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Evaluation of the new capture vaporizer for Aerosol Mass Spectrometers (AMS)

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

Species: Organic aerosol, Sulfate

Standard vaporizer temperature (T_v): 600℃

Collection efficiency (CE) depends on :

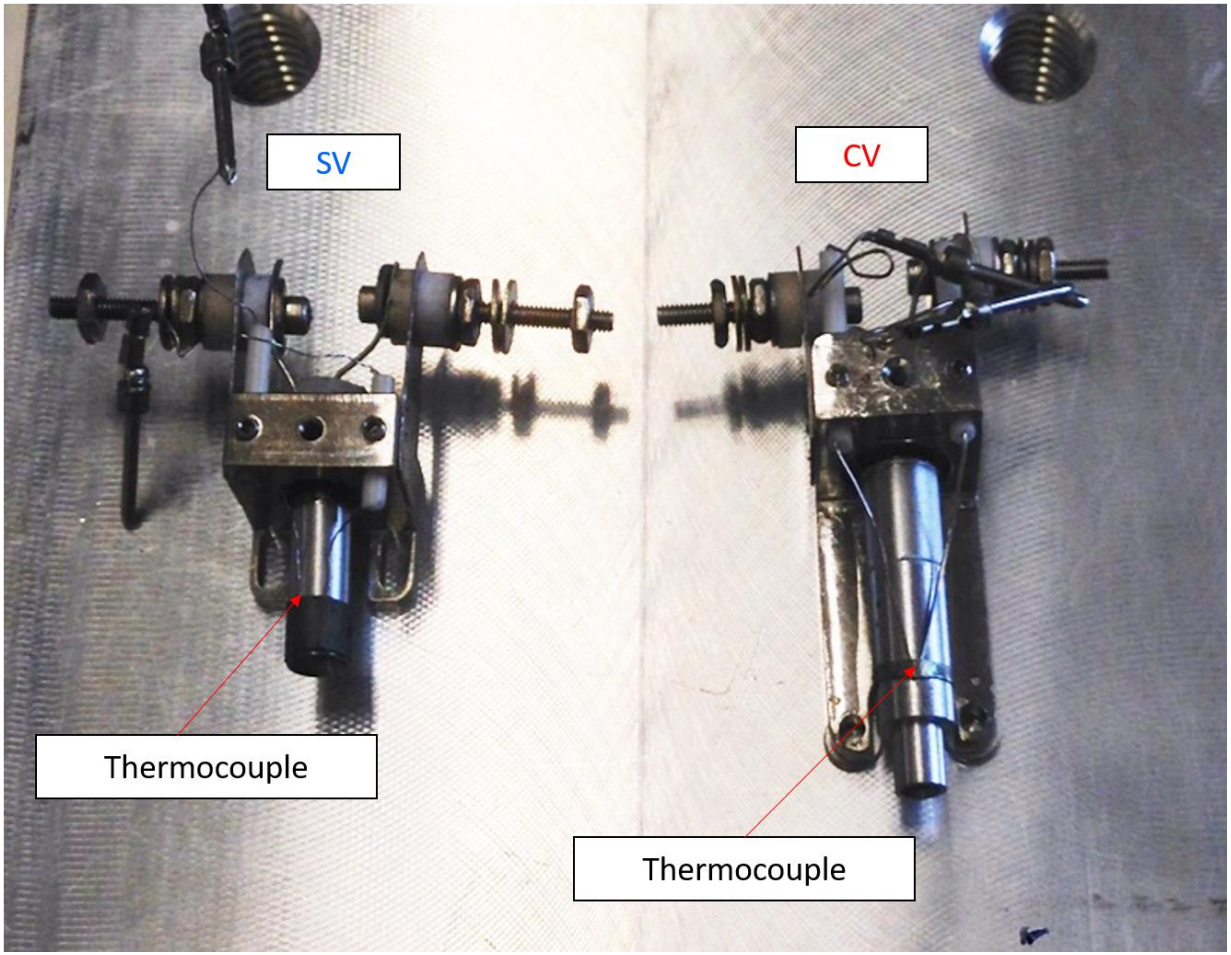
Chemical composition: e.g. NH_4NO_3 fractions, Acidity of aerosol

Aerosol phase: e.g. Solid/semisolid/liquid particle, Relative humidity

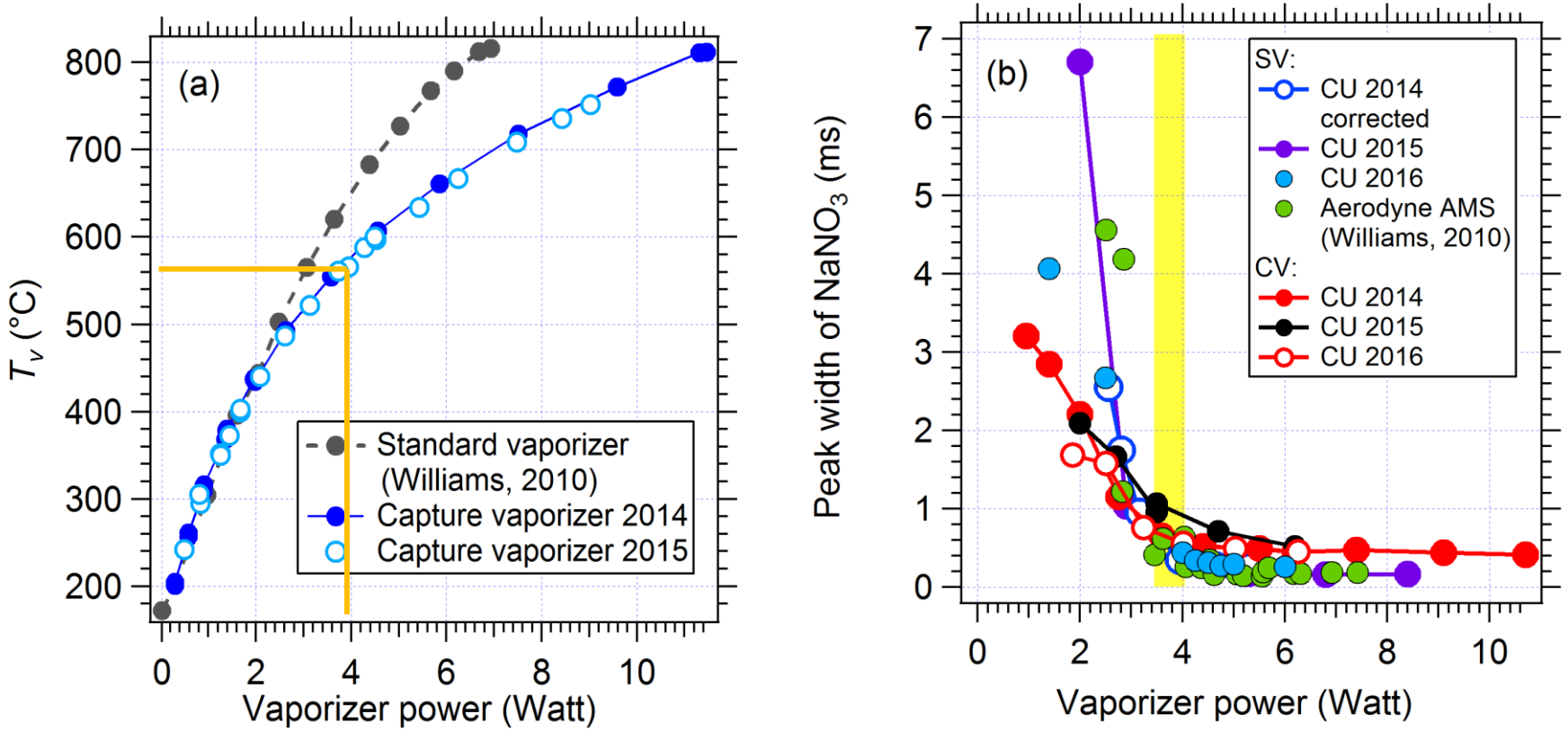
Typically contribute the most uncertainty for ambient aerosol measurement

Middlebrook et al., AST, 2012

Outlook of SV and CV



Temperature measurement for CV

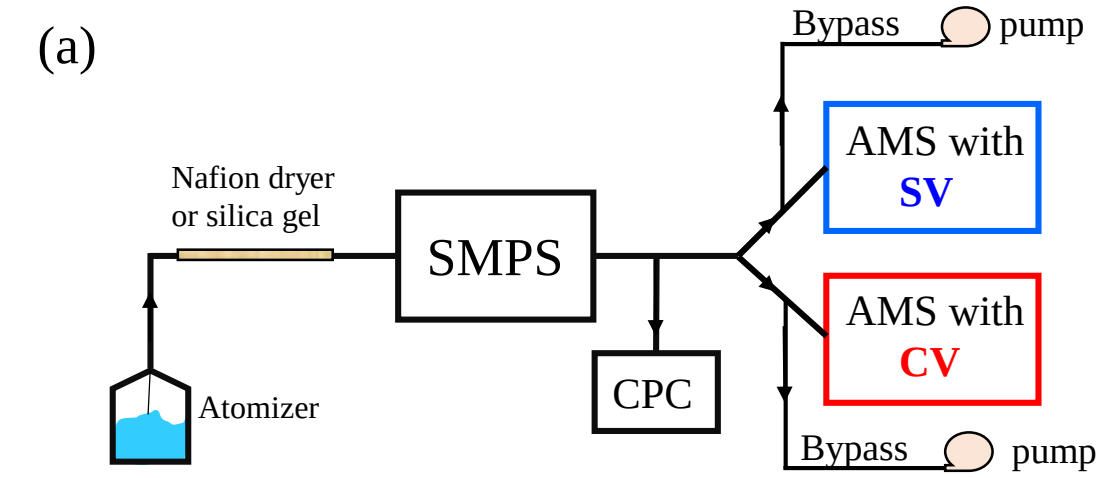


Leah William. 2010: http://cires1.colorado.edu/jimenez-group/UsrMtgs/UsersMtg11/WilliamsAMSUsersMtg_2010_VapT.pdf

