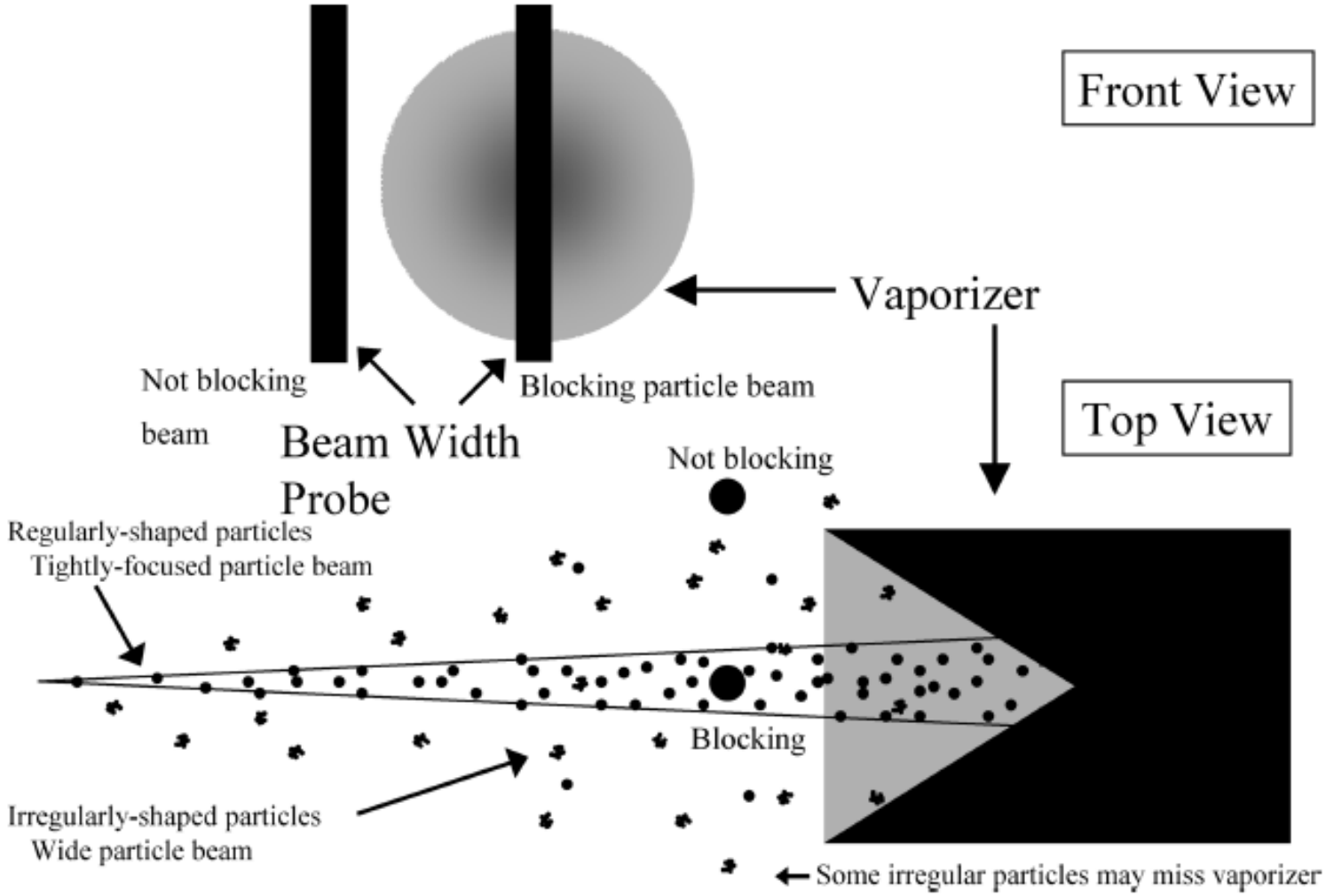
Collection efficiency definition



CE=E_L (lens) × E_s (scattering) × E_b (Bounce)

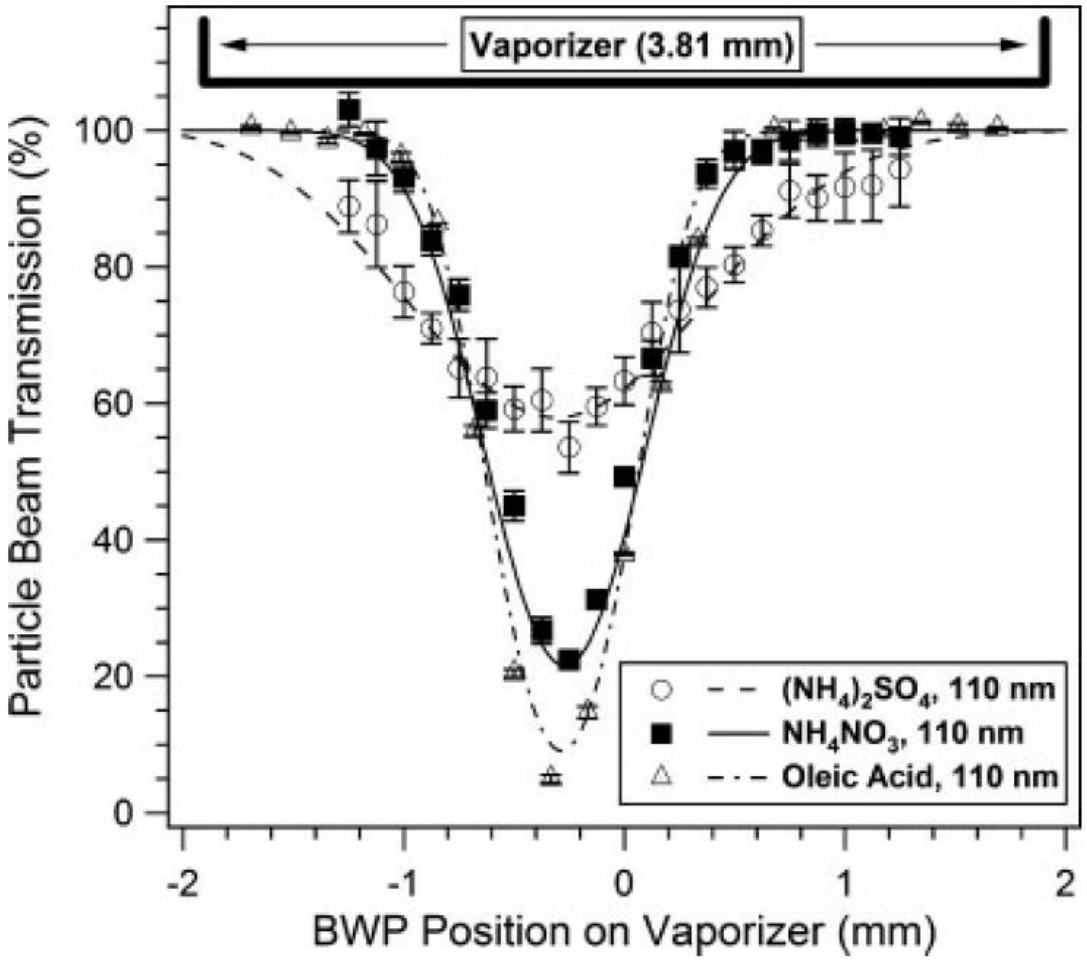
minor **minor** **Major**

Particle Beam Width Probe



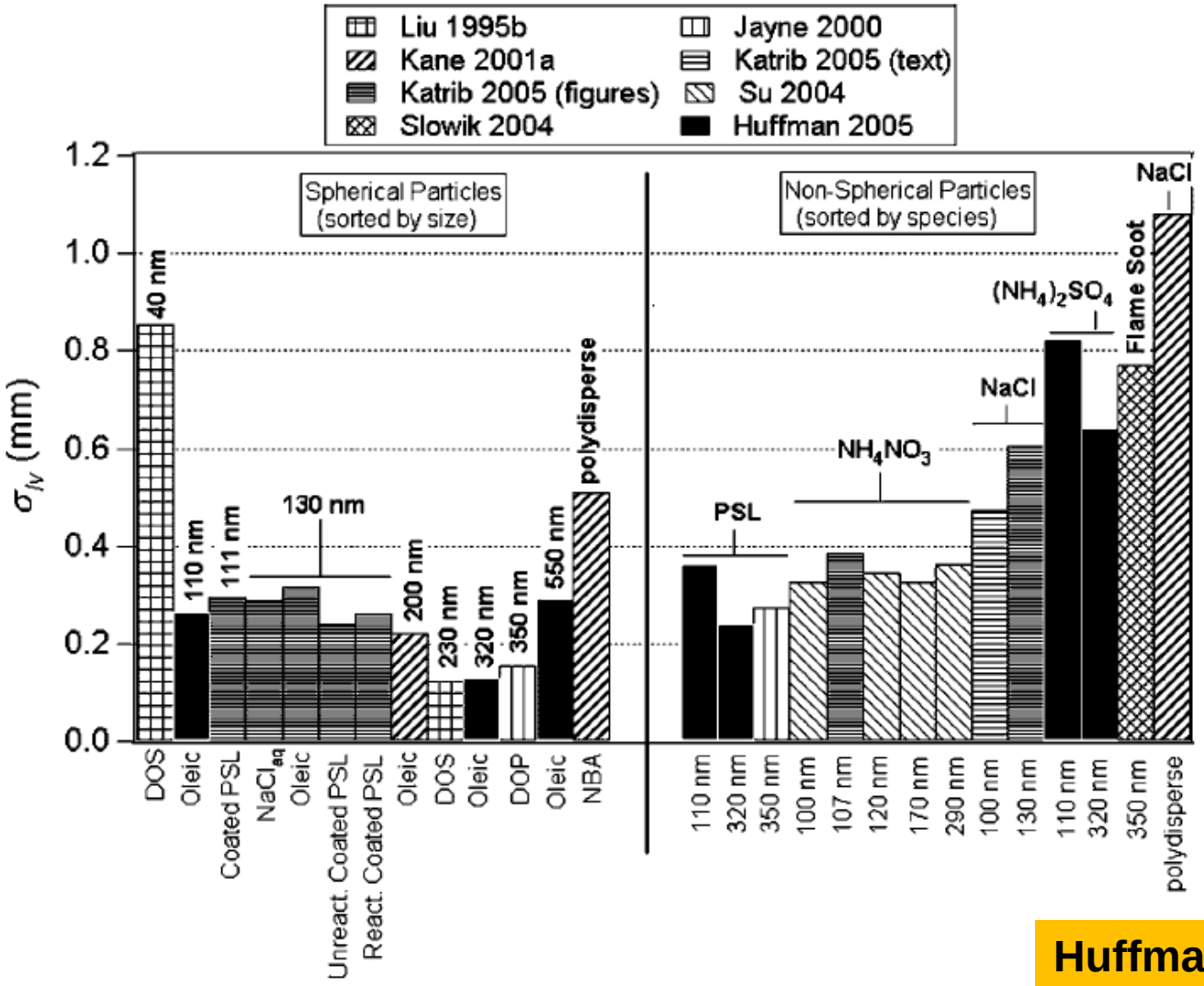
Huffman et al. 2009

Particle beam transmission



Huffman et al. 2005

Particle beam width for different particles

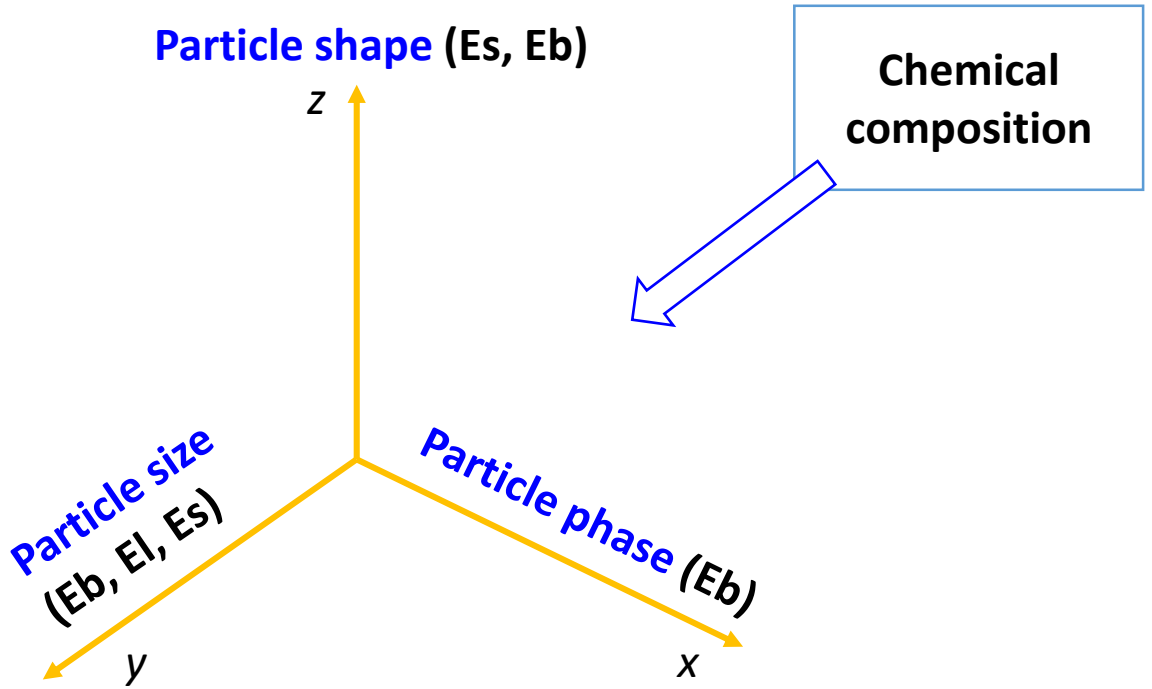


Huffman et al. 2005

Summary

- E_b *(Bounce) is the major contributor for CE;*
- E_L *(Lens) and* E_s *(scattering) are minor .*

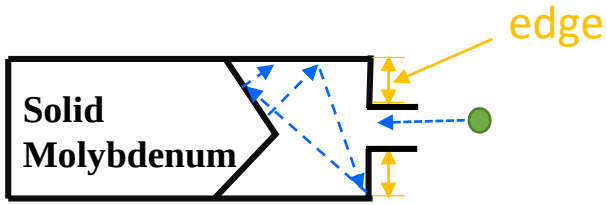
Another way to think about CE



Feature of standard vaporizer (SV) *vs* capture vaporizer (CV)

