Investigation of f_{44} variability in AMS and ACSM instruments

Update from Aerodyne Research

Experiments by Phil Croteau, Andy Lambe, Wen Xu, Tim Onasch, Lindsay Wolff, Manjula Canagaratna

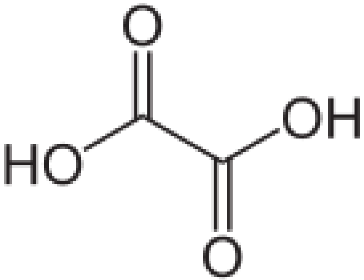
John Jayne

Mass 44
A Marker Ion for OOA

CO_2, CO and water is formed by thermal decomposition of organic acids

$$H_2C_2O_4 \xrightarrow{\Delta} H_2O + CO + CO_2$$

Oxalic acid, smallest di-acid



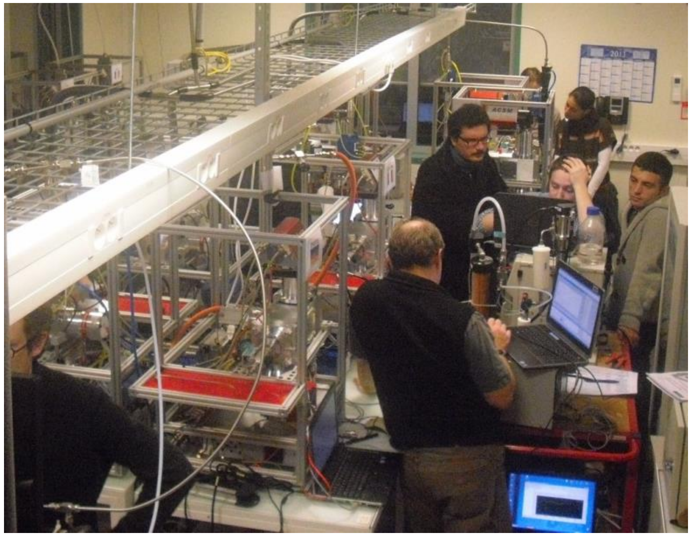
*f*44 = m/z44 / Org

Background

ACTRIS-ACSM intercomparison study

10 European countries

15 mass spectrometers
13 QACSM, TOF ACSM,
HTOF AMS



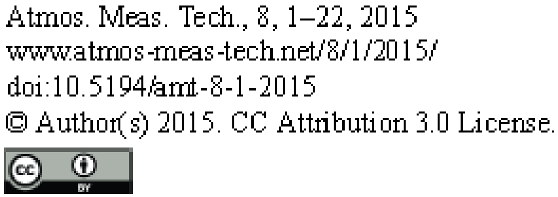
Led by Jean Sciare, Vincent Crenn (LSCE) and Olivier Favez (INERIS)

Three weeks during the fall period (Nov. – Dec. 2013)

Results of ACTRIS-ACSM intercomparison study are summarized in two AMT papers

Crenn et al
ACTRIS ACSM Intercomparison: Part I - Intercomparison of concentration and fragment results from 13 individual co-located Aerosol Chemical Speciation Monitor (ACSM)

Frohlich et al,
ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers


Atmos. Meas. Tech., 8, 1–22, 2015
www.atmos-meas-tech.net/8/1/2015/
doi:10.5194/amt-8-1-2015