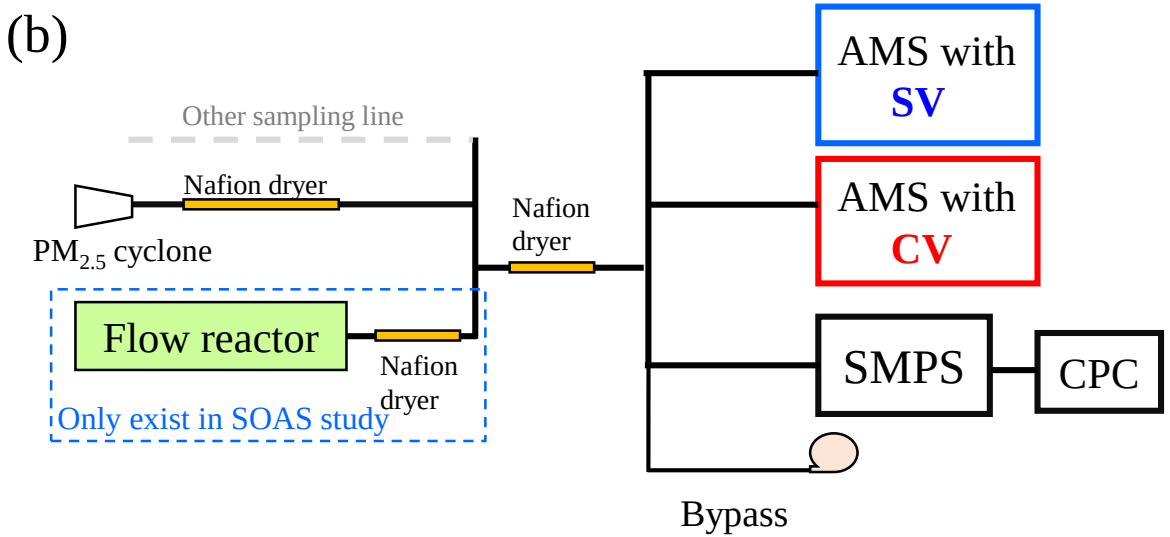
Hu et al., AMTD. 2016

Experiment setup：

Lab



Ambient

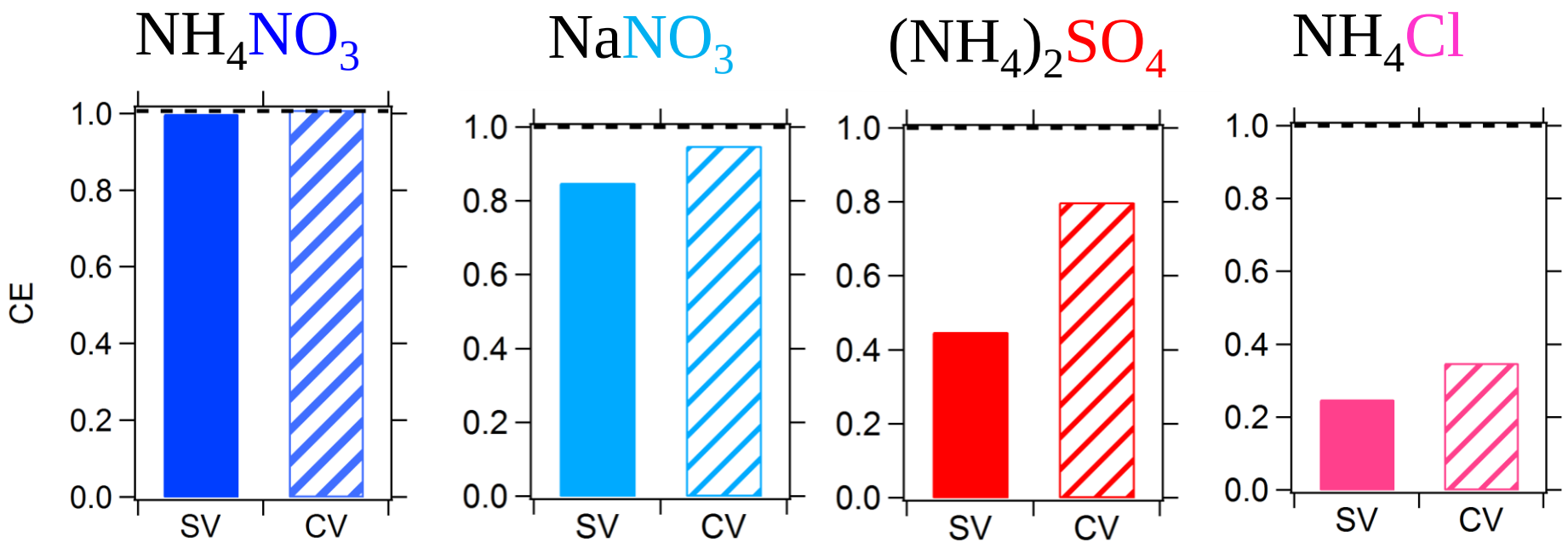


Outline

- 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?
- Pros and cons of SV vs CV

CE of standard inorganic species

CE=AMS/CPC mass ratio



An improvement in CE of inorganic species in the CV

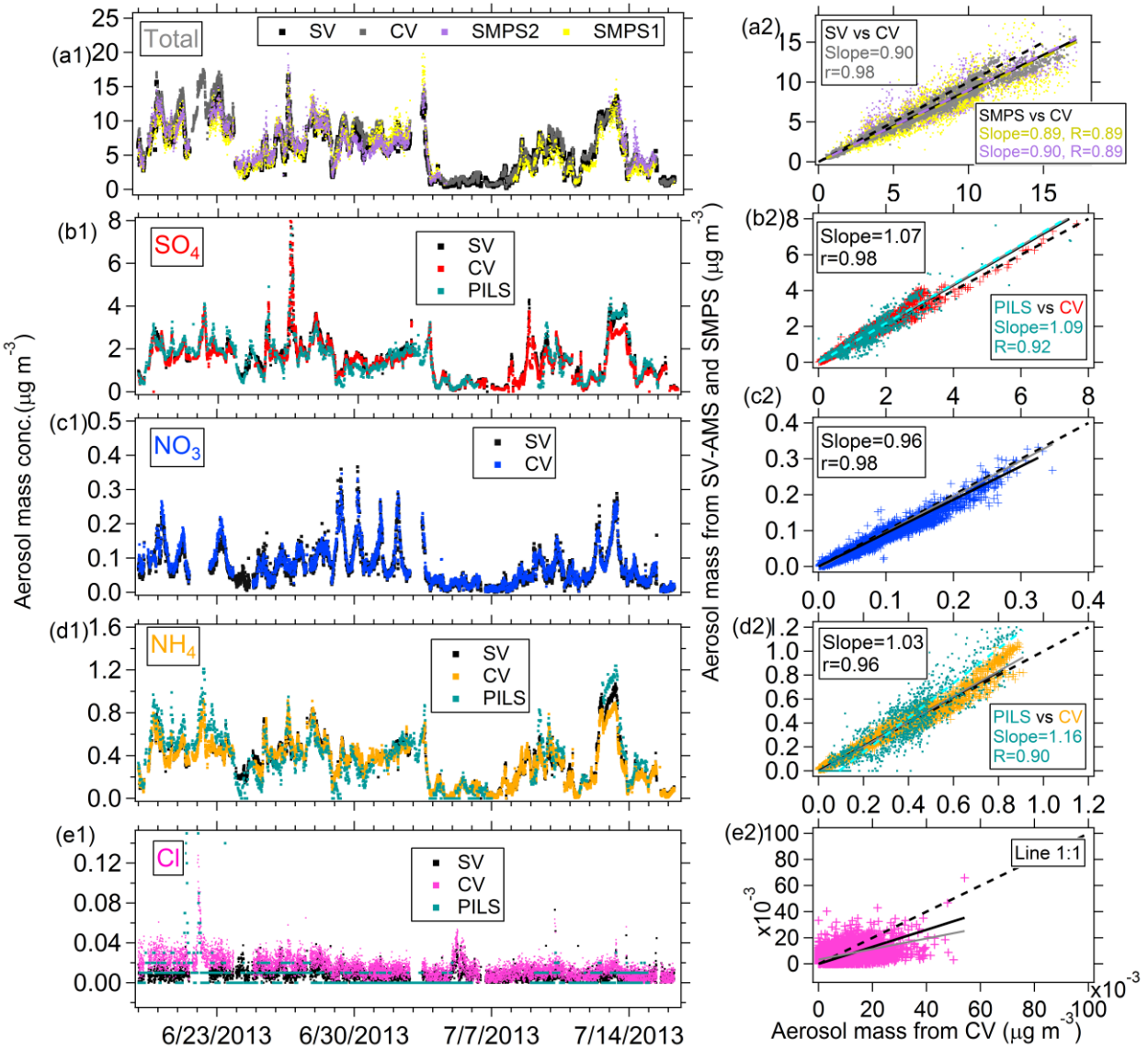
Shown results are carried out under medium vaporizer temperature 500-600C