SV

CV



Species: Organic aerosol, Sulfate

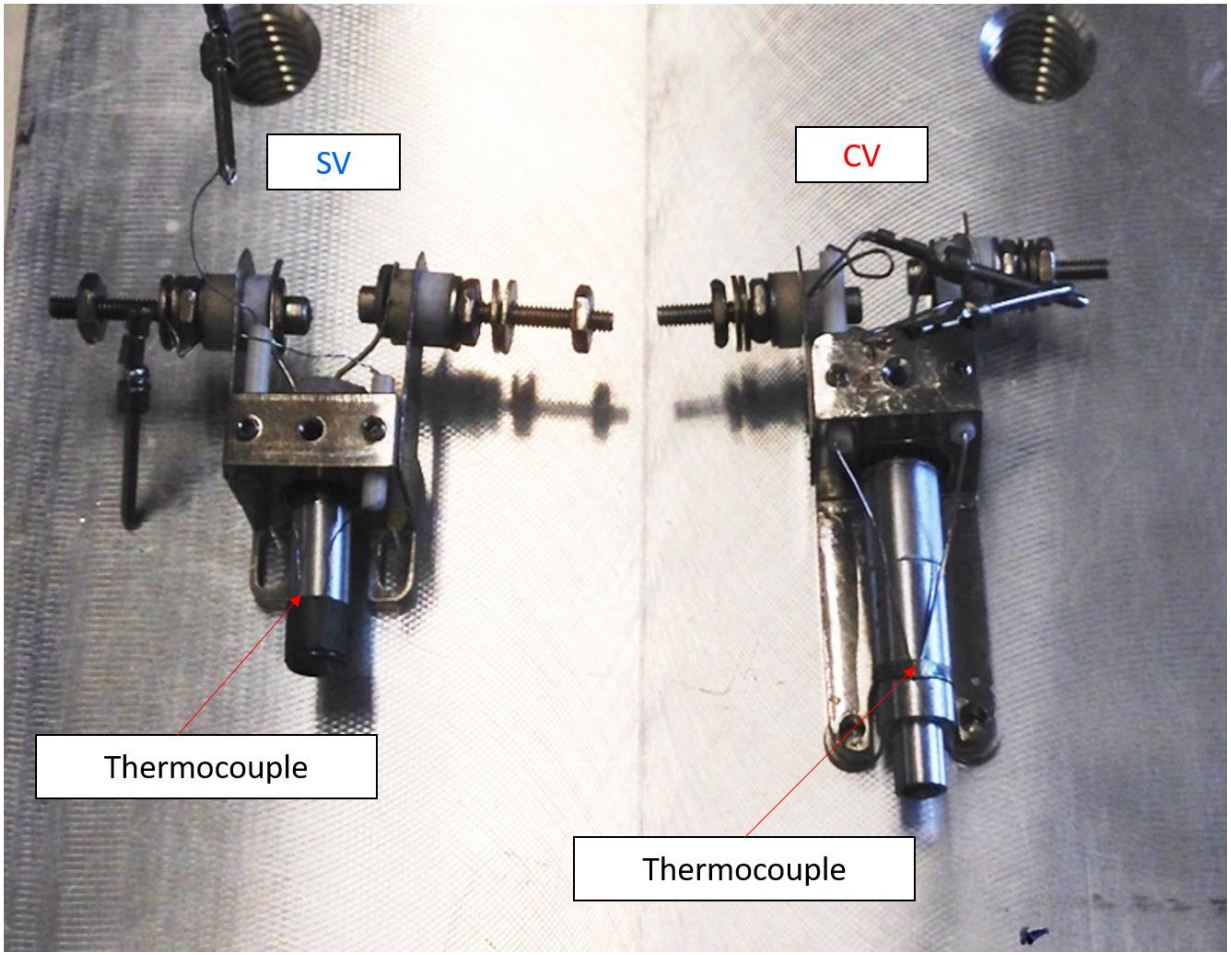
Standard vaporizer temperature (T_v): 600°C

Collection efficiency (CE) depends on : **Chemical composition\ Aerosol phase etc**

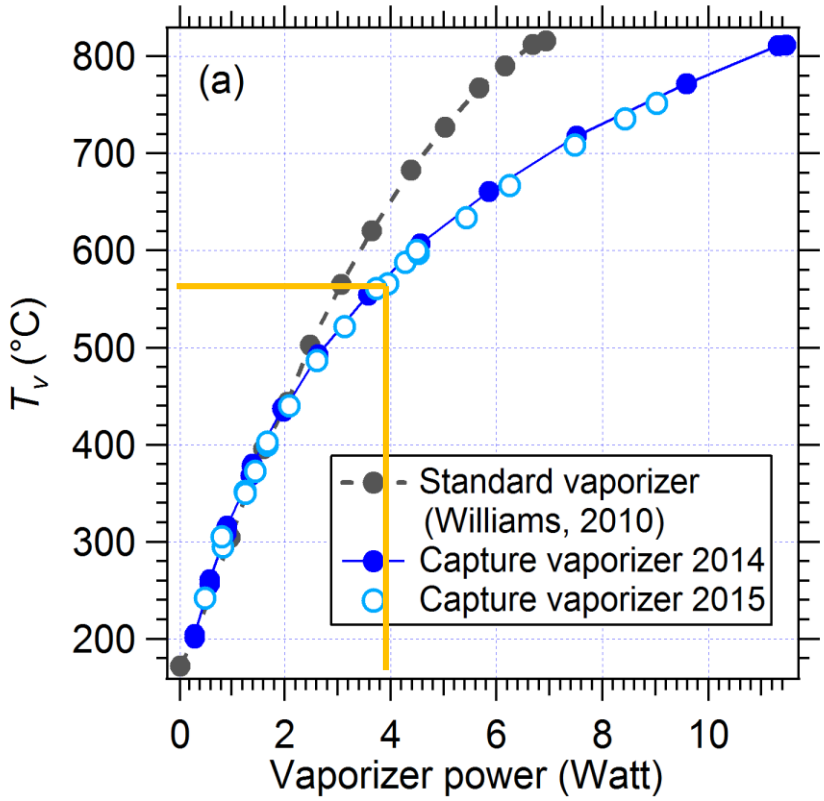
- ✓ Typically contribute the most uncertainty for ambient aerosol measurement
- ✓ AMS quantification uncertainty 30-40% of ambient aerosols.

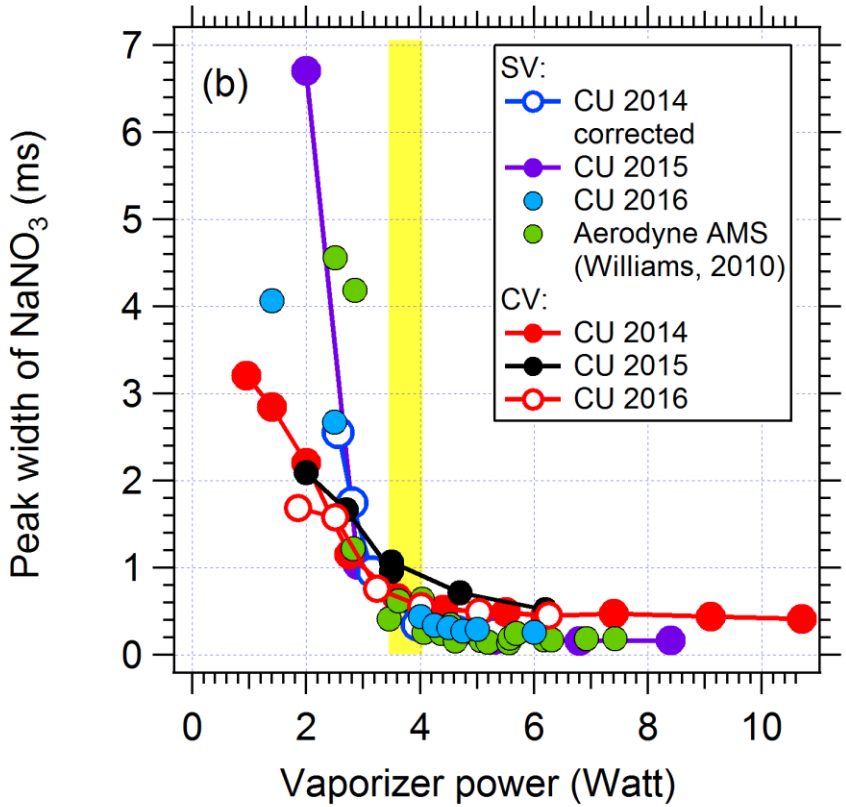
Middlebrook et al., AST, 2012; Bahreini et al. 2009

Outlook of SV and CV



Temperature measurement for CV



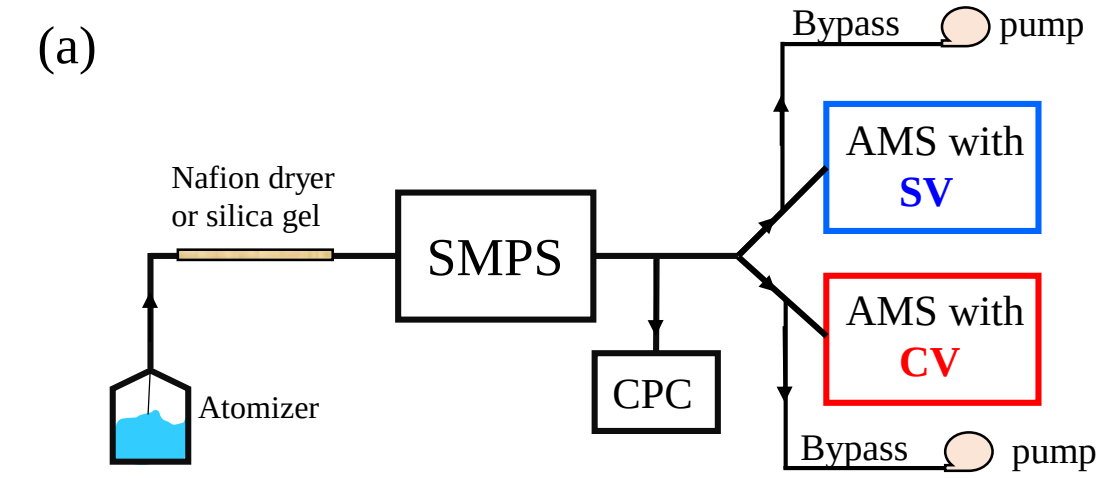


Leah William. 2010: http://cires1.colorado.edu/jimenez-group/UsrMtgs/UsersMtg11/WilliamsAMSUsersMtg_2010_VapT.pdf

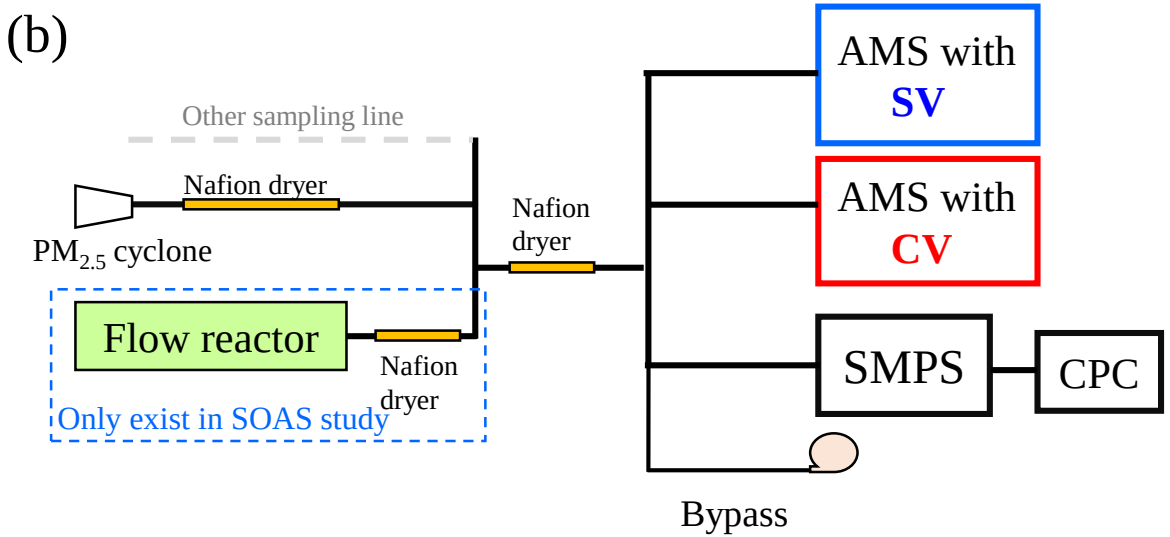
Hu et al., AMT. 2017

Experiment setup：

Lab



Ambient



Lab Ambient

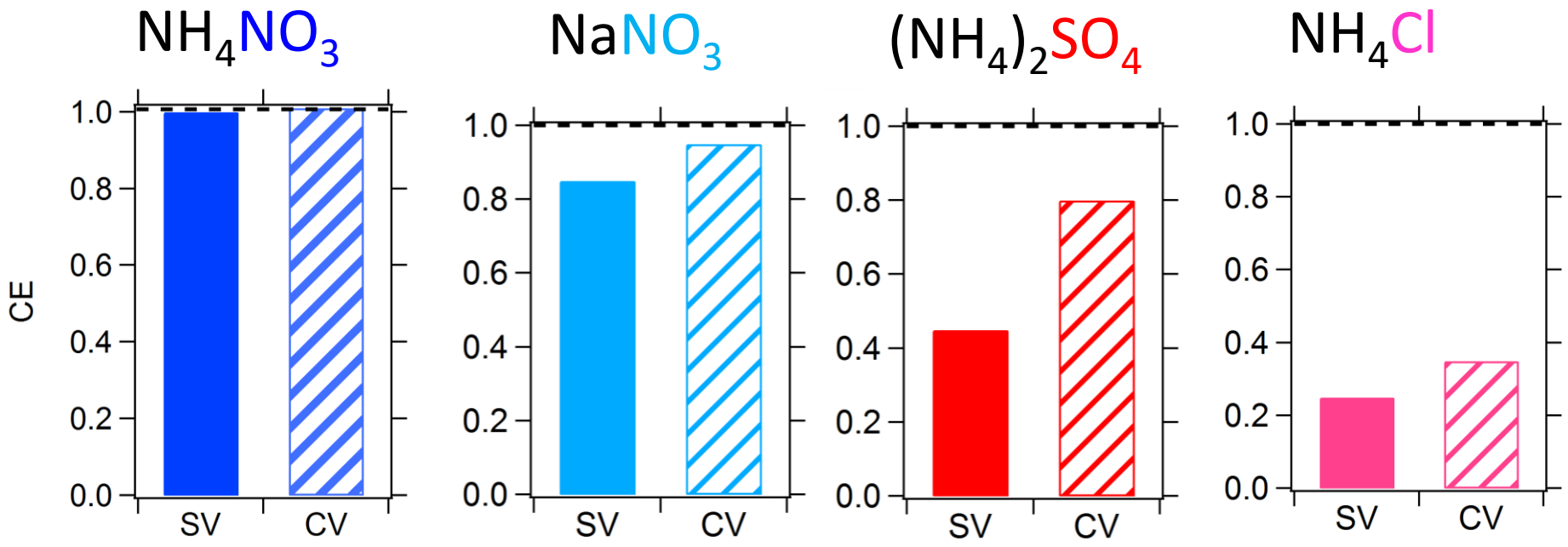
Outline

- Does capture vaporizer make CE~1 ?
- Does the capture vaporizer preserve or diminish the chemical and physical information from AMS?
  - Fragmentation and OA source identification?
  - Size distribution
  - Gas-phase $CO_2(g)$ and artifact chloride formation in CV
- Pros and cons of SV vs CV