Atmospheric
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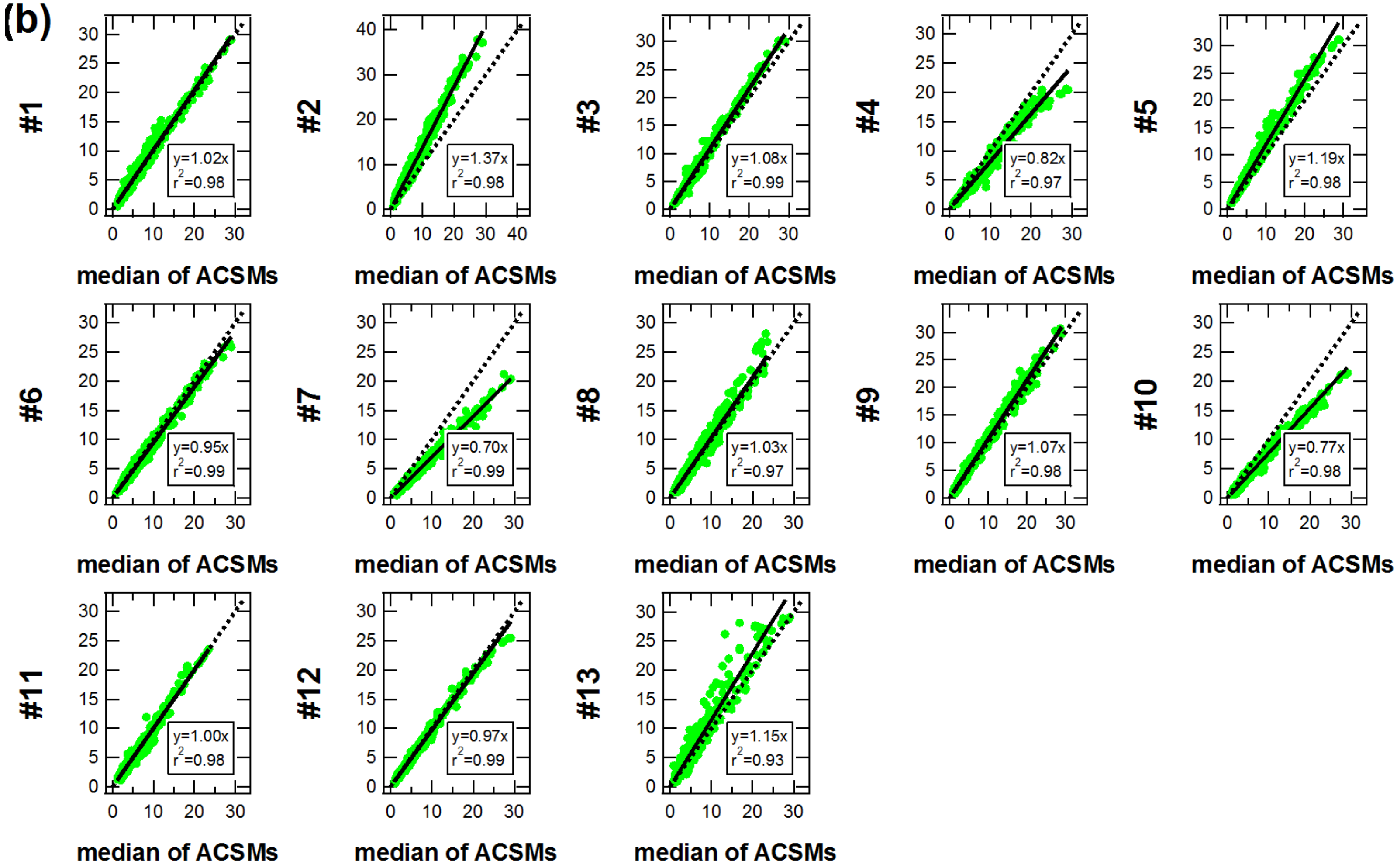
ACSM – Org versus ACSM median-ORG values for the 13 QACSM Instruments



Crenn et al (2015)