Hu et al., AMTD. 2016

CE of ambient aerosols

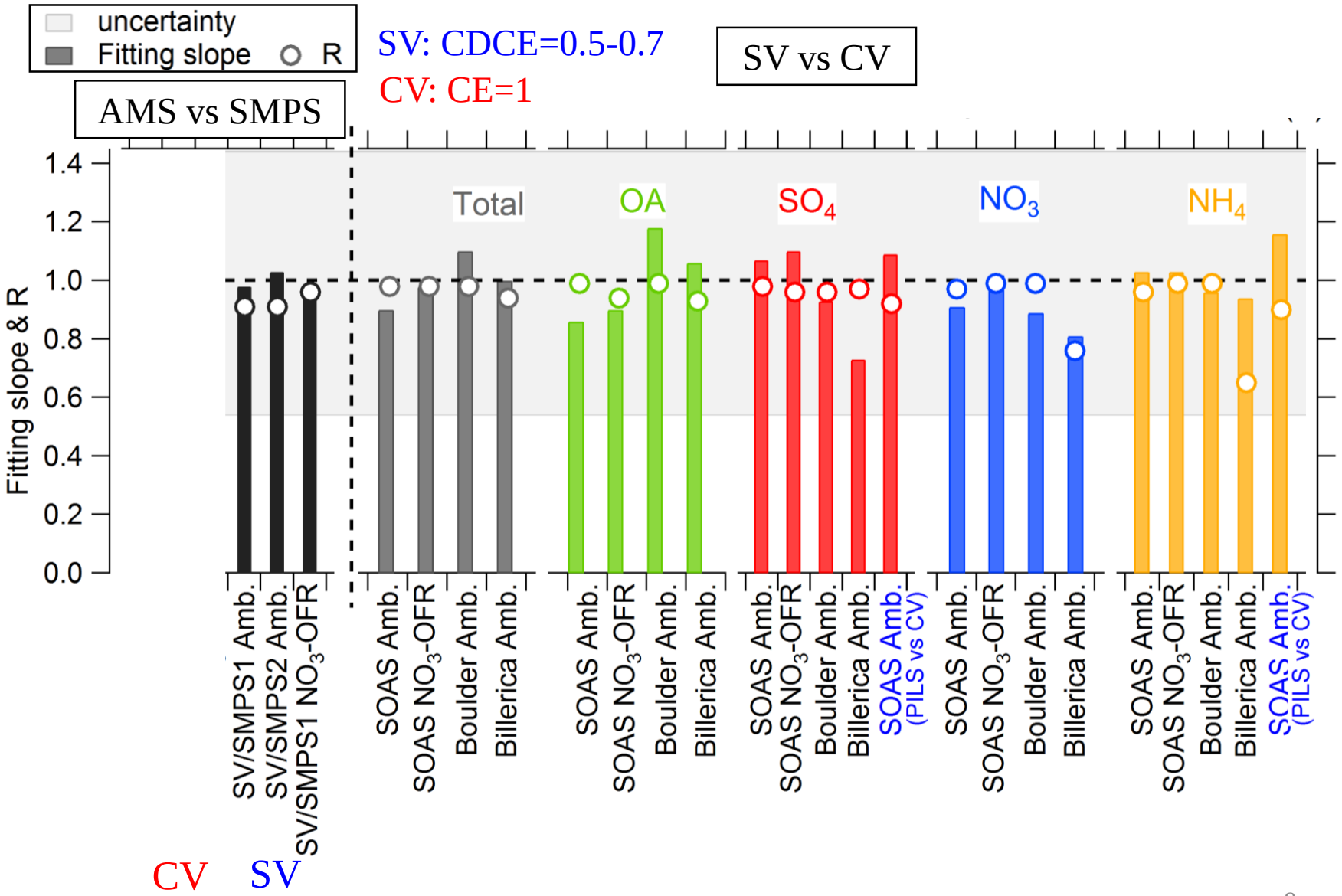
SV: CE: 0.5-0.7

CV: CE=1



Hu et al., AS&T. 2017

Multiple results support ambient CE in CV =1



Hu et al., AS&T, 2017

Outline

- Does capture vaporizer make CE~1 ?
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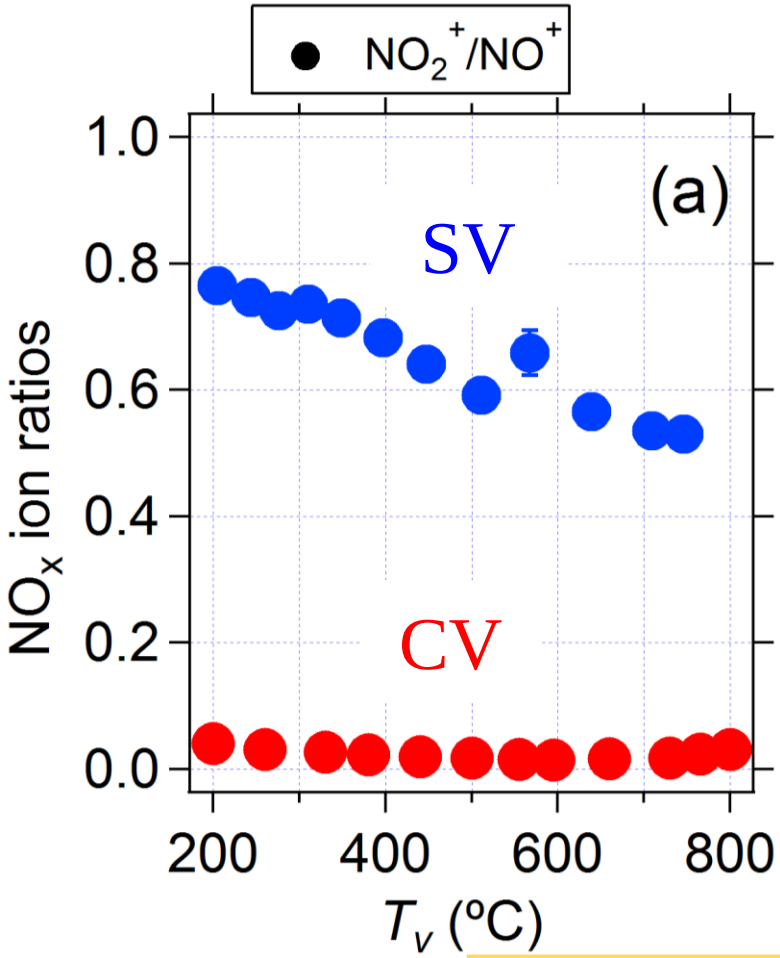
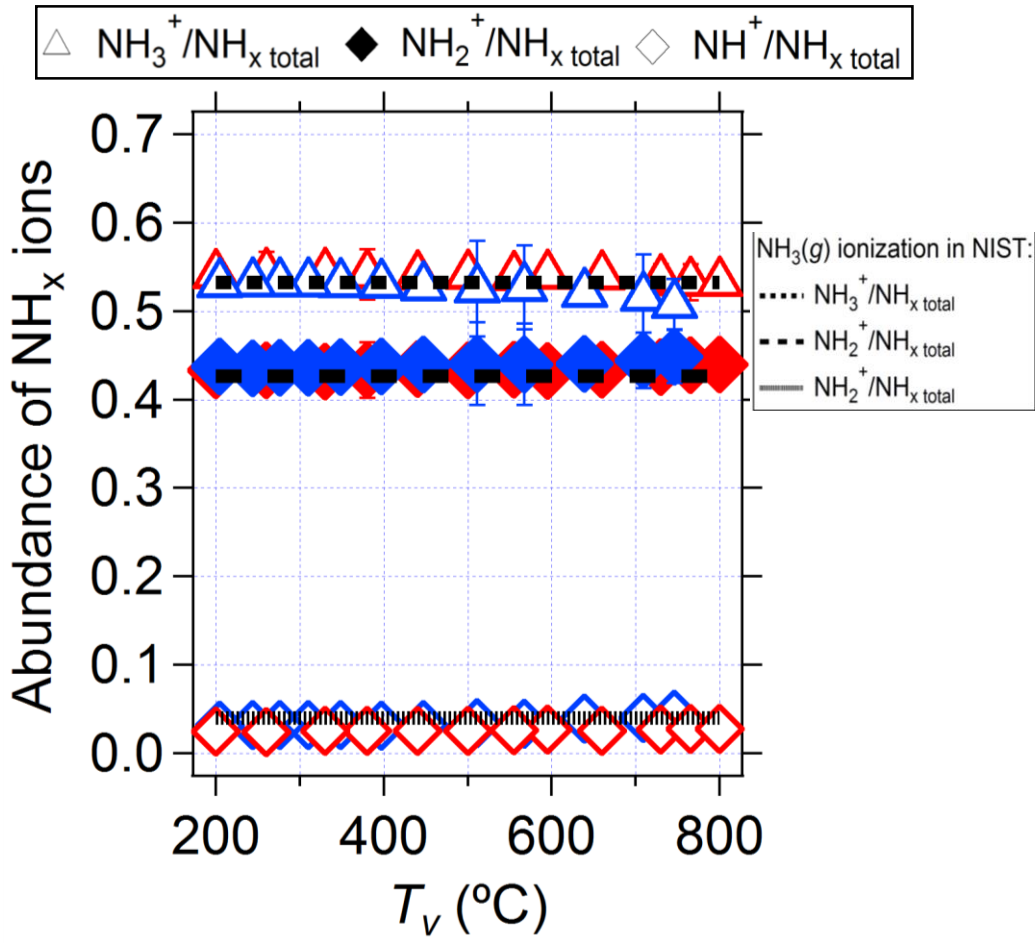
Fragmentation pattern of inorganic NH_4NO_3

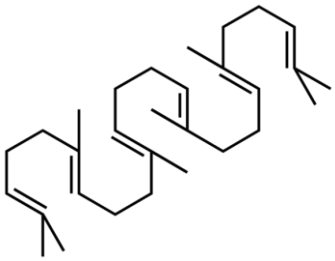




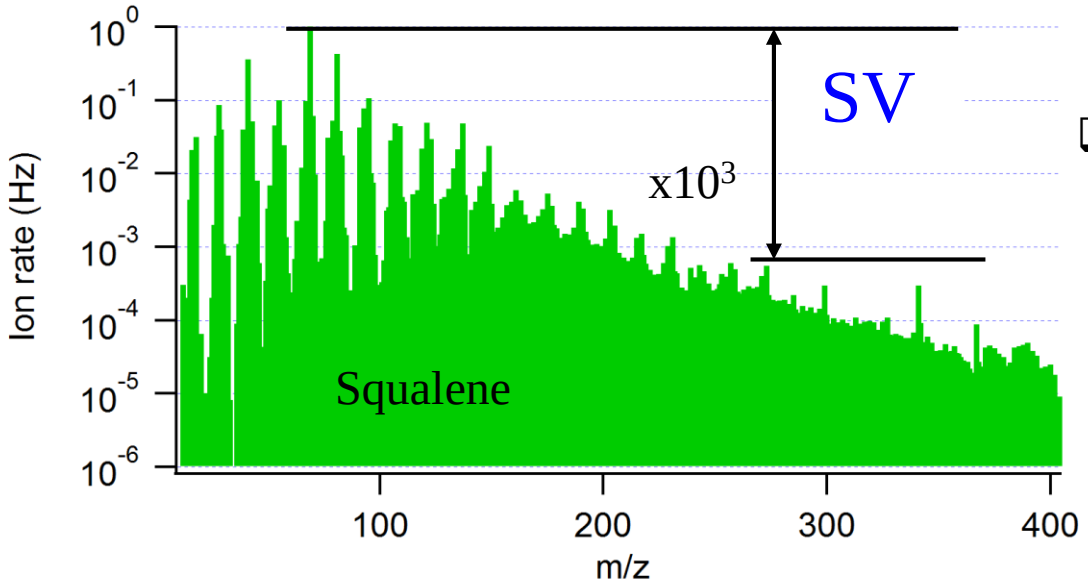
Inorganic does not evaporate as intact salts E.g., $NH_4NO_3(s) \rightarrow NH_4NO_3(g)$ but go through thermal decomposition.
E.g., $NH_4NO_3(s) \rightarrow NH_3(g)+HNO_3(g)$; $HNO_3(g) \rightarrow NO_2(g)+H_2O(g)+O_2(g)$ (Drewnick et al., 2015)