Lab

CE of standard inorganic species

CE=AMS/CPC mass ratio

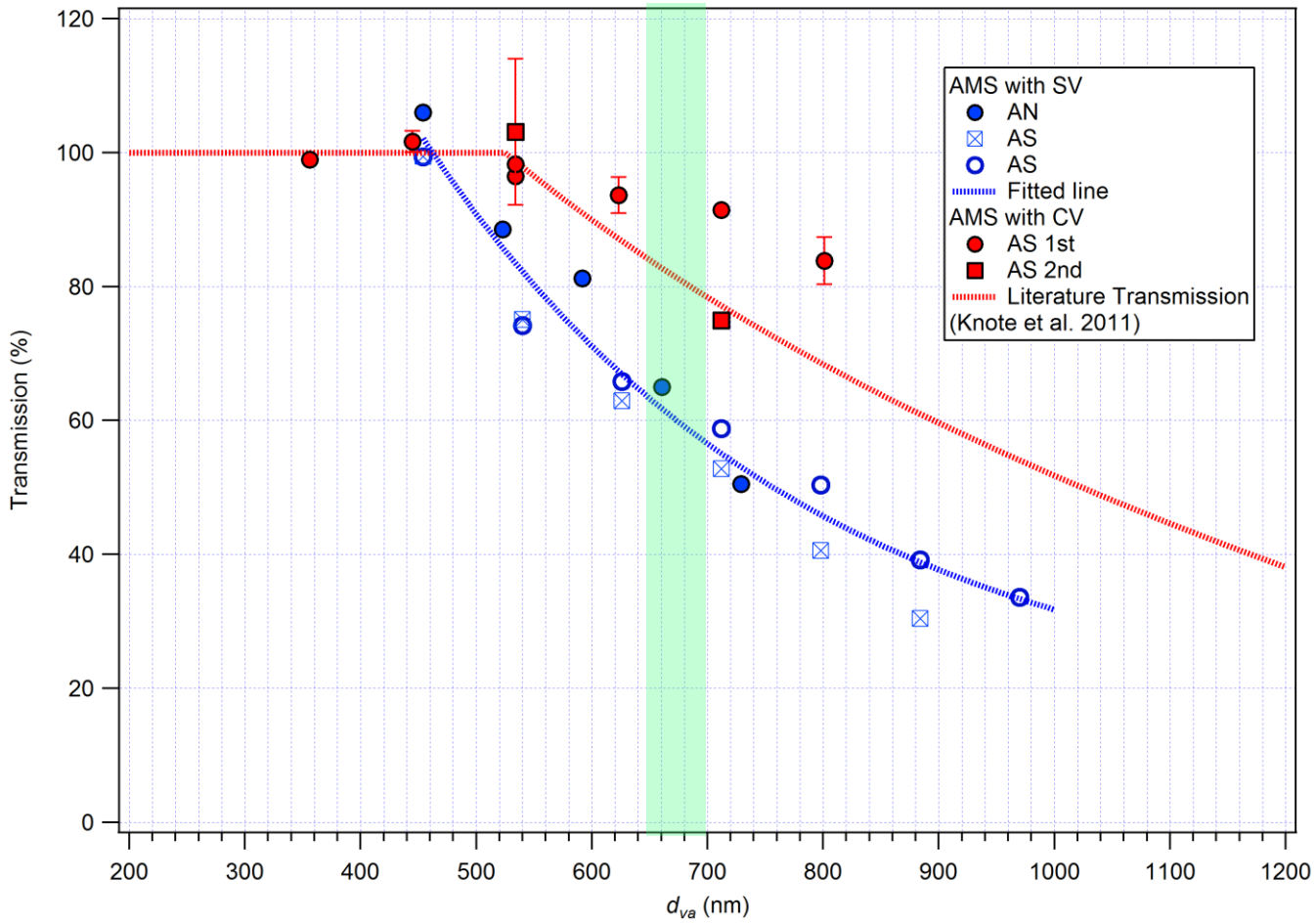


An improvement in CE of inorganic species in the CV

Shown results are carried out under medium vaporizer temperature 500-600C

Hu et al., AMT. 2017

Lens transimission corrections for $NaNO_3$
d_m=300nm→d_{va}=670 nm



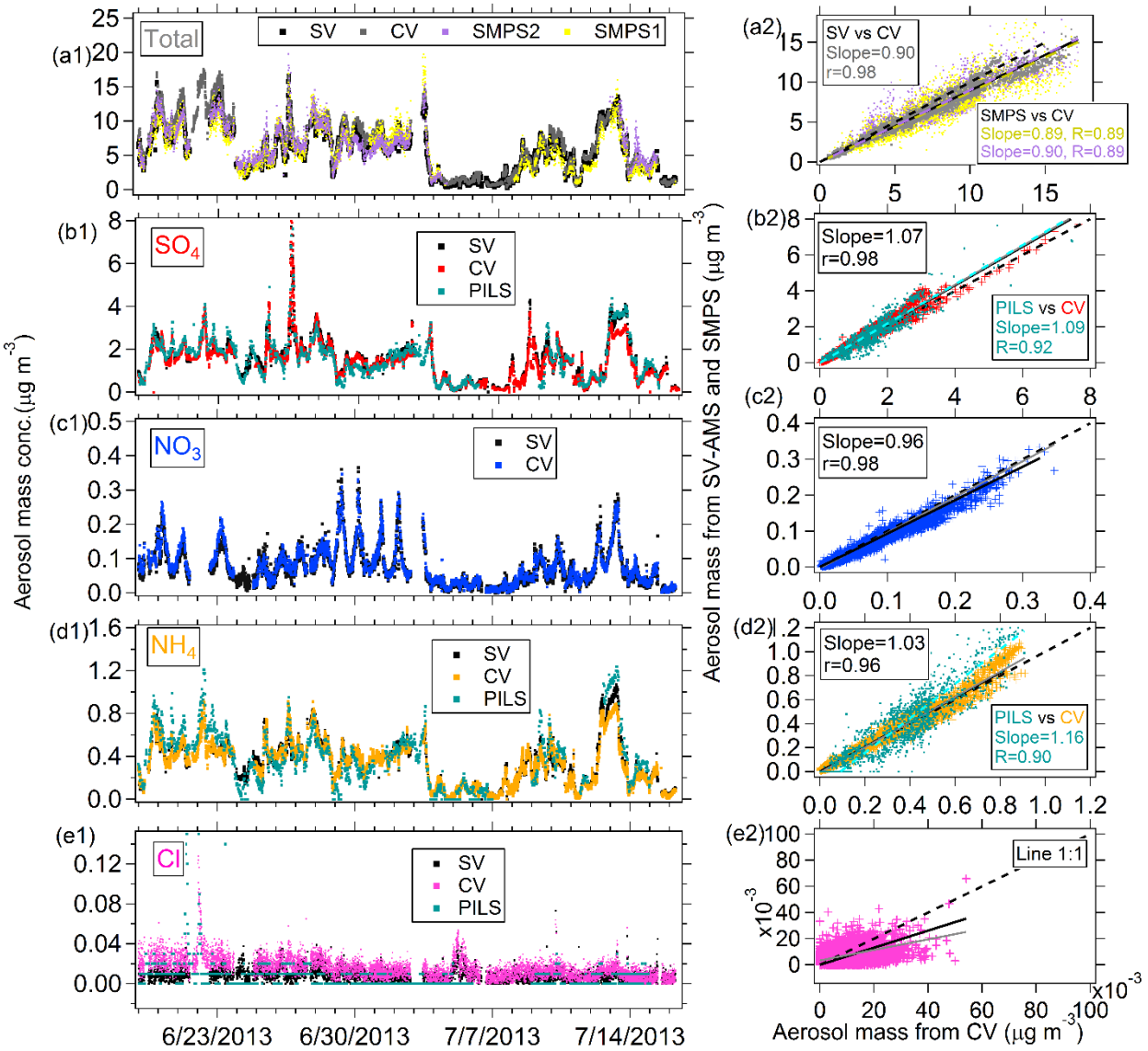
Hu et al., AMT 2017

Ambient

CE of ambient aerosols

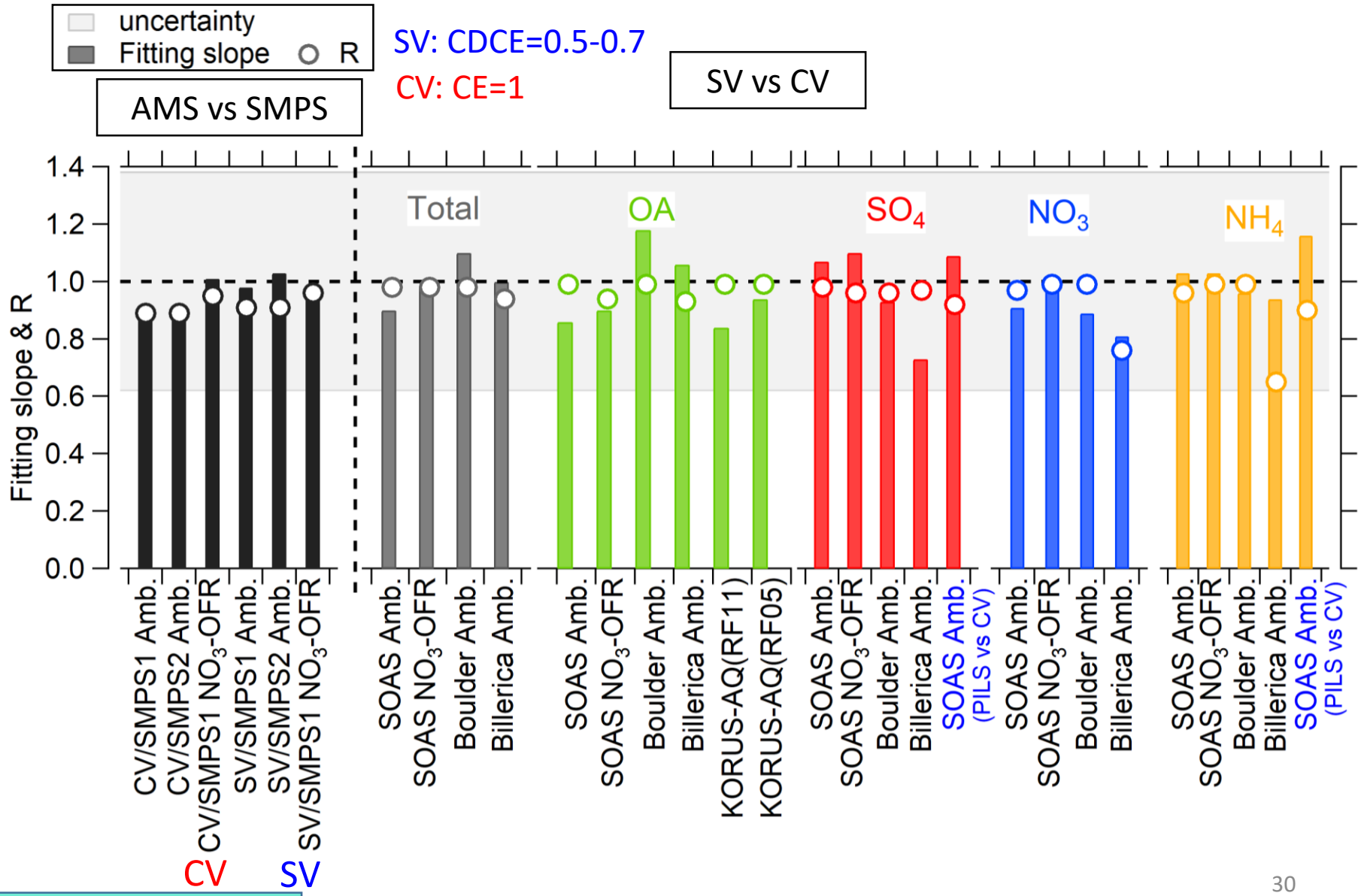
SV: CE: 0.5-0.7

CV: CE=1



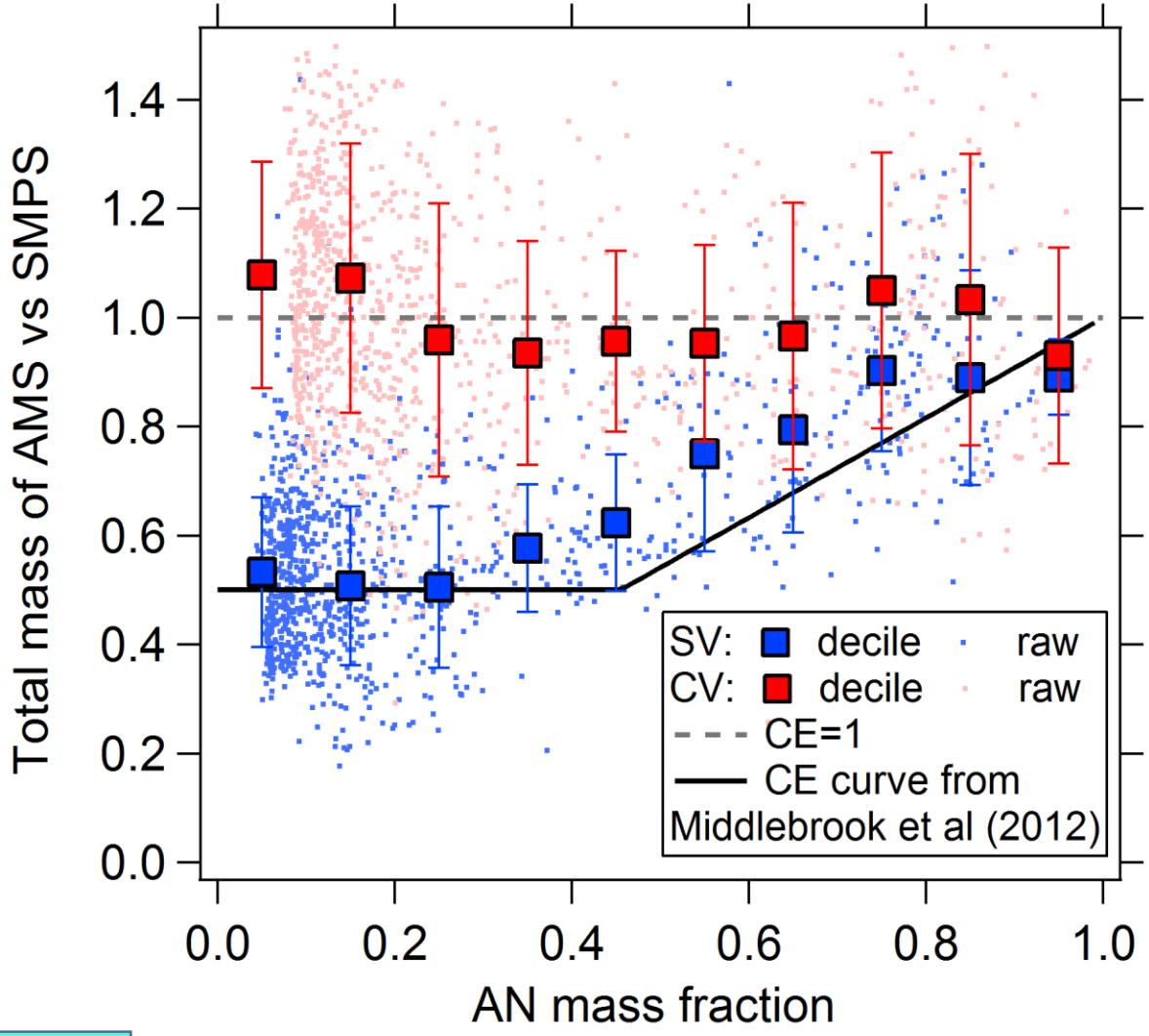
Hu et al., AS&T. 2017

Multiple results support **ambient** CE in CV =1



Hu et al., AS&T, 2017

Evaluation on chemical composition CE correction



Hu et al AST 2017

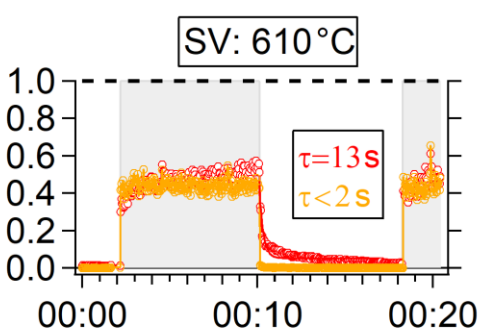
RIE between SV versus CV

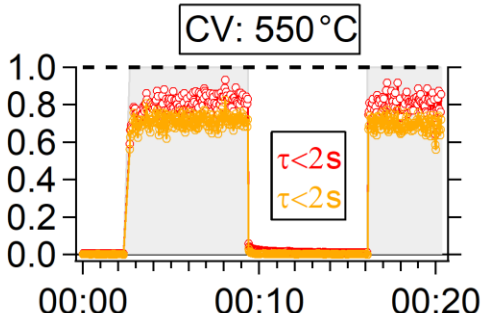
	SV	CV	
NO3	1.1	1.1	Default
NH4	3-6 (3-15 for ToF-ACSM)	3-6	Experimental measured (NH_4NO_3)
SO4	1.1-1.3	1.1-2.4	Experimental measured ($(NH_4)_2SO_4$)
chloride	1.3	1.4	Experimental measured (NH_4Cl)
OA	?	?	

Hu et al AST 2017; Hu et al AMT 2017;Xu et al. AS&T 2018