Deviation of Selected Organic Ion Fragments from the Median Values

f44 follows an opposite pattern compare to the other organic fragments

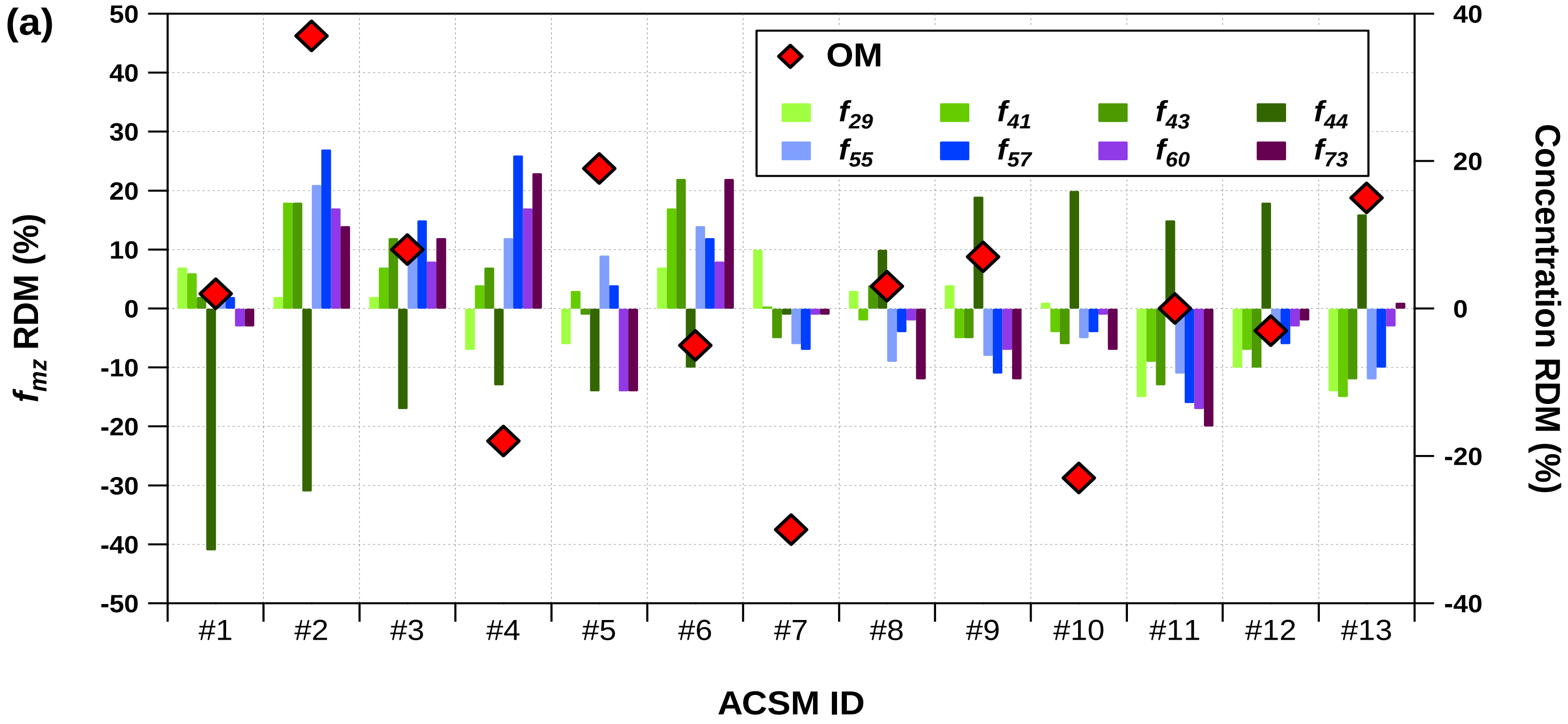
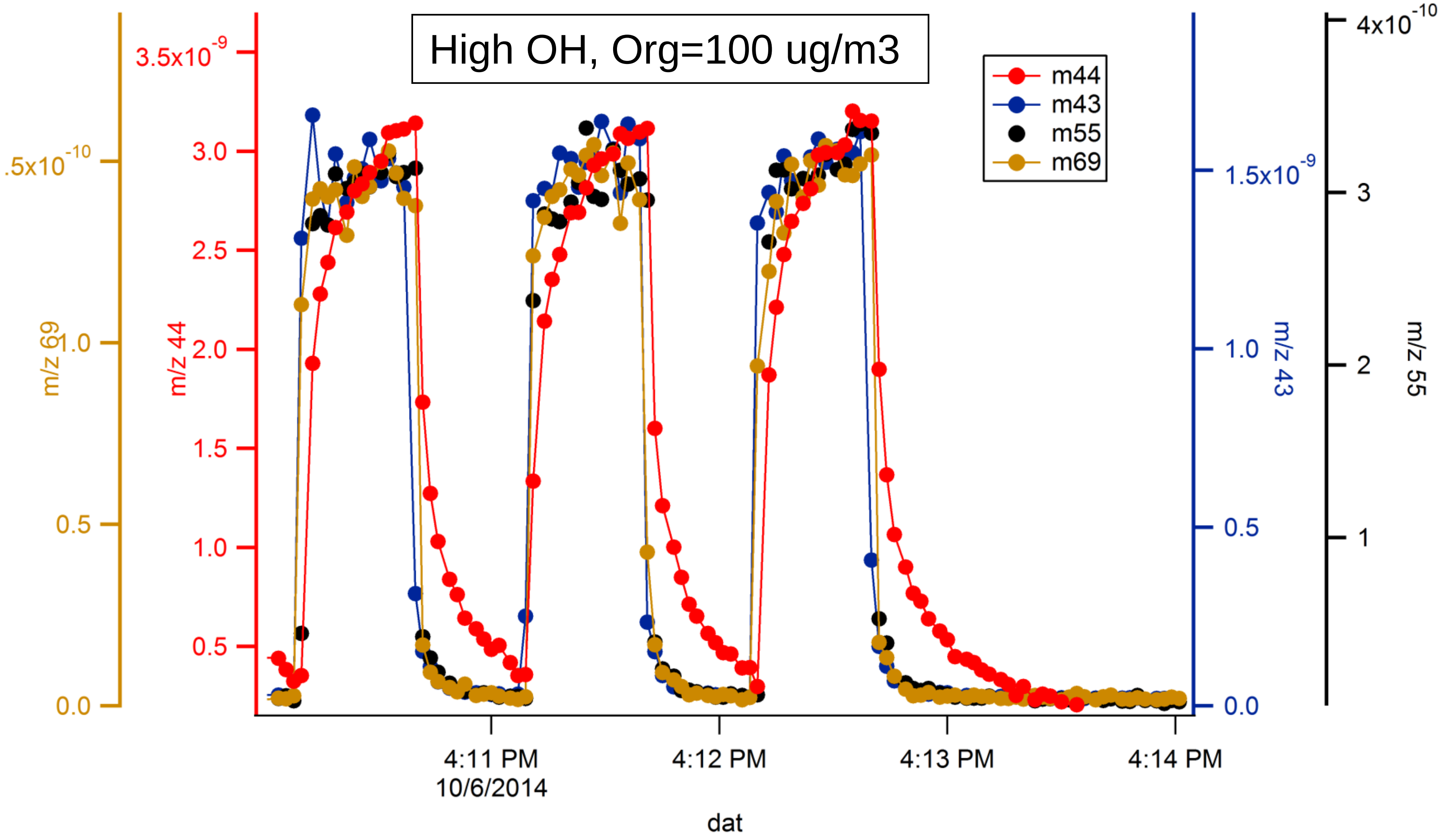