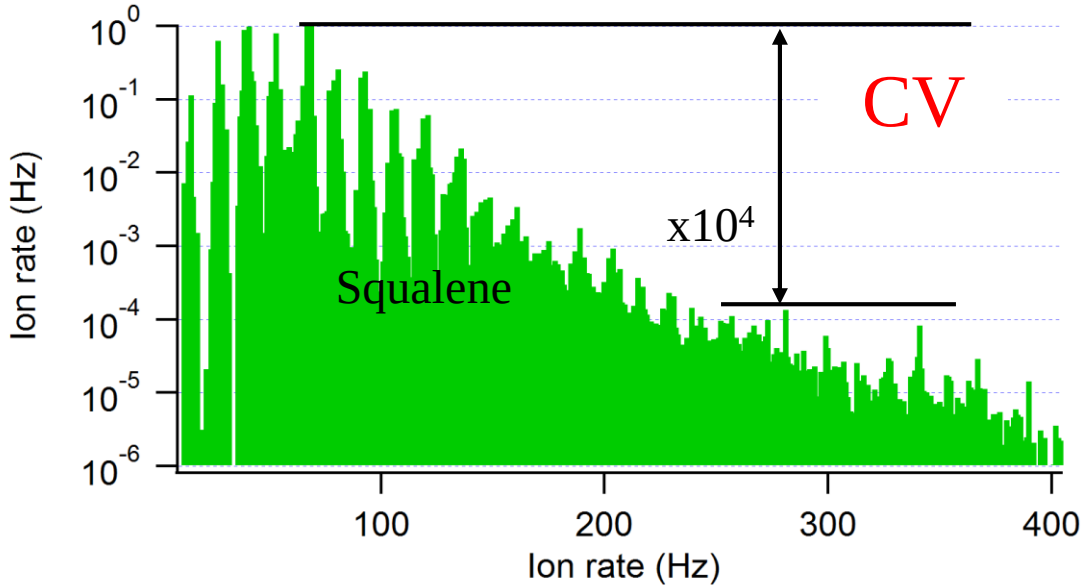
Hu et al., AMTD. 2016

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.

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Fragmentation pattern of organic species

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

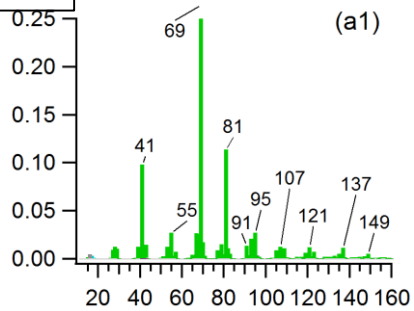
Squalene ($C_{30}H_{50}$)

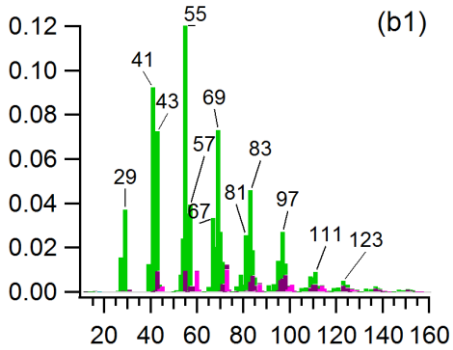
Oleic acid ($C_{18}H_{34}O_2$)

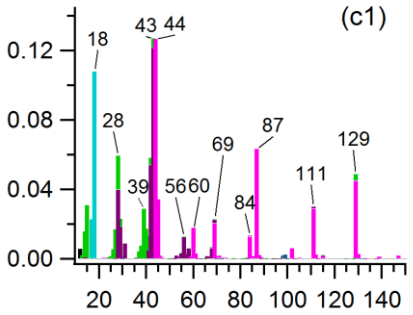
Citric acid ($C_6H_8O_7$)

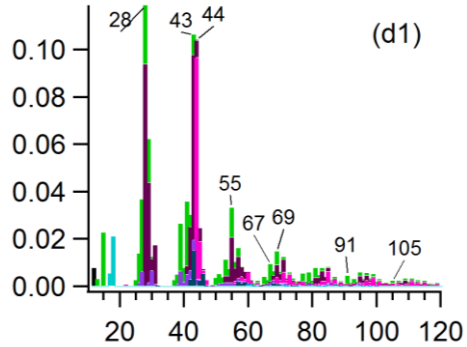
Ambient OA (KORUS-AQ)

SV

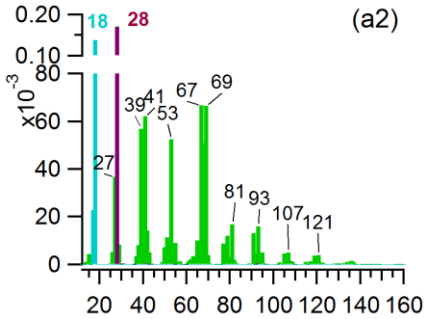


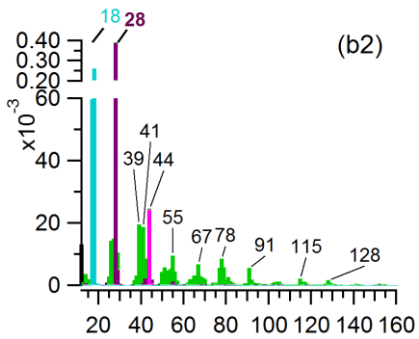


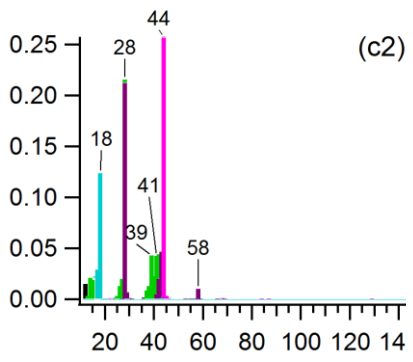


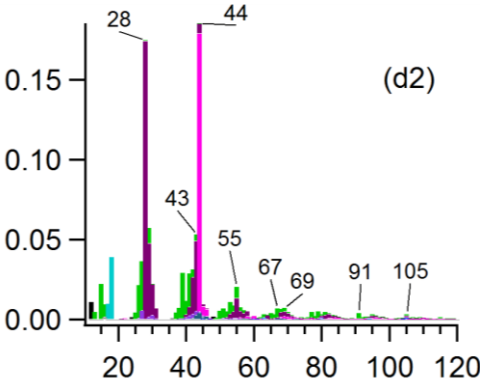


CV



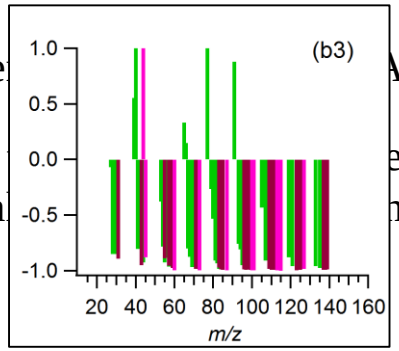


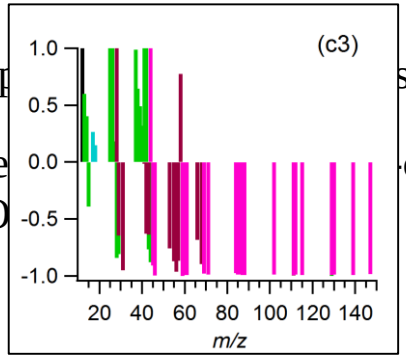


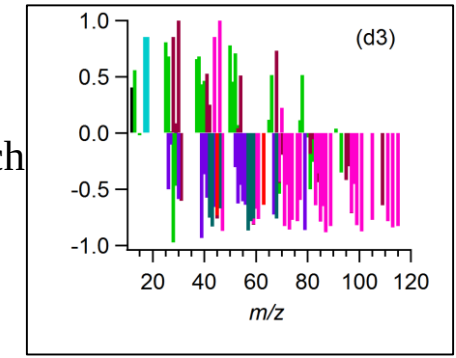


- This shifting happe… A typ… s
- Excess CO^+ (H_2O^+ … erve… ch… species, not in high… nt O…