Brief reasons for different RIE

- **More masses collected**
- Faster decay
- Different ionization precursors from thermal decomposition (SV: $H_2SO_{4(g)}/SO_{2(g)}/SO_{(g)}$ **vs** CV: $SO_{(g)}/SO_{2(g)}$)
- Other possible reasons





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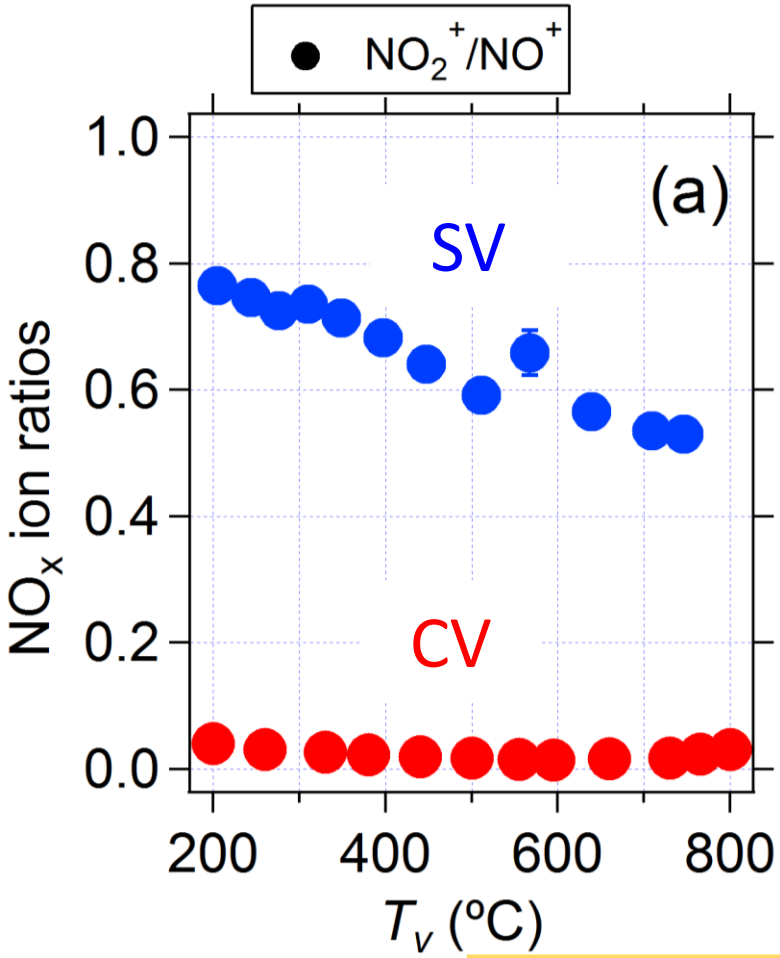
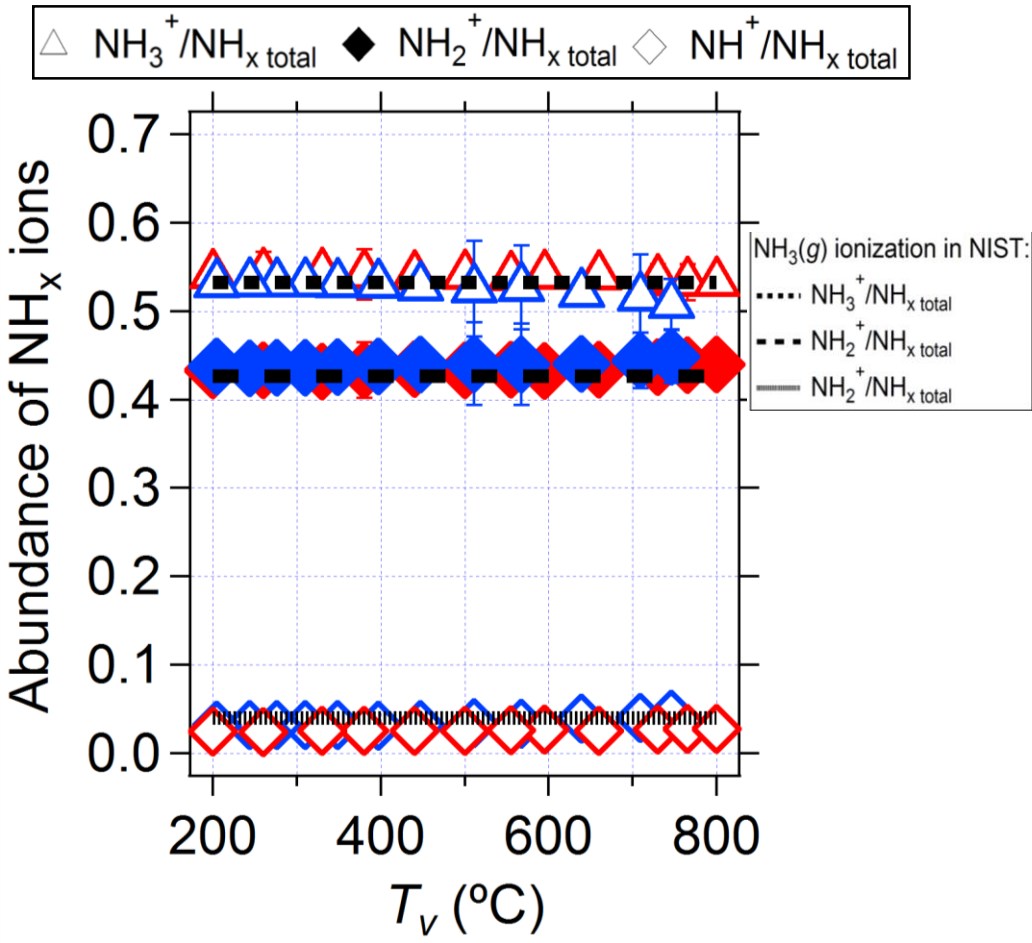
Lab

Fragmentation pattern of inorganic NH_4NO_3

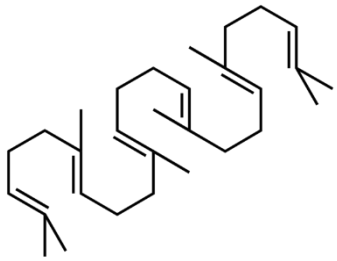




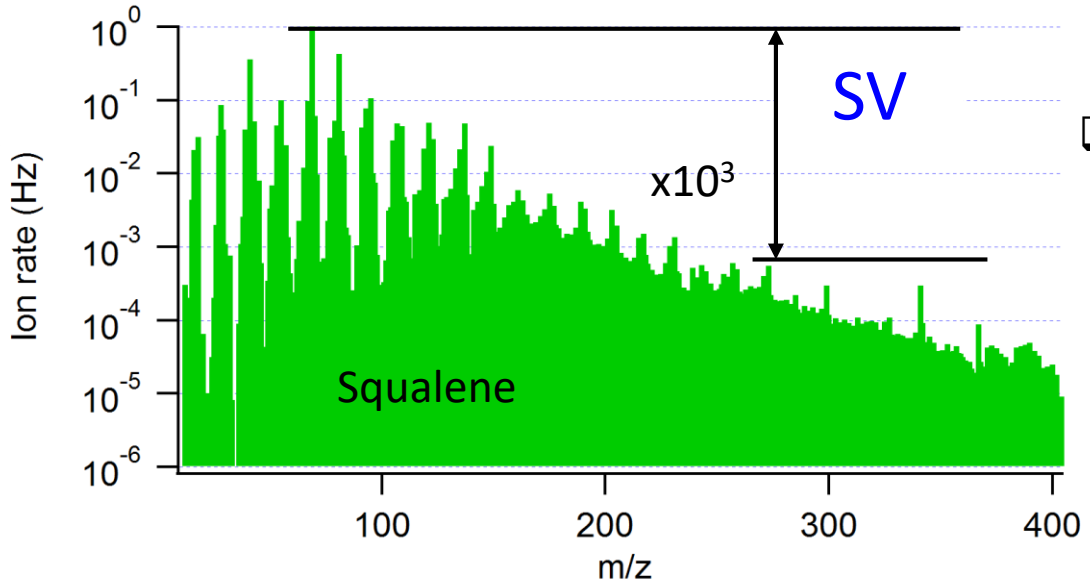
Inorganic does not evaporate as intact salts E.g., $NH_4NO_3(s) \rightarrow NH_4NO_3(g)$
but go through thermal decomposition.
E.g., $NH_4NO_3(s) \rightarrow NH_3(g)+HNO_3(g)$; $HNO_3(g) \rightarrow NO_2(g)+H_2O(g)+O_2(g)$
(Drewnick et al., 2015)

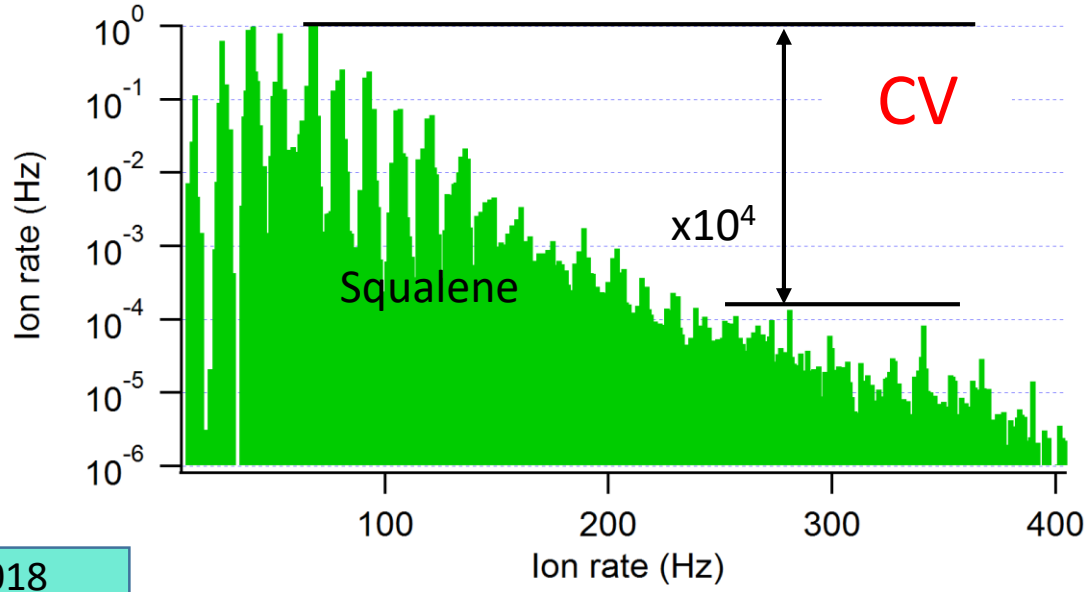
Hu et al., AMT. 2017

Fragmentation pattern of organic species



$C_{30}H_{50}$
Squalene





- the larger molecular-weight fragments of OA tend to shift toward smaller ions in the CV due to additional thermal decomposition.