Figure 7. Relative deviation to the median (RDM) of ACSM concentrations and major fragments (f_{mz}) for (a) OM (f_{29}, f_{43}, f_{44}, f_{55}, f_{57}, f_{60} and f_{73}), (b) NH_4 (f_{16} and f_{17}), (c) NO_3 (f_{30} and f_{46}), and (d) SO_4 (f_{48}, f_{64}, f_{80}, f_{81} and f_{98}) obtained from orthogonal distance regression fits with zero intercept.

Crenn et al (2015)

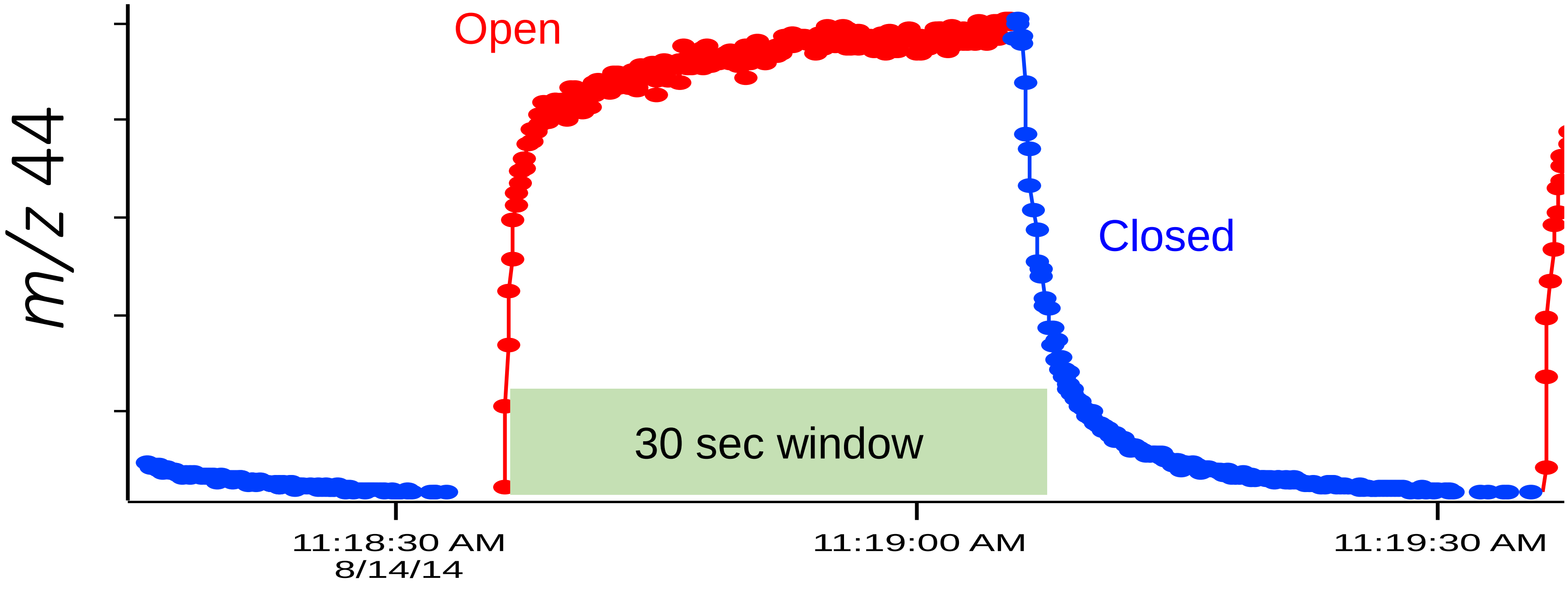
1c. *f*44 Timescales for PAM α-pinene SOA (ACSM)



“Slow” CO_2 rise and fall. Other org masses are “fast”