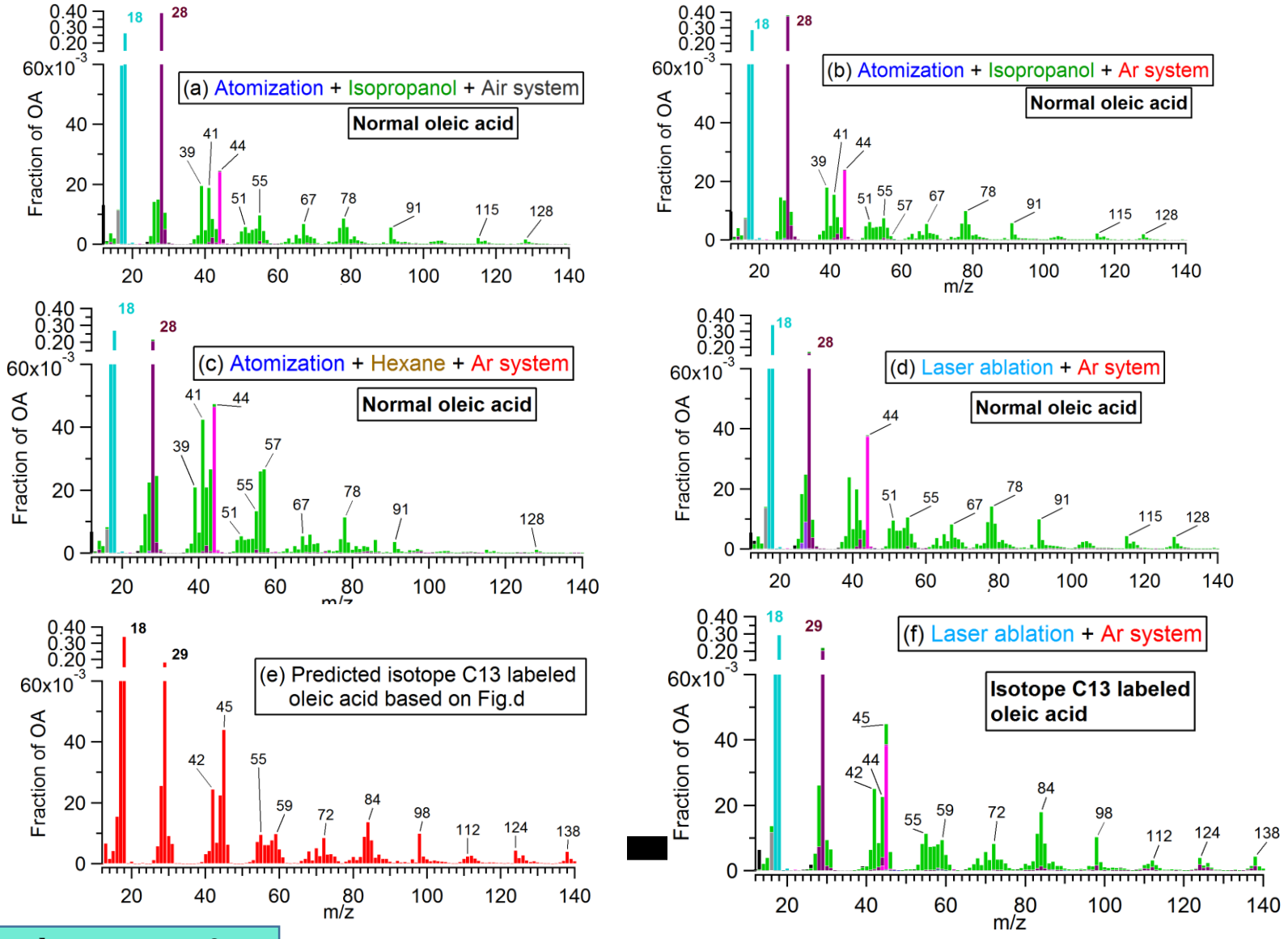
(CV-SV) /SV





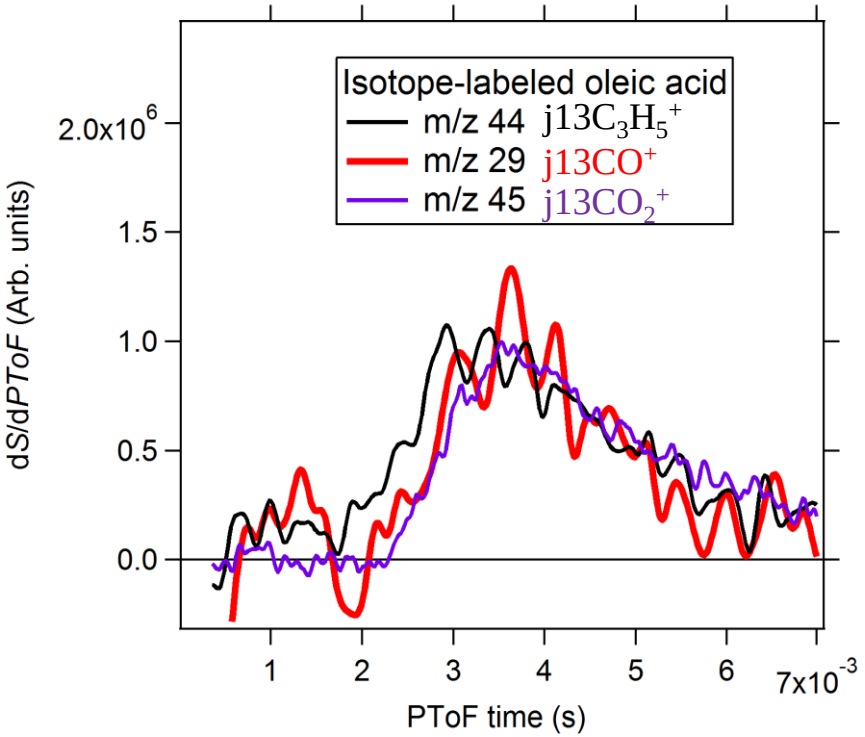


Excess H_2O^+ and CO^+ ions in the CV

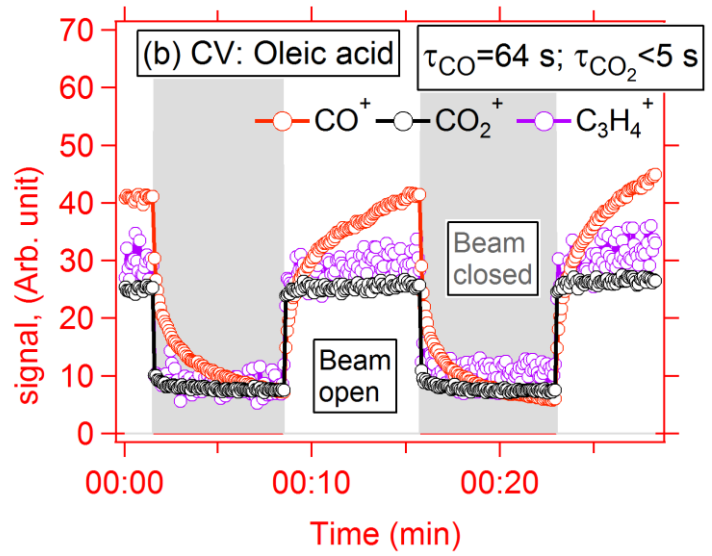


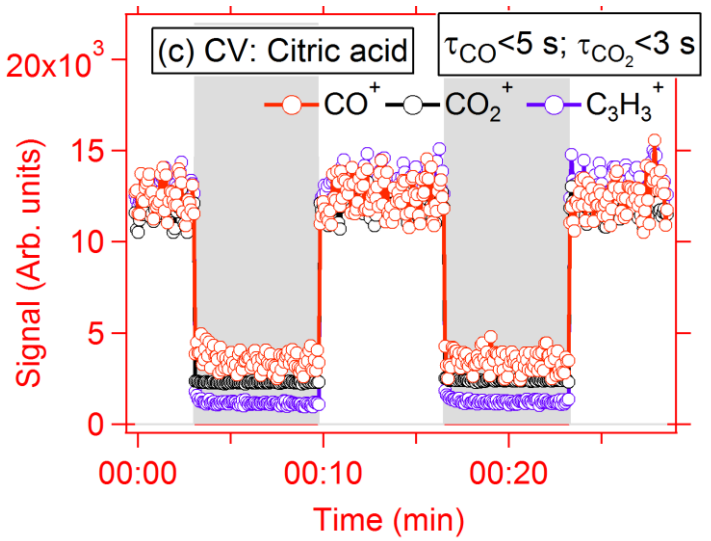
Hu et al., in prep. 2017

PToF show CO peak similar with aerosol phase



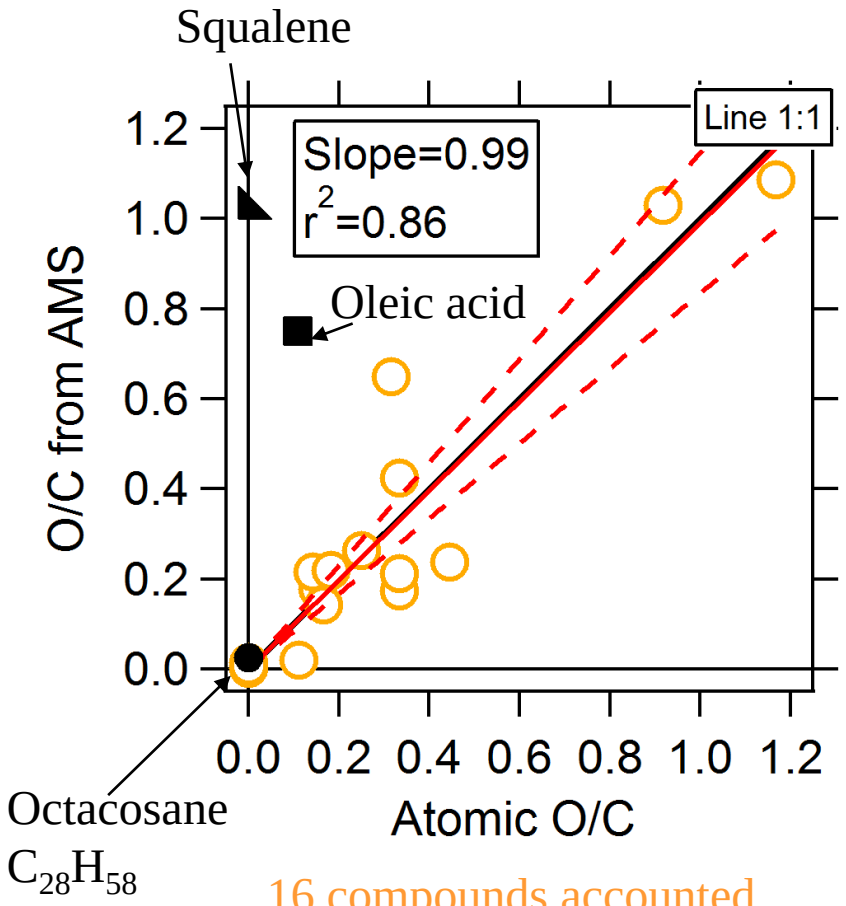
- Unexpected CO^+ (H_2O^+) ion formation might be caused by catalytic reaction on the vaporizer surfaces.