Hu et al., AST 2018

Lab

Fragmentation pattern of organic species

$C_xH_y^+$
$C_xH_yO^+$
$C_xH_yO_2^+$

Squalene ($C_{30}H_{50}$)

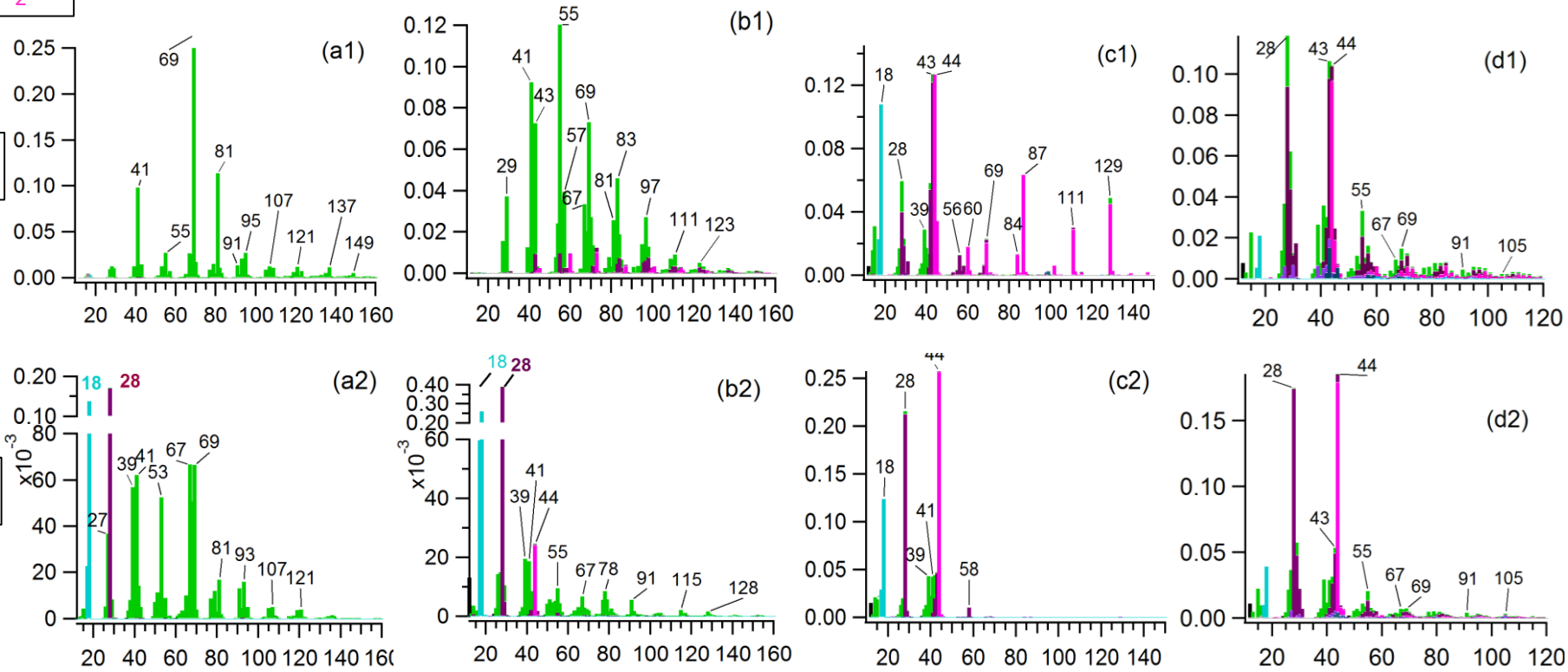
Oleic acid ($C_{18}H_{34}O_2$)

Citric acid ($C_6H_8O_7$)

Ambient OA (KORUS-AQ)

SV

CV

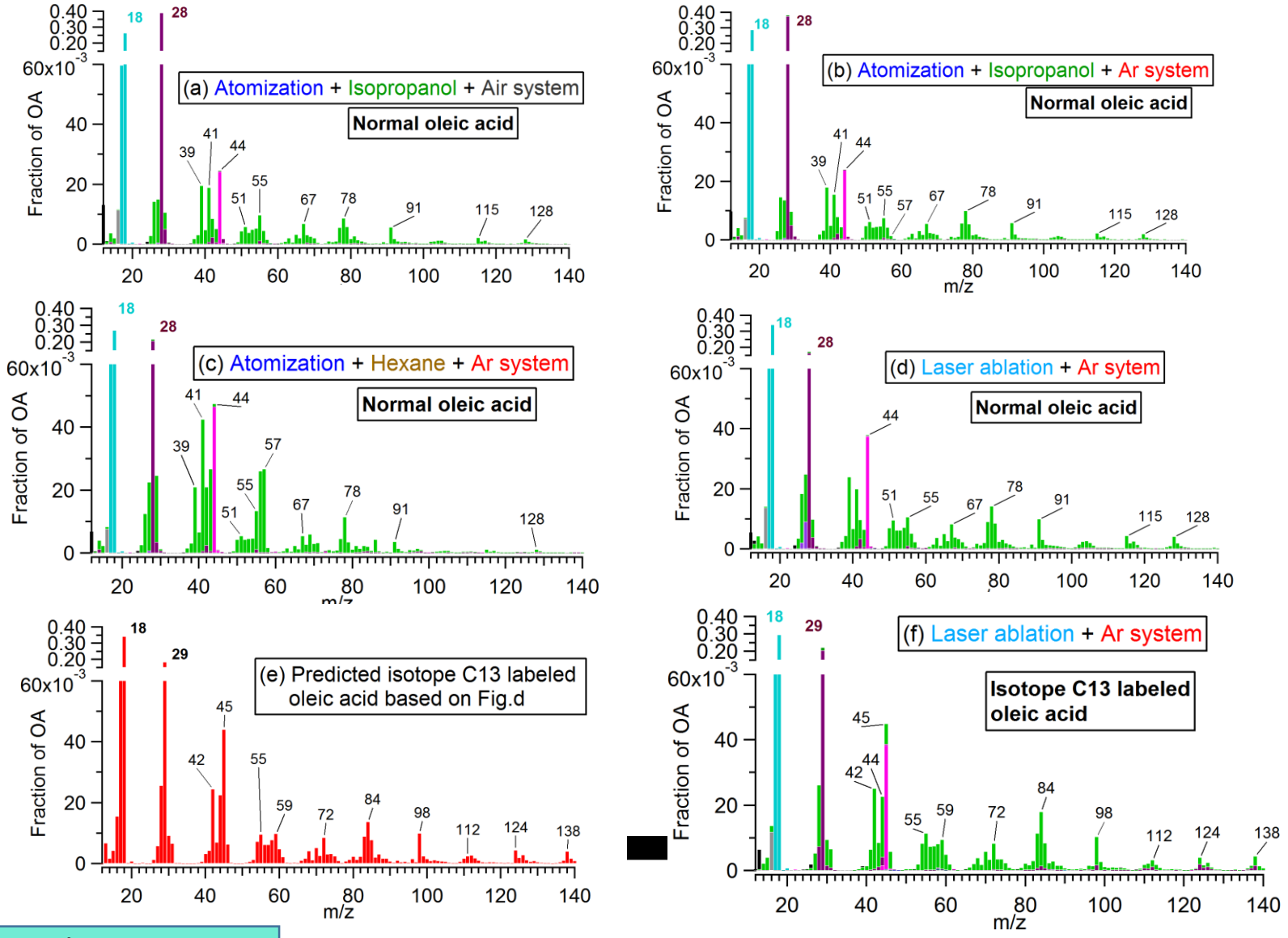


- This shifting happened independent of OA types and oxidation levels
- Excess CO^+ (H_2O^+ to a less extent) is observed when sampling long-chain alkene/alkane like species, not in highly oxidized and ambient OA
- Unexpected CO^+ (H_2O^+) ion formation might be caused by chemical reaction on the vaporizer surfaces.

Hu et al., AST. 2018

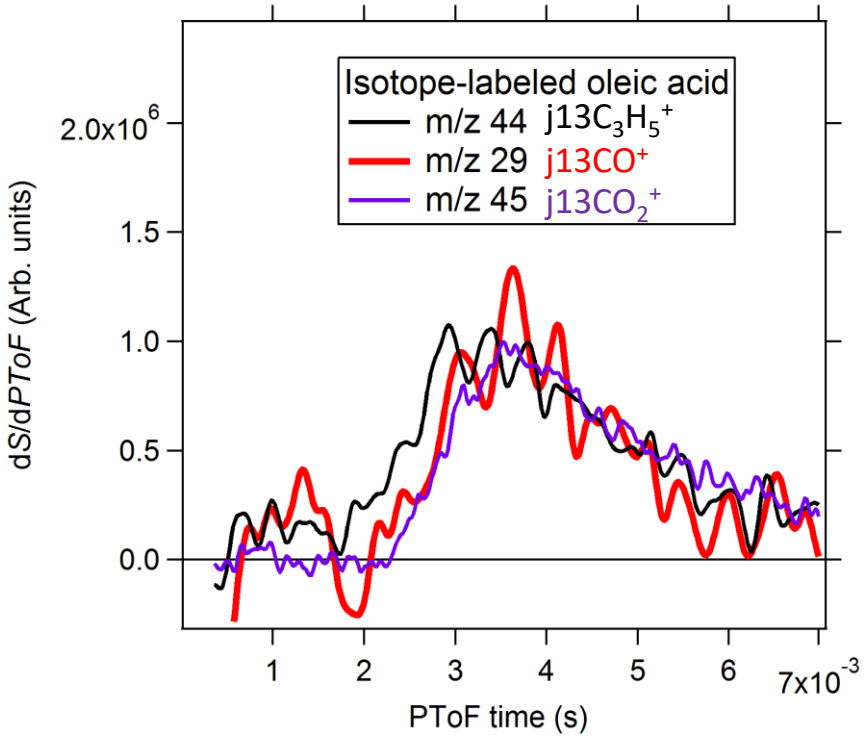
Lab

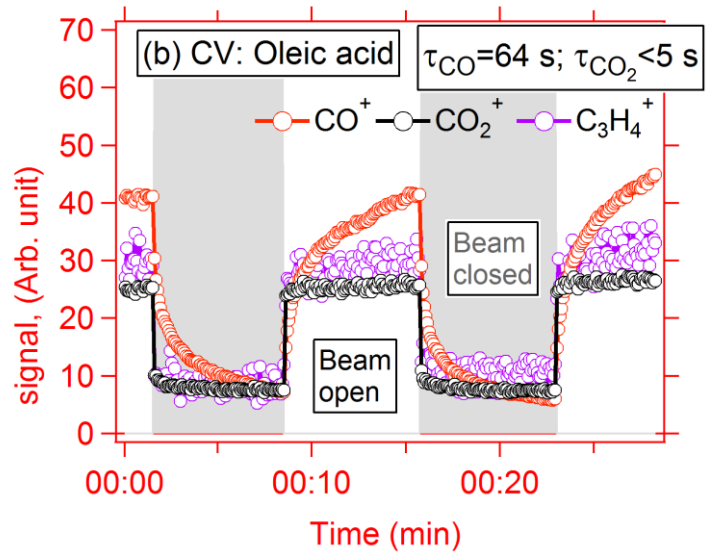
Excess H_2O^+ and CO^+ ions in the CV

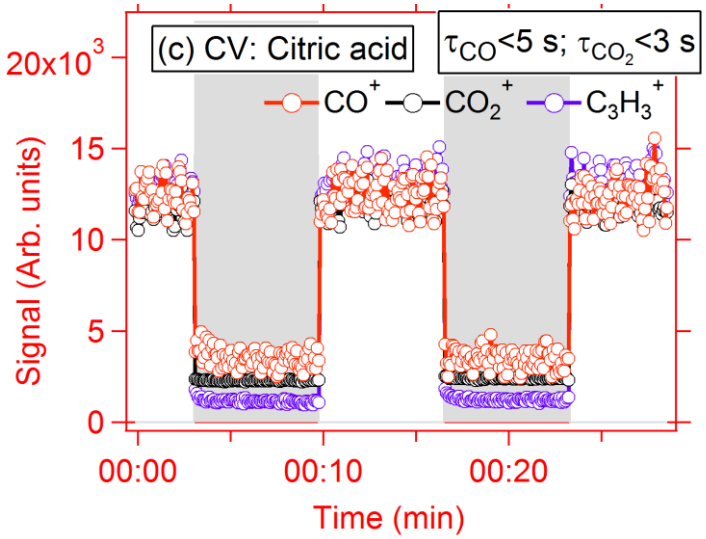


Hu et al., AST. 2018

PToF show CO peak similar with aerosol phase







- Unexpected CO^+ (H_2O^+) ion formation might be caused by catalytic reaction on the vaporizer surfaces.

Hu et al., AST. 2018

Causes for artifact CO enhancement

$Mo + 3/2\ O_2 \rightarrow MoO_3$

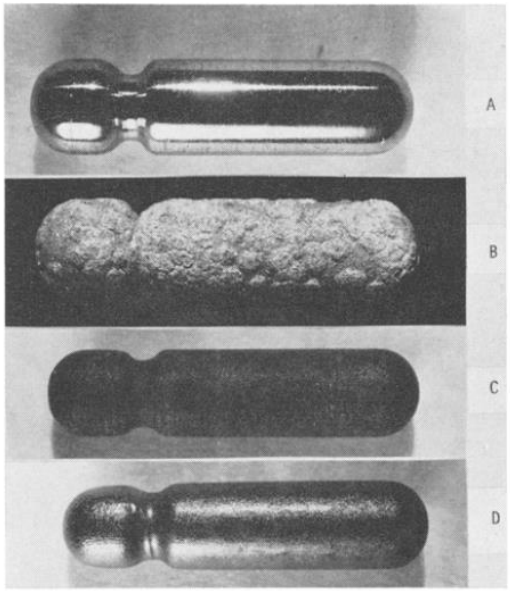
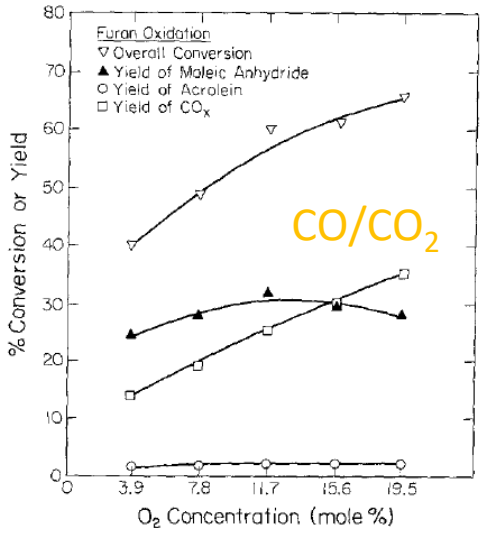


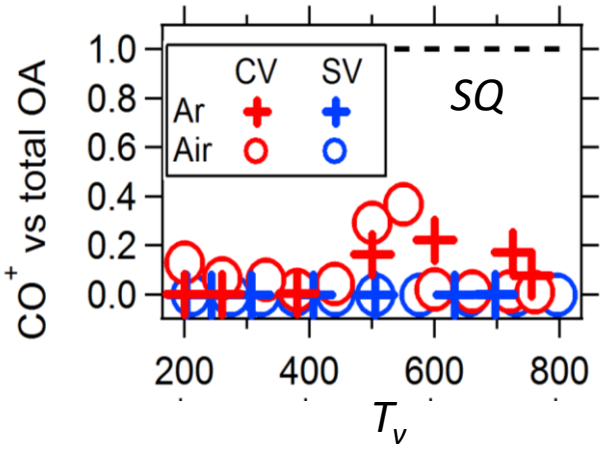
Fig. 2. Photographs of molybdenum specimens: A, unreacted; B, 600°C; 76 Torr, 420 min; C, 1200°C, 76 Torr, 8½ min; D, 1600°C, 76 Torr, 7 min. Magnification, approximately 5X.

Class	Reaction conditions	Oxidation phenomena
1	Below 450°C	Adherent oxide films or scales form.
2	500°-700°C	Oxide scales form also oxide volatilizes, low pressure favors volatility of oxide.
3	801°C to transition temperature	Liquid oxide can form, volatilizes as soon as oxide forms.
4	Above transition temperature	Oxide volatilizes as fast as it forms.