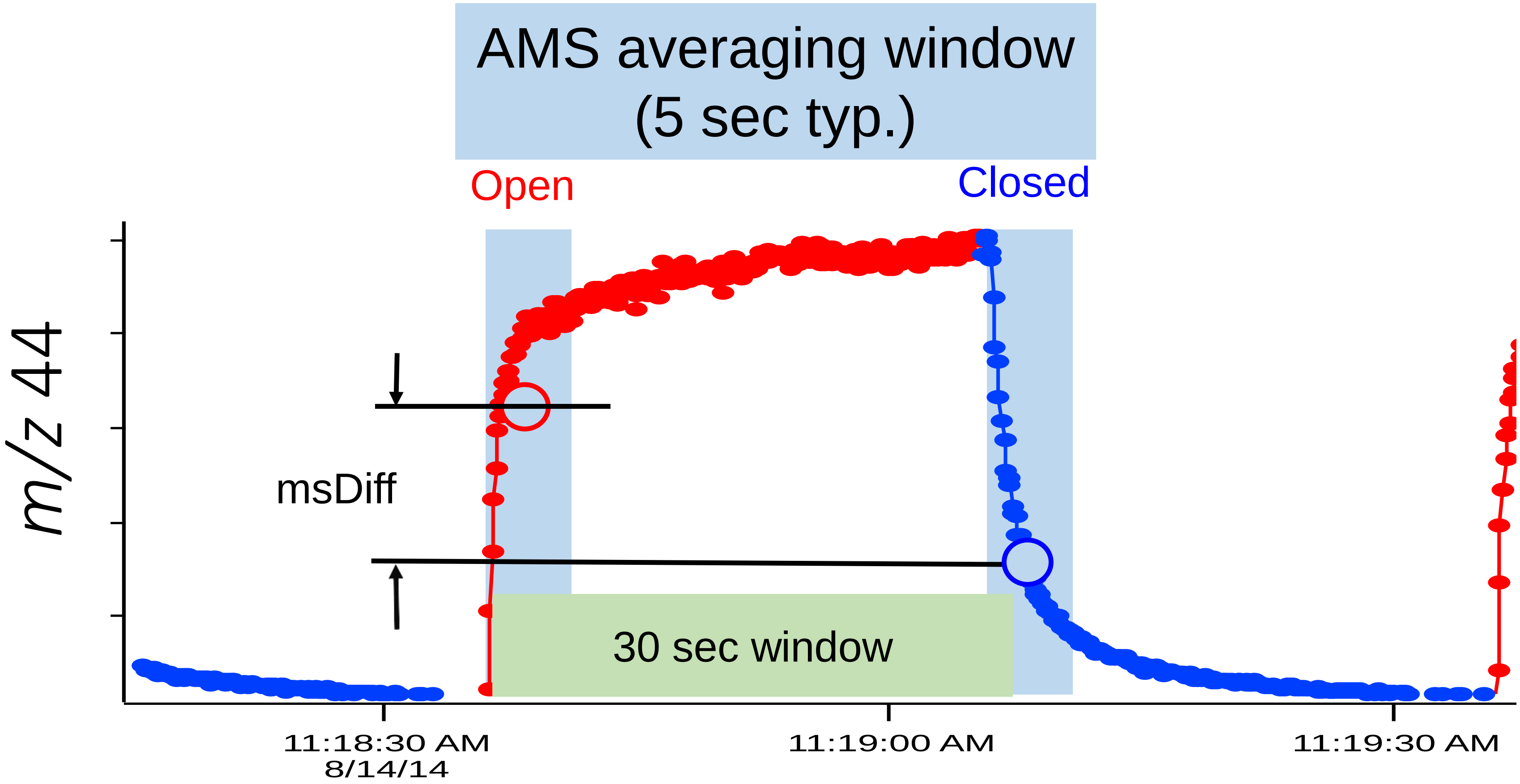
Anantomy of the m/z 44 Signal
Slow rise and fall times on seconds timescale