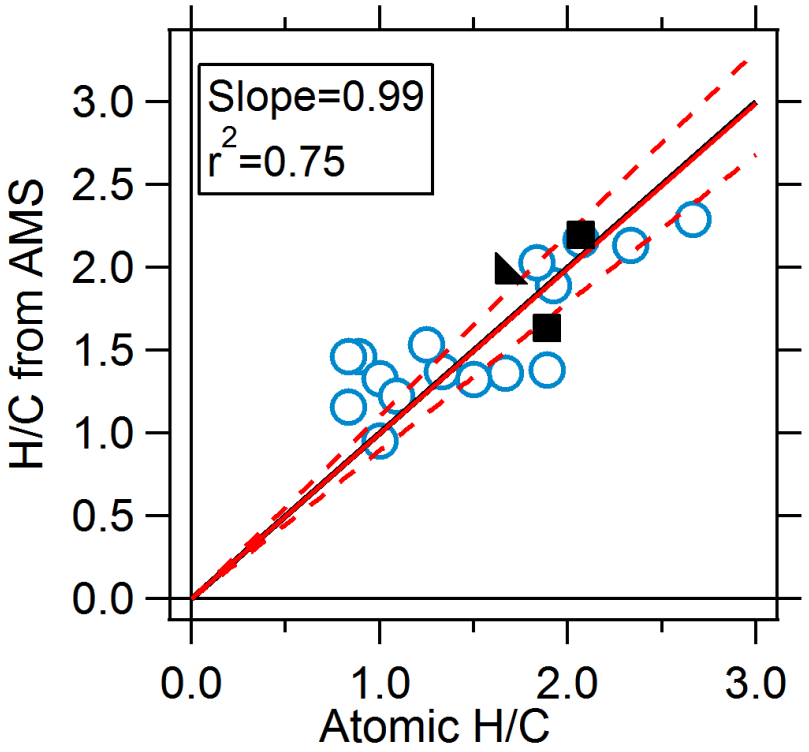




Hu et al., in prep. 2017

Elemental ratio calibration: standard species





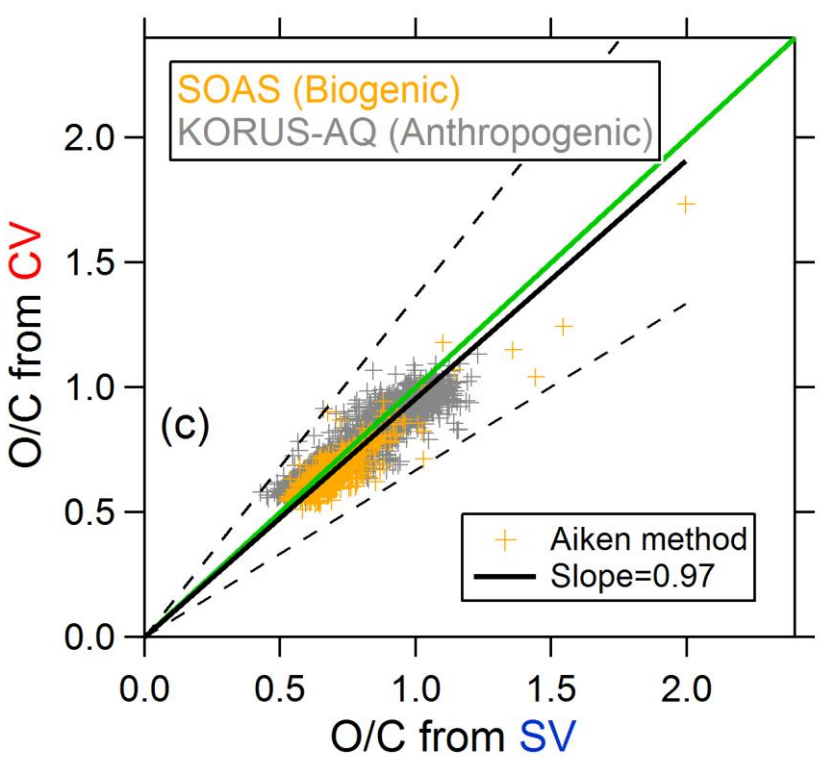
16 compounds accounted

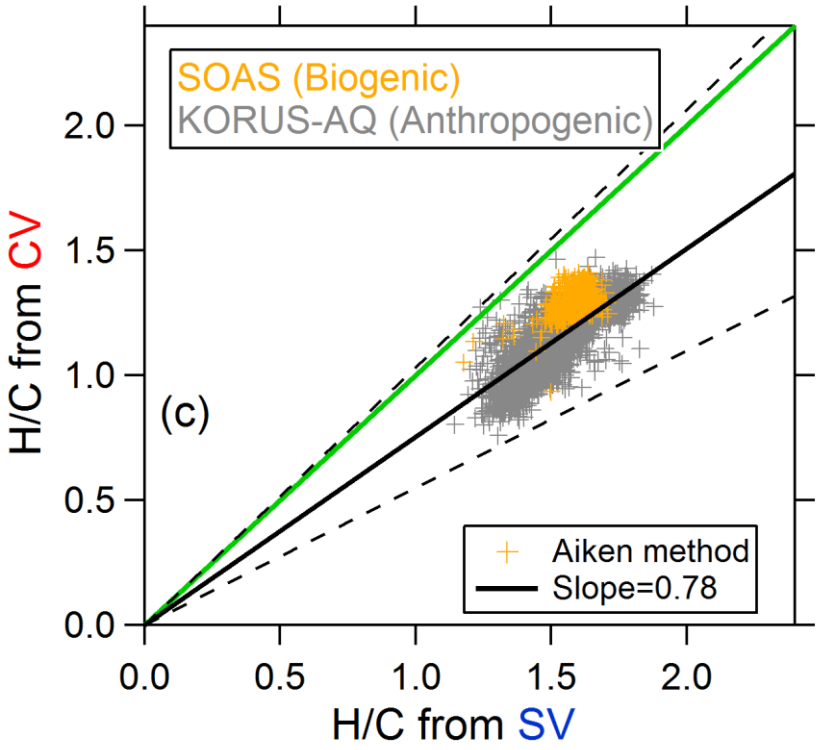
- Aiken explicit calibration method (Aiken et al. 2007;2008)

Hu et al., in prep. 2017

Elemental ratio comparison: ambient OA

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



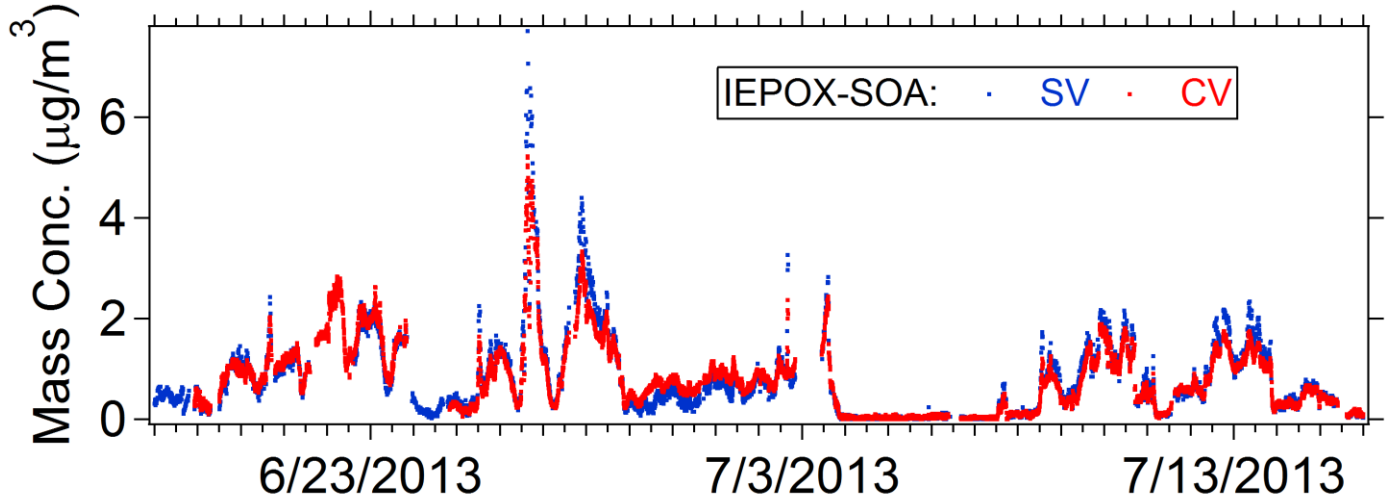


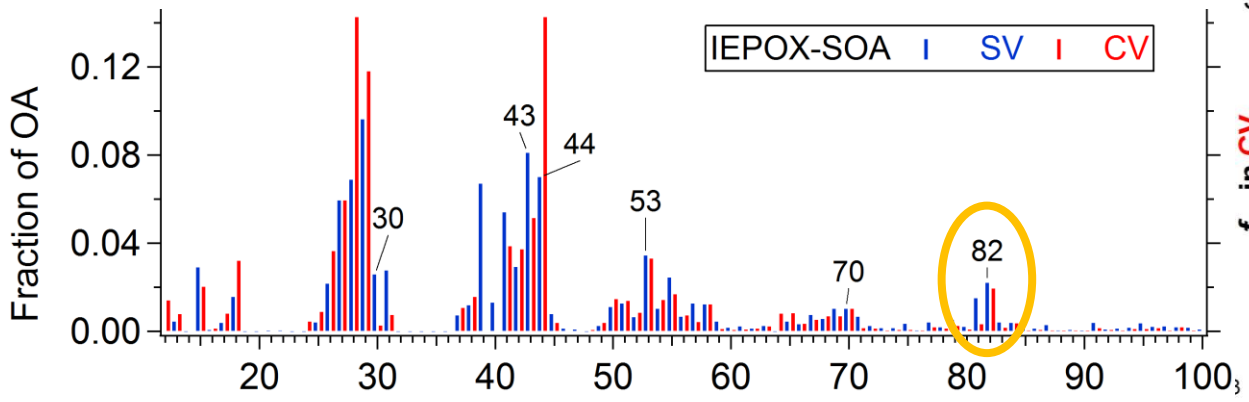
- The elemental composition of ambient OA can be accurately measured with the CV, with suitable modifications to the quantification procedure.