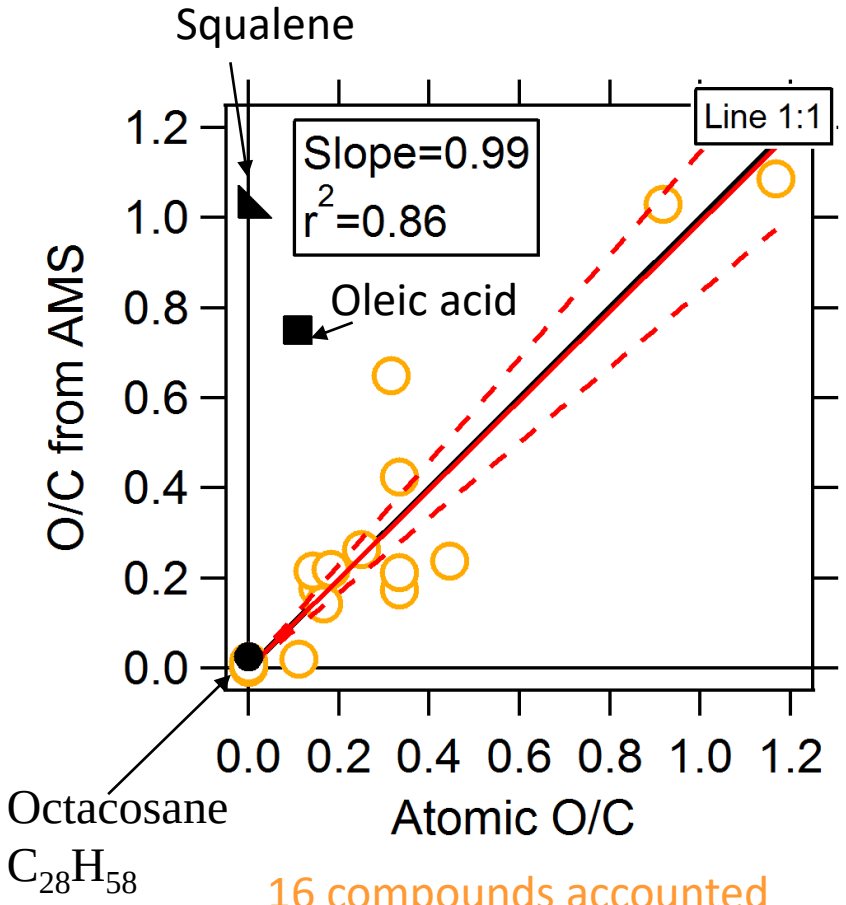
Ozkan et al., 1990

Gulbransen et al. 1963

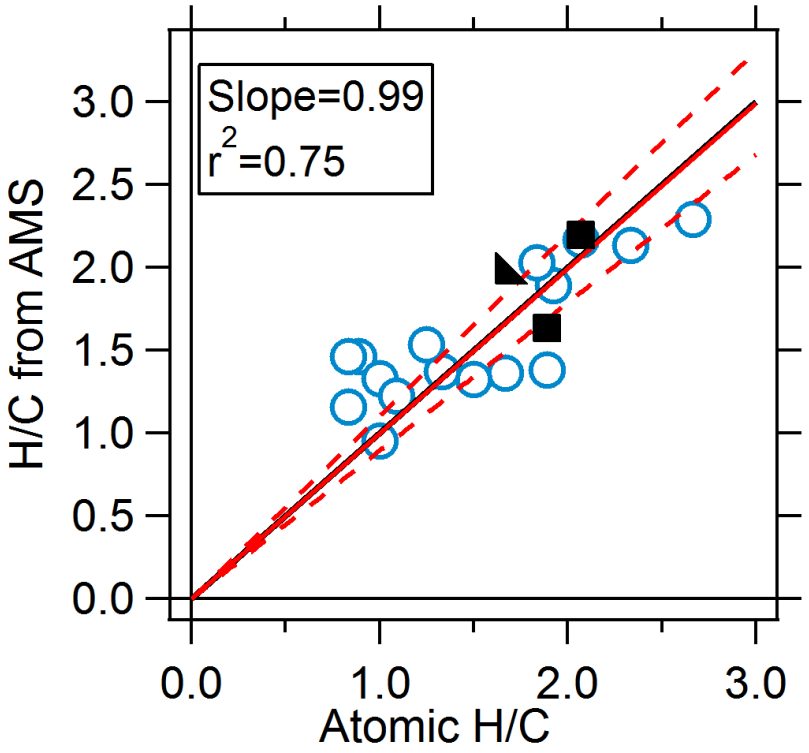


Hu et al., AST 2018

Elemental ratio calibration: standard species



16 compounds accounted



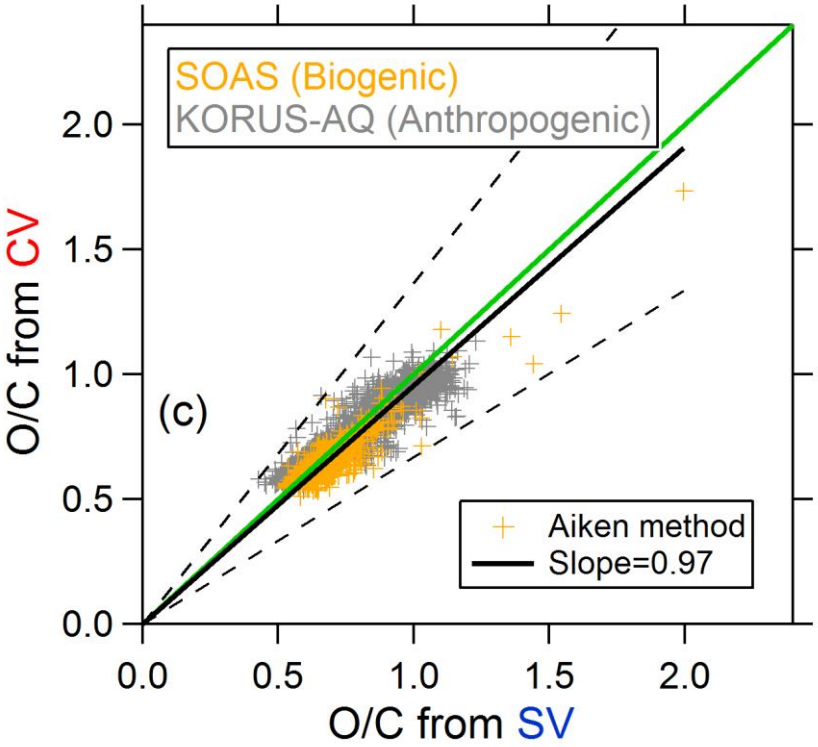
- Aiken explicit calibration method (Aiken et al. 2007;2008)

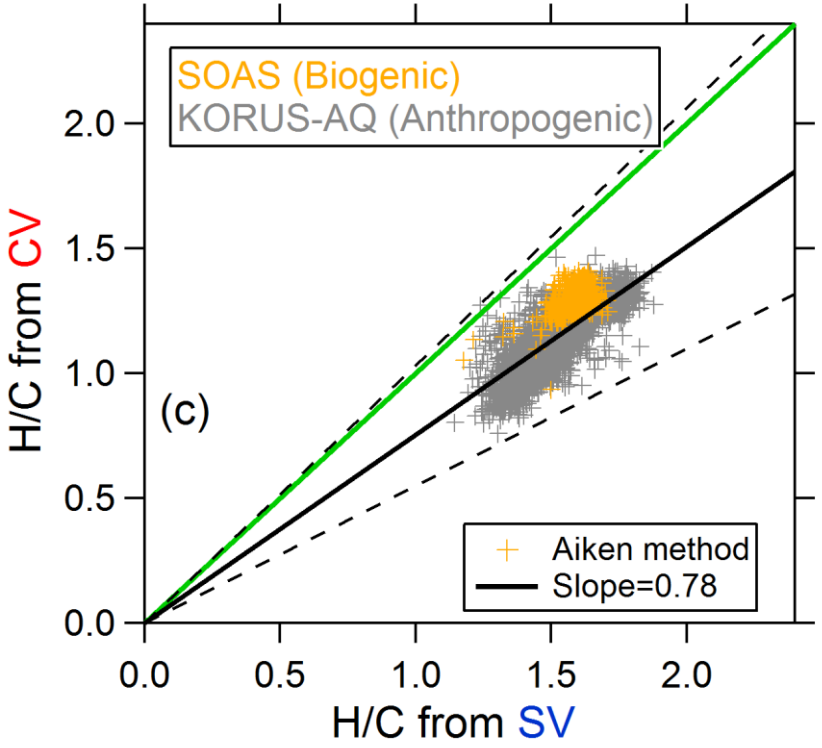
Hu et al., ACS ES&C. 2018

Ambient

Elemental ratio comparison: ambient OA

Aiken ambient method for CV: CO^+/CO_2^+=1; H_2O^+/CO_2^+=0.225; IA method for SV





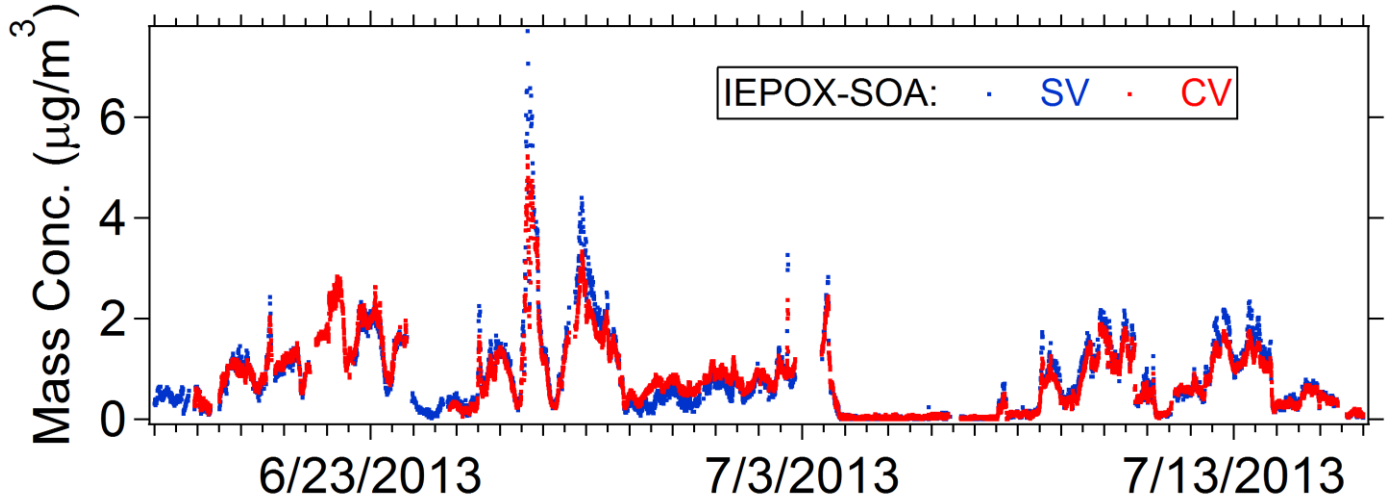
- The elemental composition of ambient OA can be accurately measured with the CV, with suitable modifications to the quantification procedure.

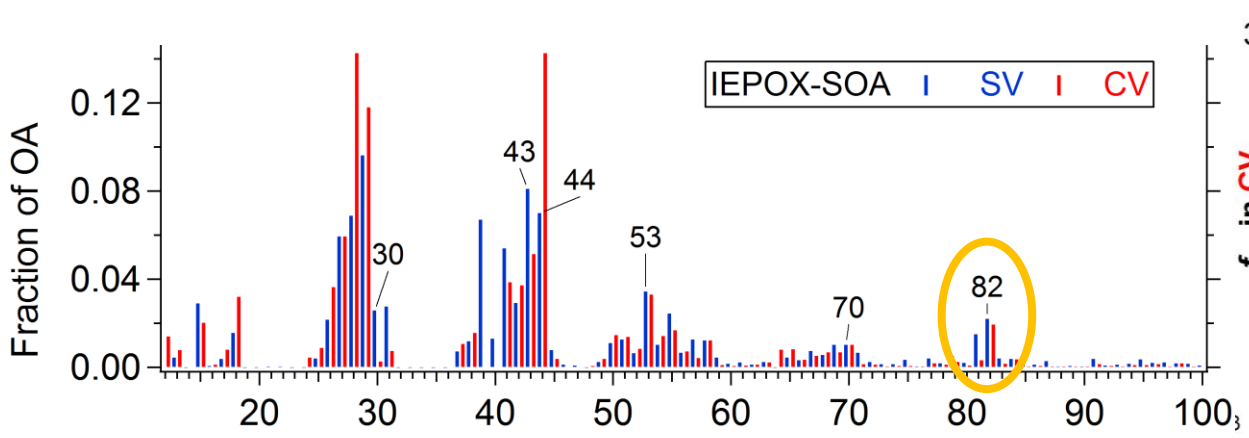
Hu et al., ACS ES&C. 2018

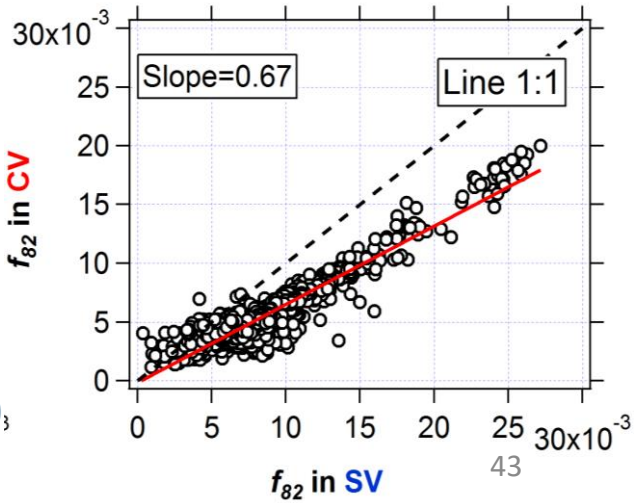
Ambient

Similar PMF results for SV vs CV

IEPOX-SOA: Isoprene epoxydiols-derived SOA







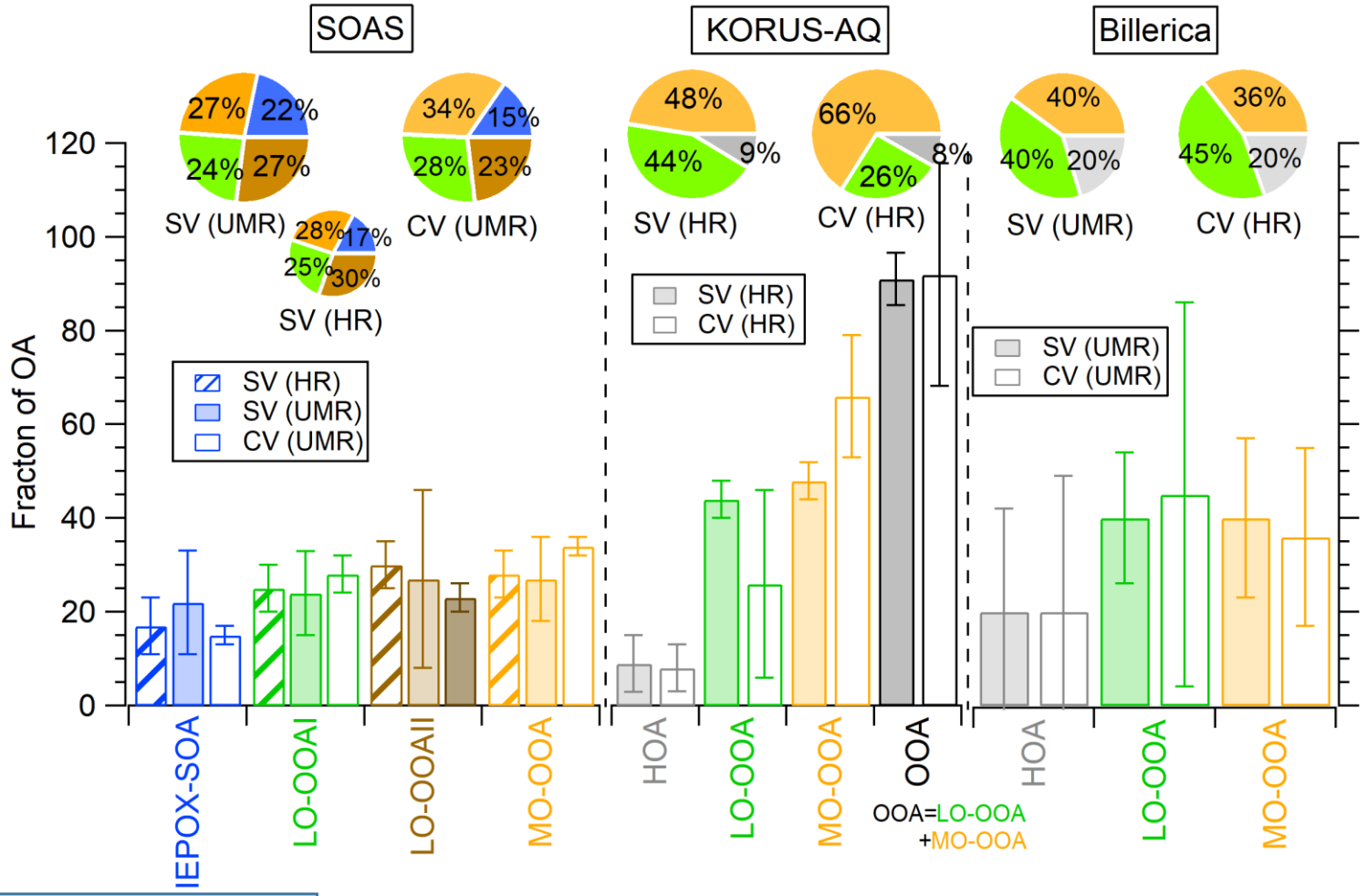
Hu et al., ACS ES&C. 2018

Summary of PMF comparison

Biogenic emission dominated. SE US forest

Aircraft urban + aged regional plumes. South Korean

Suburban site, Boston



Hu et al., ACS ES&C. 2018

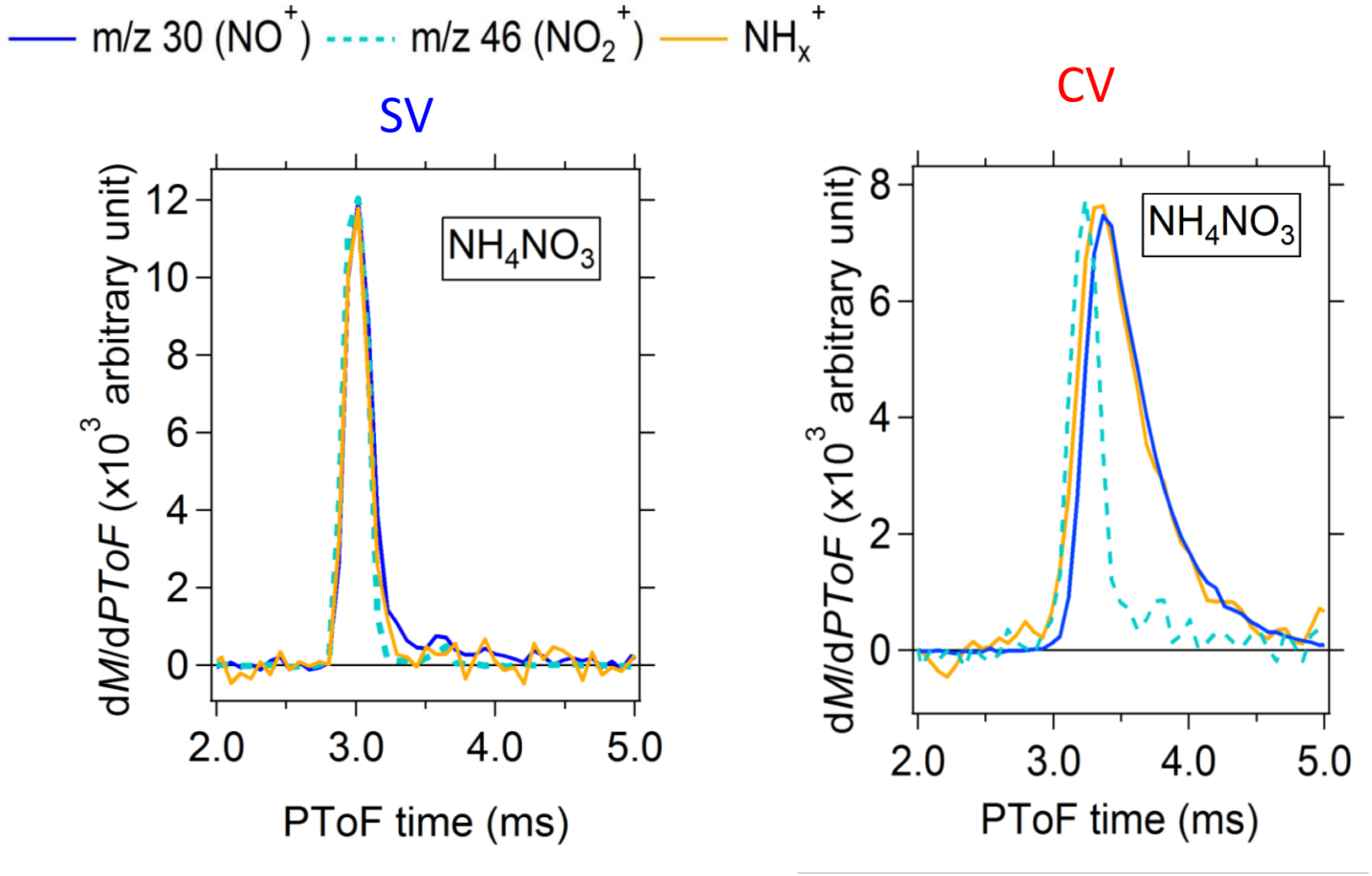
Lab Ambient

Outline

- Does capture vaporizer make CE~1 ?
- Does the capture vaporizer preserve or diminish the chemical and physical information from AMS?
  - Fragmentation and OA source identification?
  - Size distribution
  - Gas-phase $CO_2(g)$ and artifact chloride formation in CV
- Pros and cons of SV vs CV

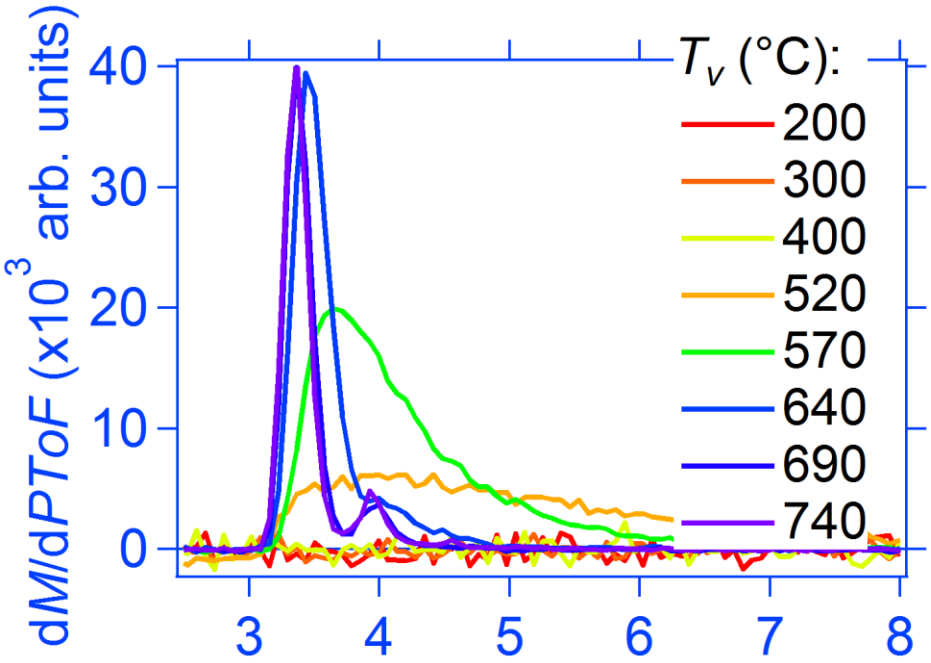
Degradation of size-resolved detection in CV