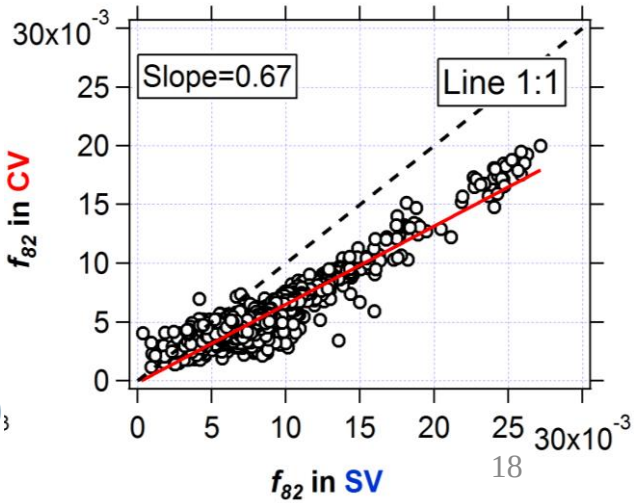
Hu et al., in prep. 2017

Similar PMF results for SV vs CV

IEPOX-SOA: Isoprene epoxydiols-derived SOA







Hu et al., in prep. 2017

Outline

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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 AN, similar for SN
Nitrate → Chloride artifact	Observable but small	Smaller than SV

Hu et al., AS&T. 2017

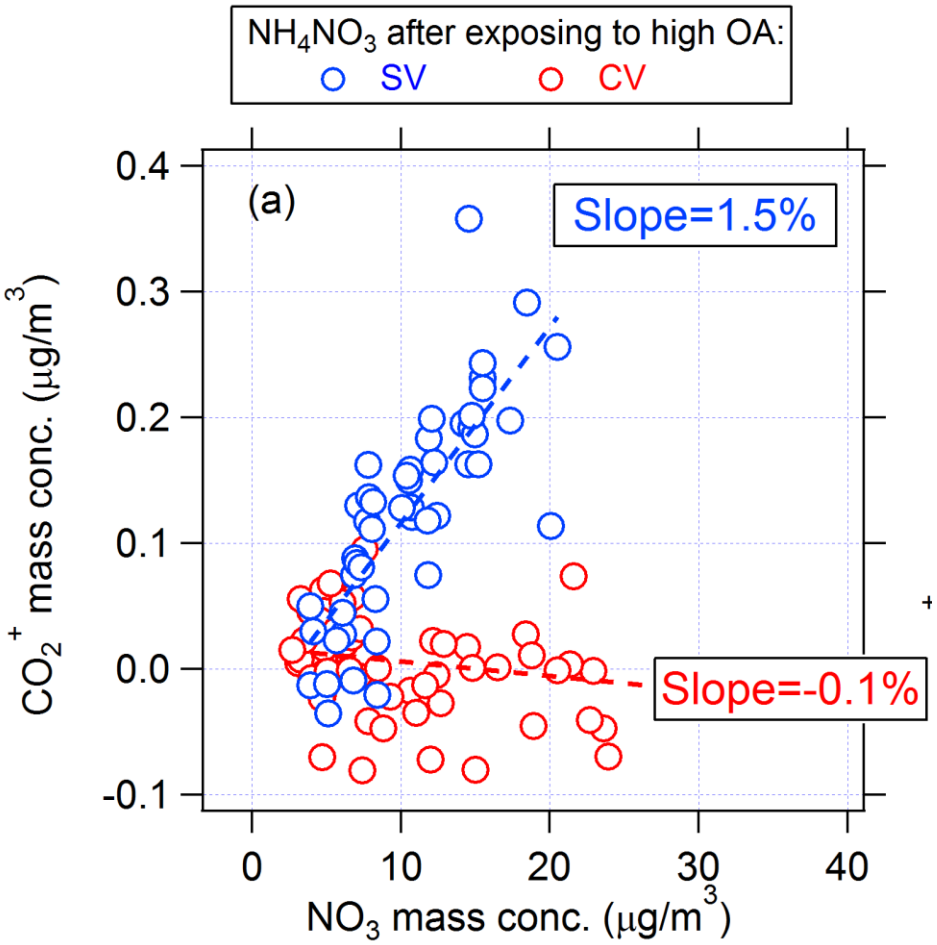
Summary

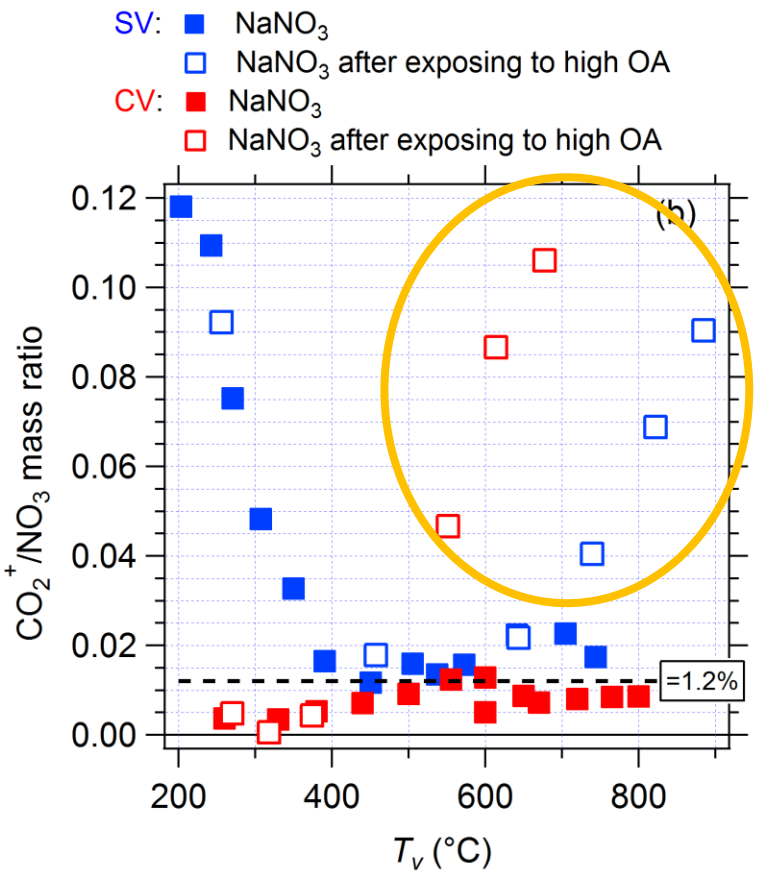
- CE ~1 !
- Mass spectra shifted to smaller fragments.
  - But information content (e.g. OA sources and elemental ratios) not lost!!
  - Unexpected CO^+ (H_2O^+) when sampling long chain alkane/alkene-like OA (e.g. squalene), whereas no such enhancement for ambient OAs.
- Slower evaporation impacts size distributions
  - Still OK for ambient air.
  - Much broader for monodisperse lab exp.
- **Future analysis**: OA quantification in the CV: oxidation vs morphology; CO^+ interference; Chamber SOA quantification/fragmentation/elemental ratio
- **References for more details about CV:**

- Hu, W. W. et al. (2016). Evaluation of the new capture vaporizer for Aerosol Mass Spectrometers (AMS) through laboratory studies of inorganic species Atmos. Meas. Tech. Discuss. 2016, 1-55, 10.5194/amt-2016-337; http://www.atmos-meas-tech-discuss.net/amt-2016-337/
- Hu, W.,W et al. (2017). Evaluation of the new capture vaporizer for aerosol mass spectrometers (AMS) through field studies of inorganic species, Aerosol Sci Tech, 0-0, 10.1080/02786826.2017.1296104. http://www.tandfonline.com/doi/full/10.1080/02786826.2017.1296104
- Xu, W, et al. (2017). Laboratory characterization of an aerosol chemical speciation monitor with PM2.5 measurement capability, Aerosol Sci Tech. 51, 69-83, 10.1080/02786826.2016.1241859. http://www.tandfonline.com/doi/abs/10.1080/02786826.2016.1241859

Thanks for your attention.