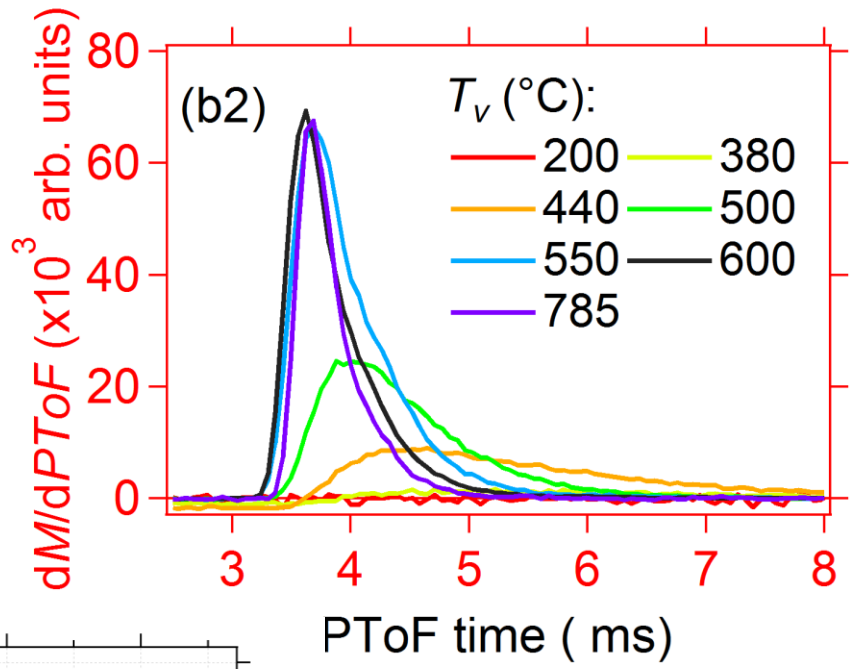
300 nm monodisperse particle NH_4NO_3

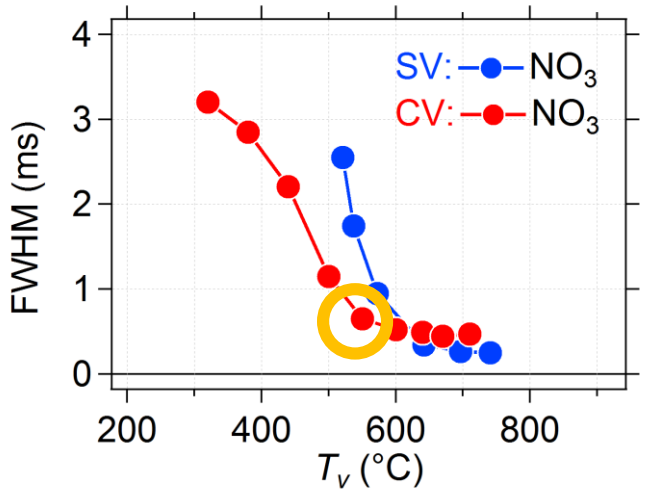


Hu et al., AMT. 2017

Temperature dependent size distribution

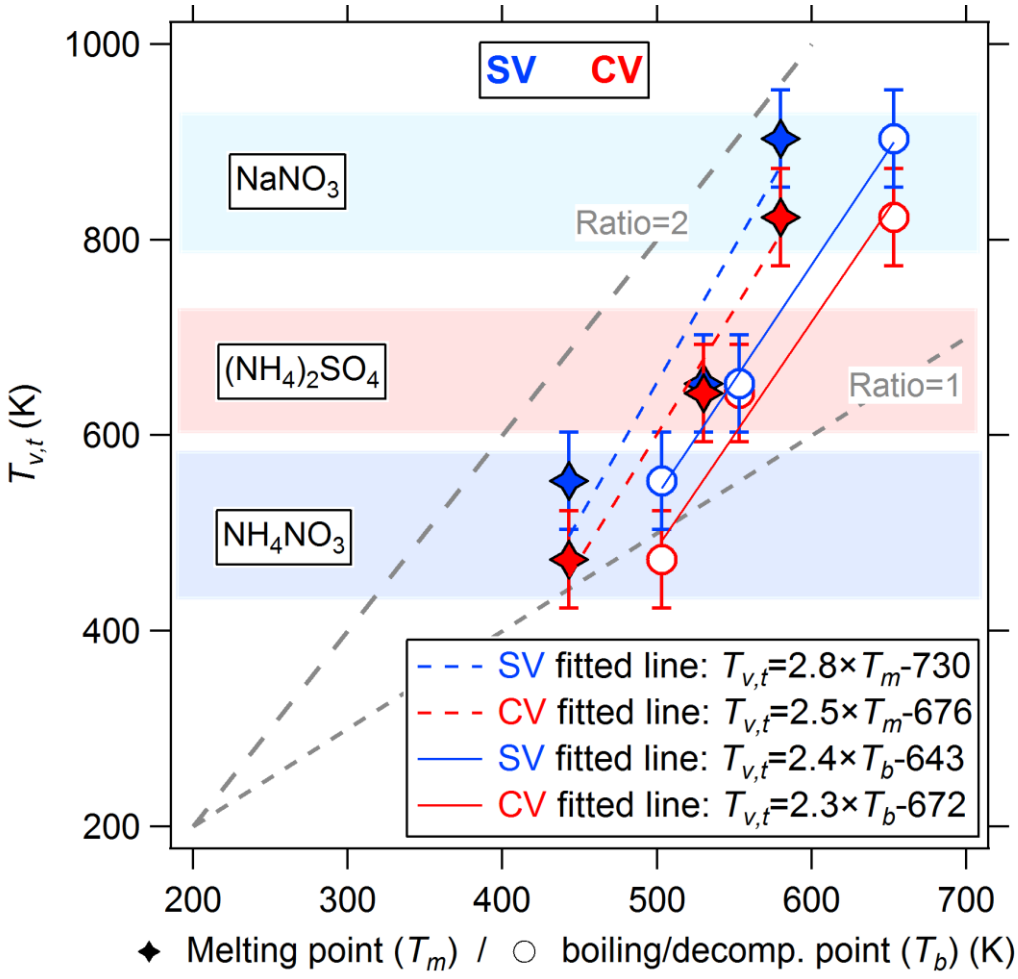






Hu et al., AMT. 2017

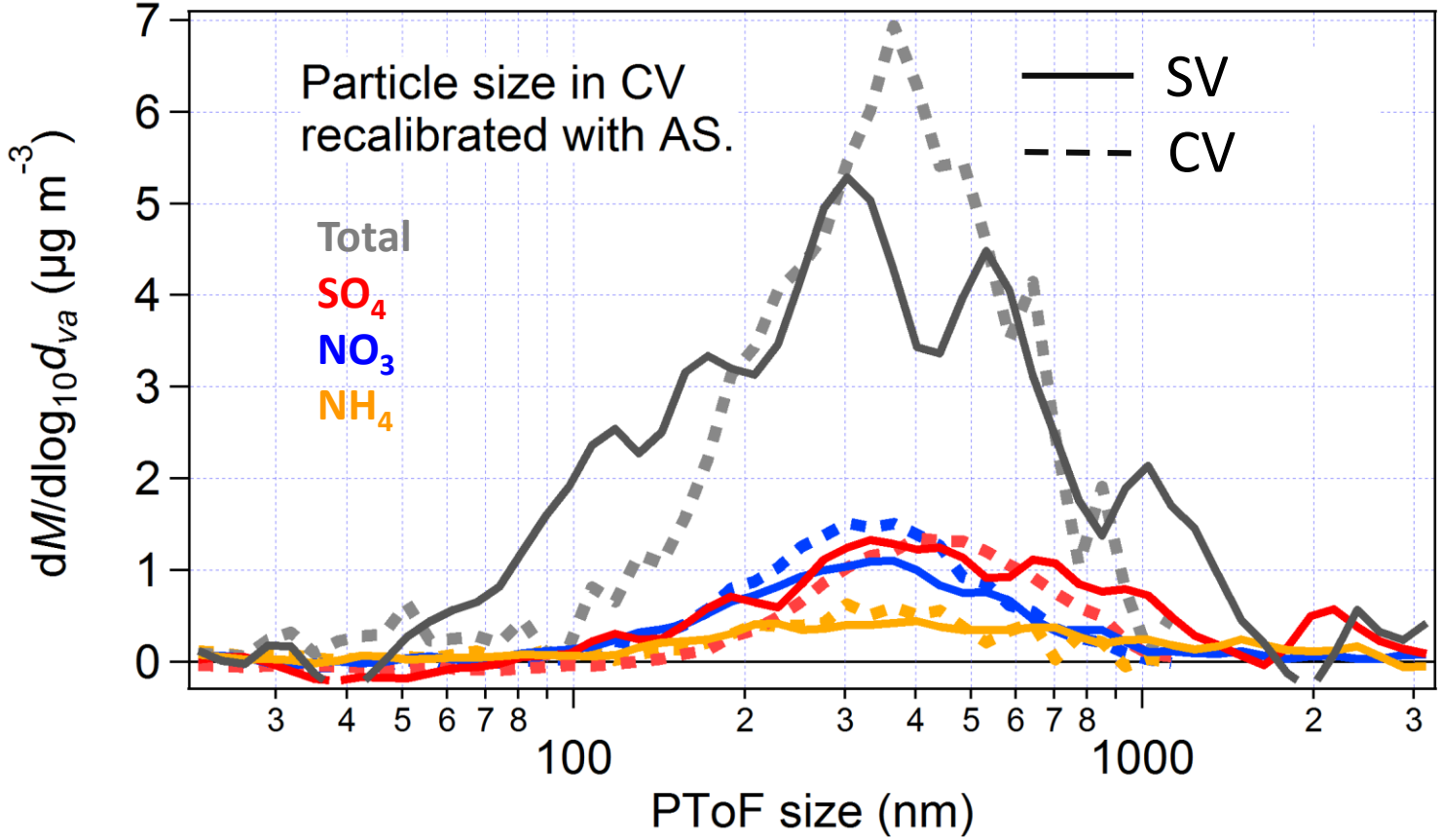
Estimating vaporizer temperature for detecting species in size mode



Hu et al., AMT. 2017

Ambient

Size distribution of ambient aerosol in CV still work



Hu et al., AST. 2017

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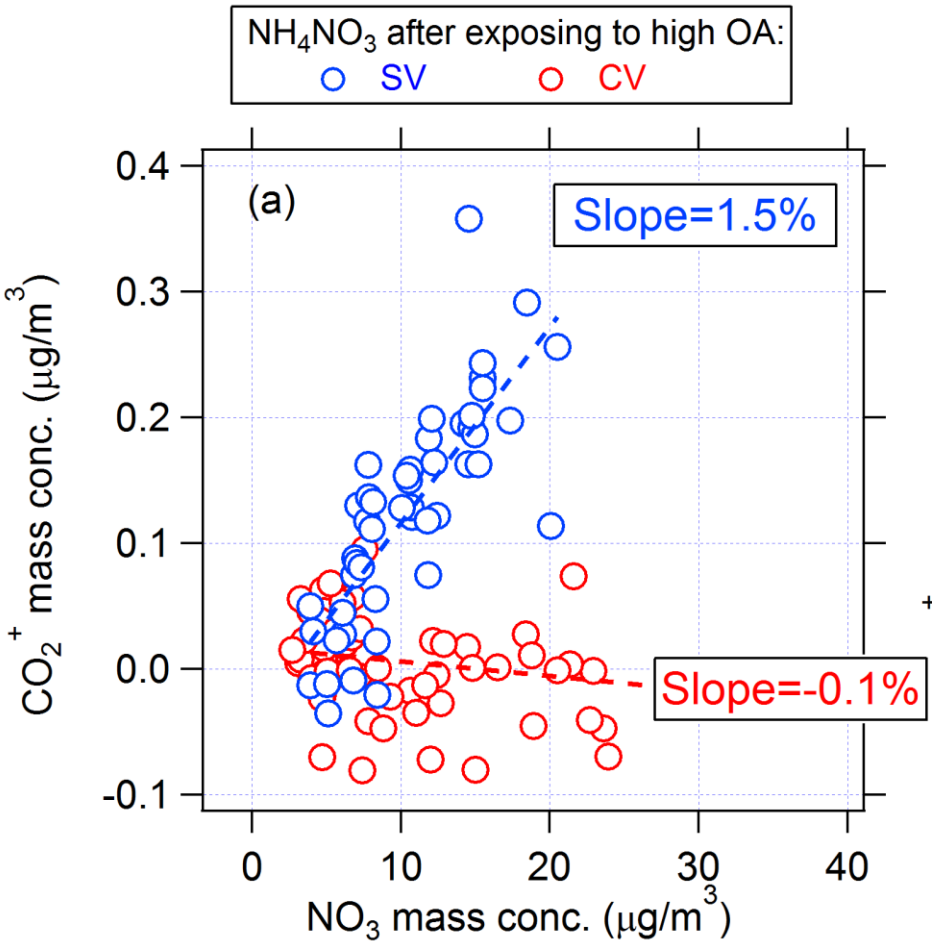
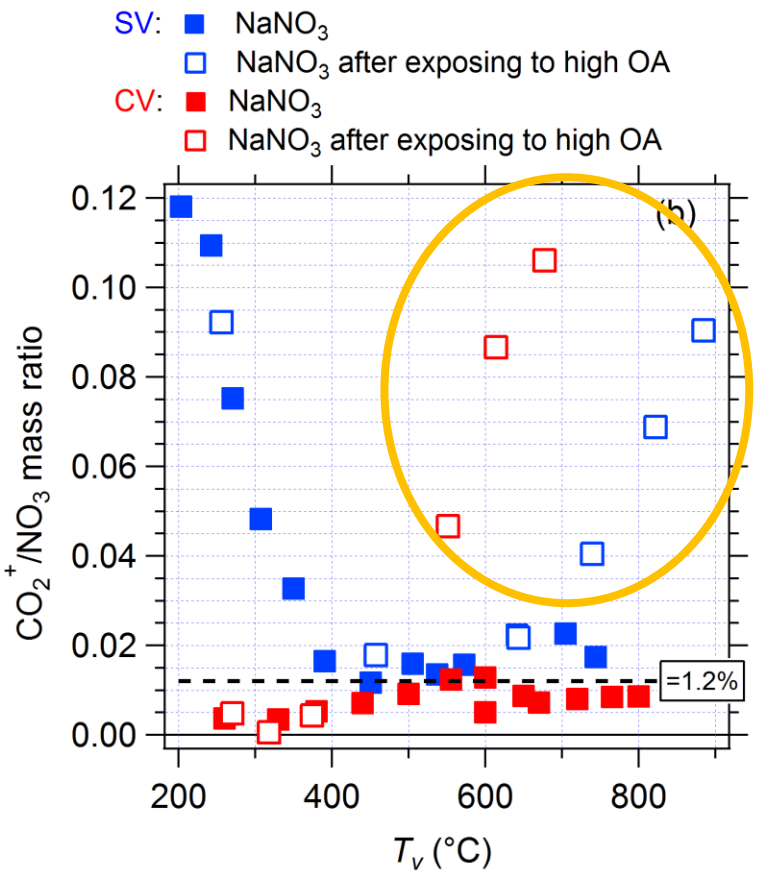
  - Size distribution
  - Gas-phase $CO_2(g)$ and artifact chloride formation in CV
- Pros and cons of SV vs CV

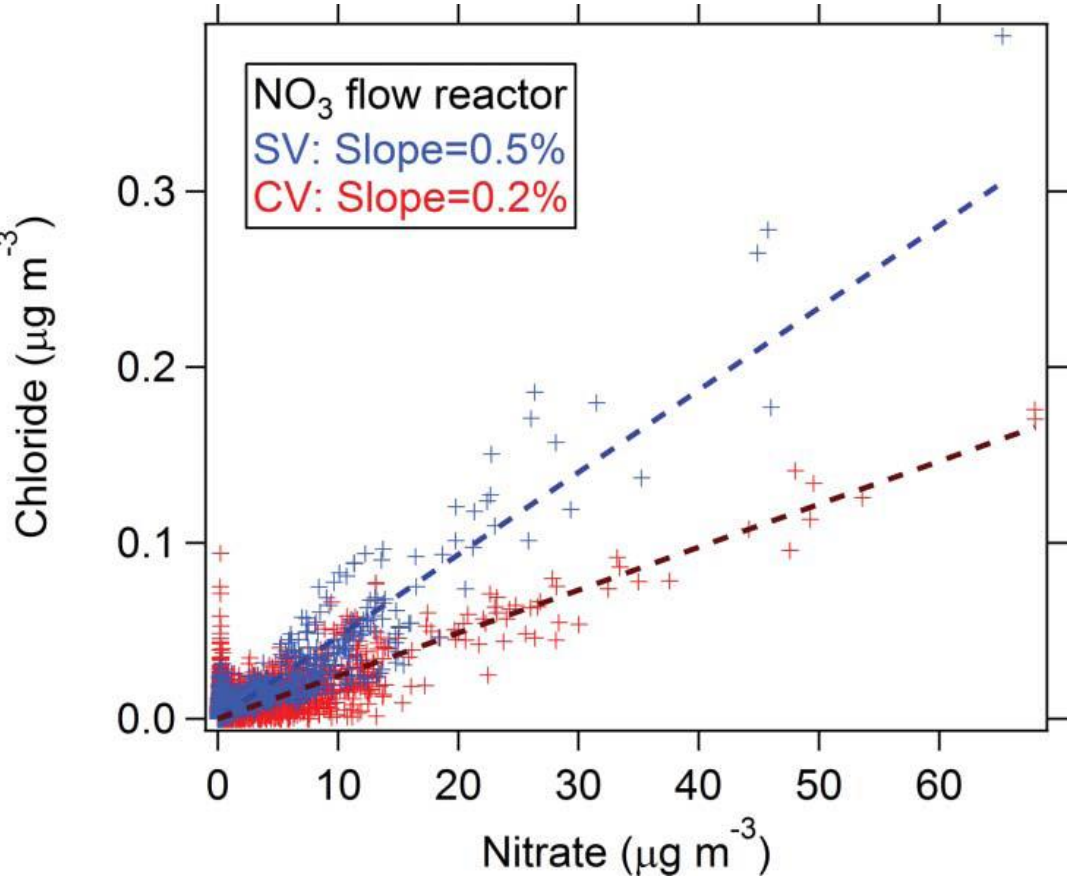
Production of $CO_2(g)$ is negligible for the CV for NH_4NO_3 and comparable to the SV for $NaNO_3$.





Hu et al., AMT 2017

Chloride artifact



$NaCl(s)+HNO_3(g) \rightarrow HCl(g)+NaNO_3(s)$ (Harkel 1997).

Hu et al., AMT. 2017

Excellent Acceptable Less desirable

	SV	CV
CE for ambient particles	Middlebrook et al. (2012)	CE=1
CE for pure inorganics in lab	Variable bounce fraction	<=1 but better than SV
Slowly evolving signals from bounced particles on colder ionizer surfaces	Significant	Nearly eliminated
Ambient size distribution	Good resolution	Sufficient resolution
Lab & Chamber size distribution	Good resolution	Low resolution for monodisperse particles
Single particle IE calibration	Routinely doable	Not yet demonstrated
CPC-based IE calibration	Routinely doable	Routinely doable
Extent of thermal decomposition	Significant	Greater than SV
Nitrate quantif. (organic vs. inorganic)	Useful even under low S/N	Less contrast and lower S/N
SO_4 UMR quantification under high OA	More OA interferences	Lower OA interferences
Nitrate → CO_2 artifact ("Pieber effect")	Important in some cases	Much lower for NH_4NO_3, similar for $NaNO_3$
Nitrate → Chloride artifact	Observable but small	Smaller than SV
CO^+/H_2O^+ artifact from OA	Not observed	Observed for reduced OA species
Elemental ratio for ambient aerosols	Good after applying referenced calibration	Good after applying referenced calibration
PMF factor separation	Reasonable	Reasonable, larger uncertainties for sub-OOA factors
OA tracer retained	Reasonable	Key tracers were preserved.

Summary

- **CE ~1 for ambient aerosols!**
- **Mass spectra shifted to smaller fragments.**
  - But information content (e.g. OA sources and elemental ratios) not lost!!
  - Unexpected CO^+ (H_2O^+) when sampling long chain alkane/alkene-like OA (e.g. squalene), potentially due to chemical reaction on the vaporizer surfaces, whereas no such enhancement for ambient OAs.
- **Slower evaporation impacts size distributions**
  - Still OK for ambient air.
  - Much broader for monodisperse lab exp.
- **Future analysis:**
  - OA quantification: Oxidation and heating effect
  - Characterization on more primary OA, e.g., biomass burning, cooking, coal combustion
  - Chamber SOA

Thanks for your attention.

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- **References for capture vaporizer:**

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