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



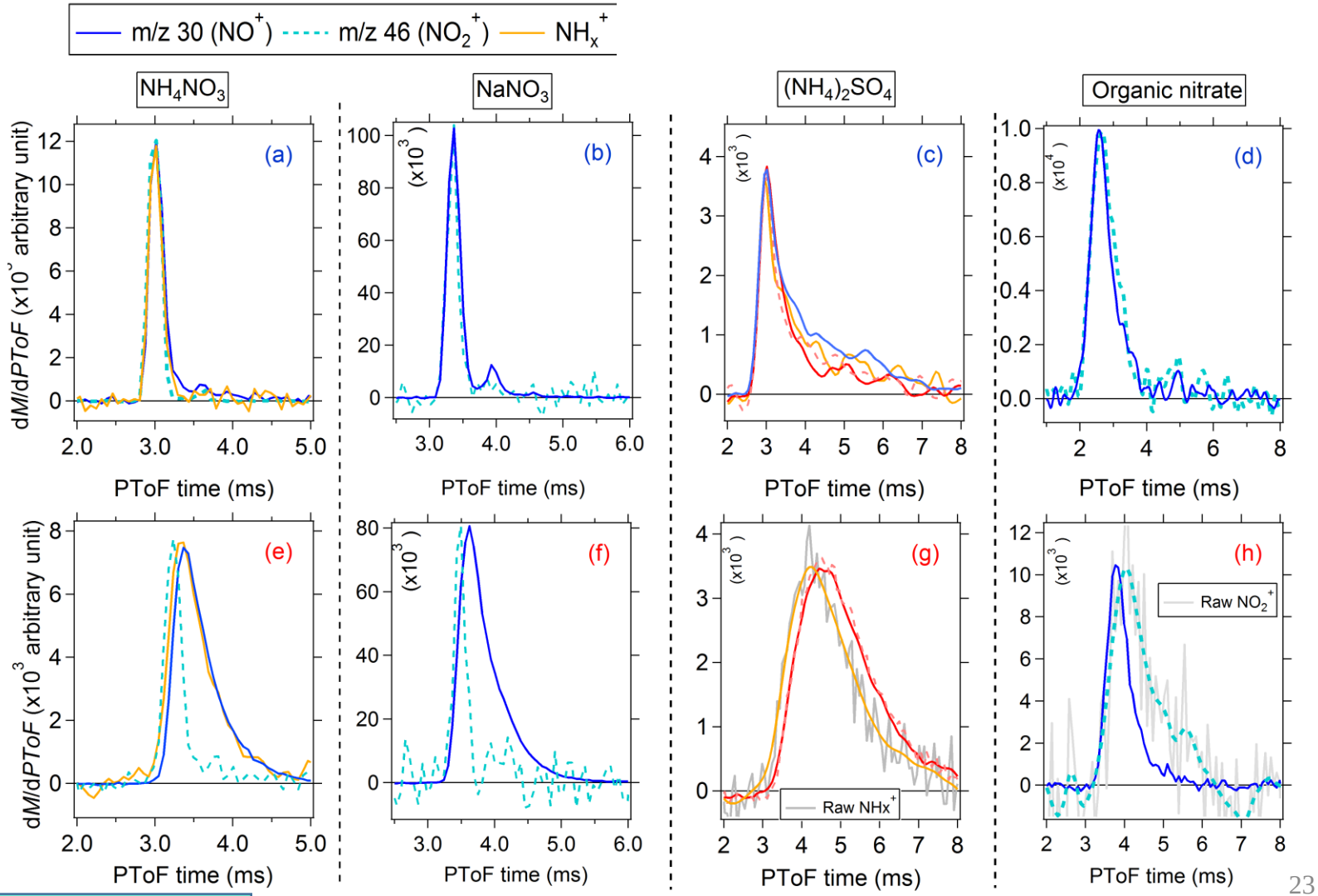


Hu et al., AMTD. 2016

Size-resolved detection of inorganic ions

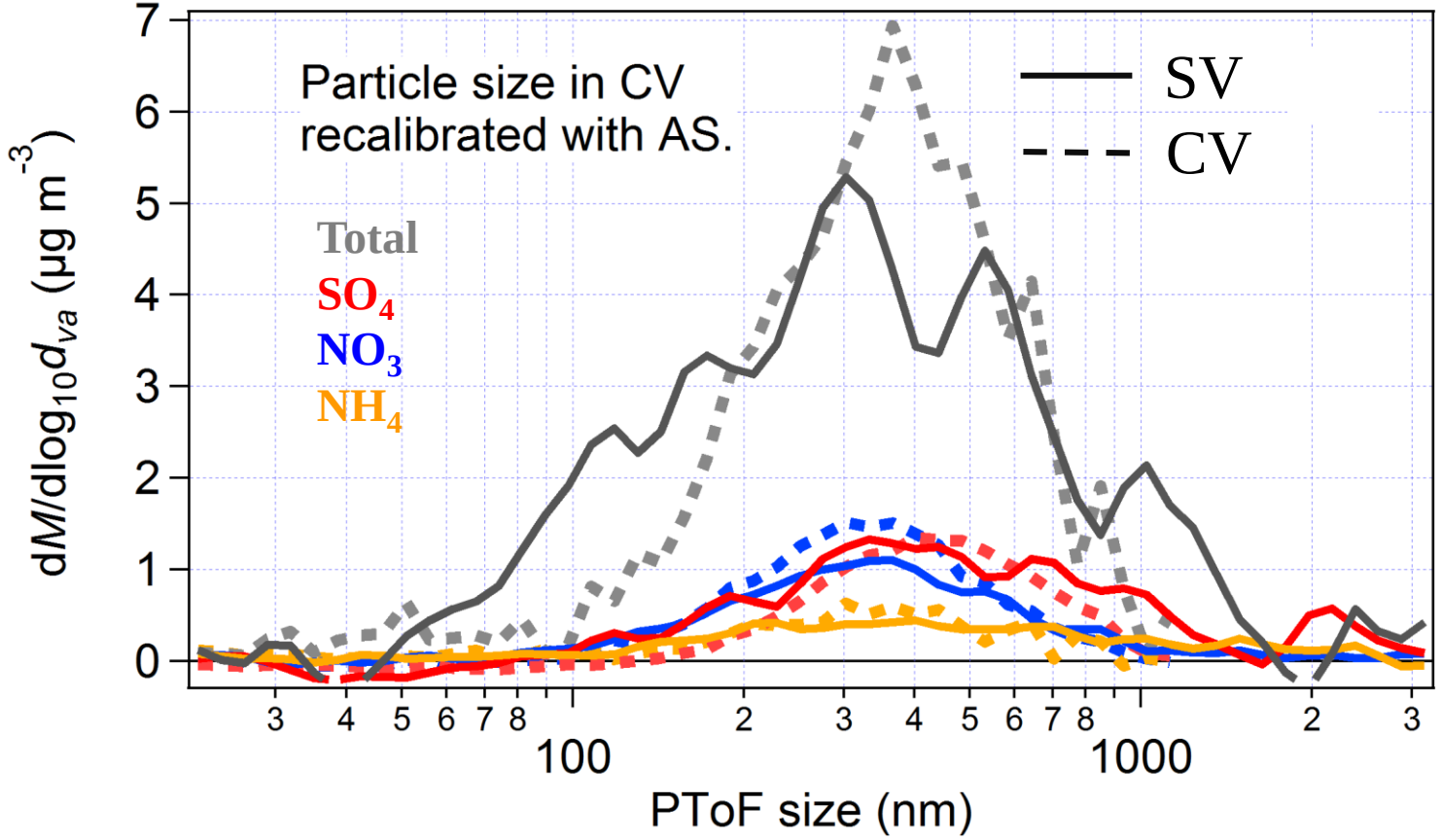
SV

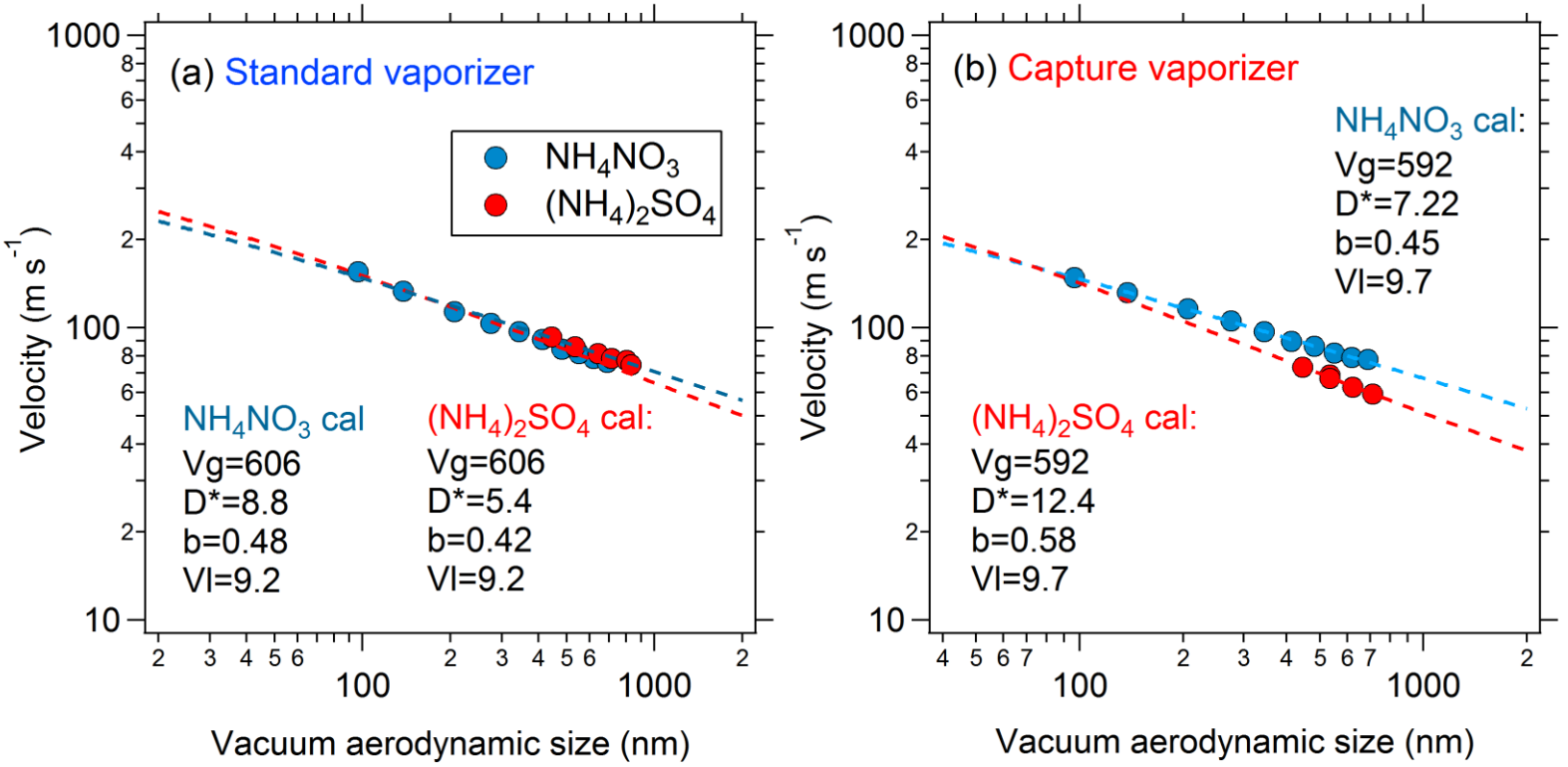
CV



Hu et al., AMTD. 2016

Size distribution of ambient aerosol in CV still work



Hu et al., AS&T. 2017

Calibration curve