msDiff = Open - Closed



Data recording mode can influence how m/z44 is sampled

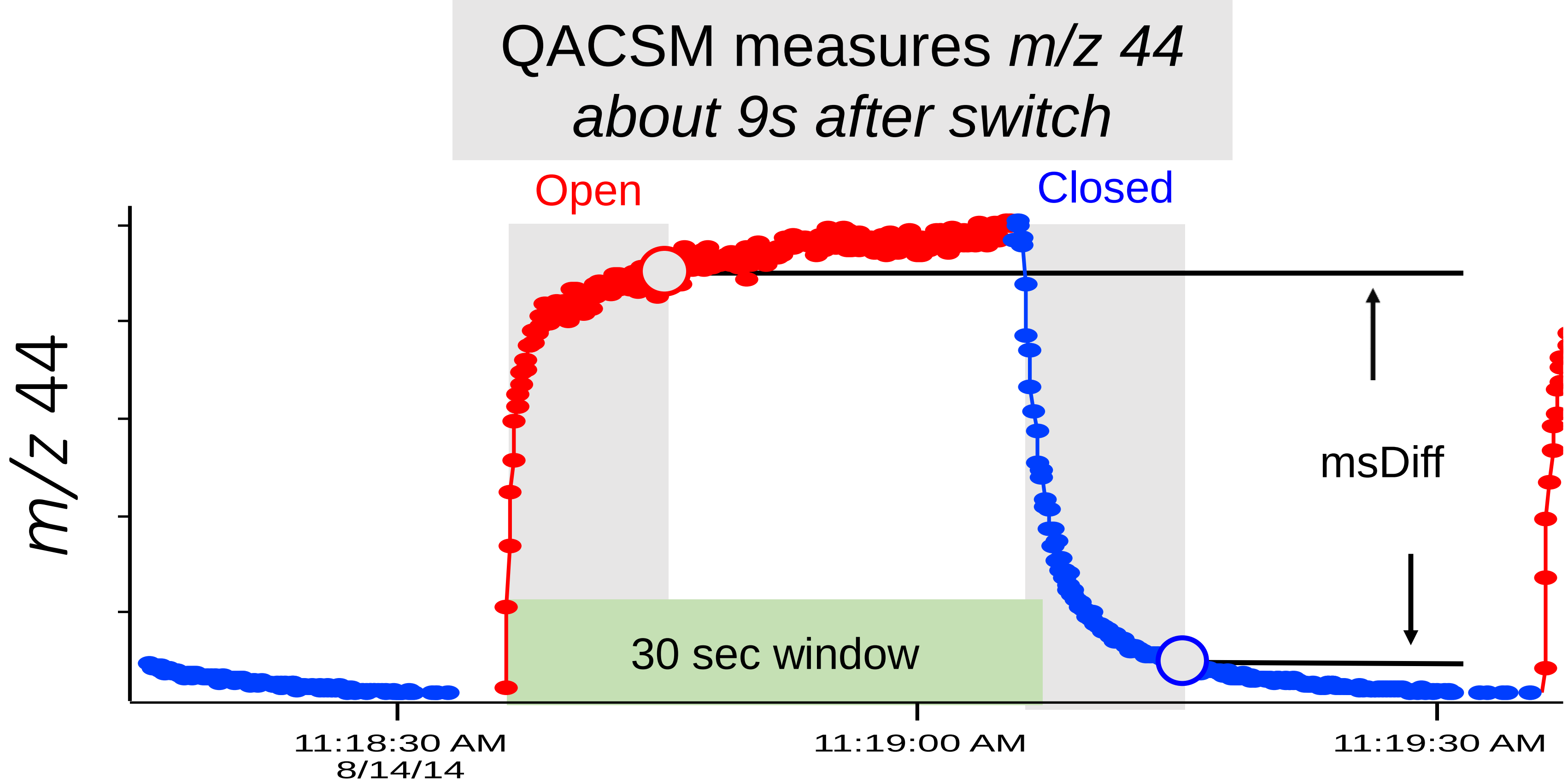
Slow rise and fall times of org44 signals on second timescales can introduce variability in f44



AMS MS open/closed : 5s (several thousand spectra)

pTOF : 2 ms, 50 μs (Single Particle)

Slow rise and fall times of org44 signals on second timescales can introduce variability in f44



QACSM 30s scan, one mass spectra 10-150 amu

Completely unrelated but happening in parallel with the ACSM Intercomparision experiment was an onging PSI SOA Chamber Experiments

Apparent Org concentration enhancements with added NH_4NO_3 seed aerosol

Work by Simone Pieber and colleagues, PSI

Past observations of this effect were always thought to be contamination of AN atomizer solution with organics!

Sources of *f*44 in AMS/ACSM Spectra

$$f_{44} = f_{44}\,(\text{F-dC}) + f_{44}\,(\text{S-dC}) + f_{44}(\text{Ox})$$

F-dC-Fast (*ms*) decarboxylation

-Flash Vaporization, single collision

-AMS O:C vs *f*44 calibration is based on this process

S-dC – Slow (*secs*) decarboxylation

-Decomposition of OM from trapped (in porous W) or bounced (ion chamber) particles.

-Capture Vaporizer accelerates/enhances this mechanism

Ox – Oxidation of trapped OM (char) on vaporizer

Oxidant from particle:

-NO_3 (fast *ms*) *(Simone's work at PSI)*

-SO4, or OOA (?)

A possible hypothesis describing the variability of *f*44

- Different data recording modes will sample the m/z 44 signal differently (main difference between AMS and ACSM).

- Long switching (open/closed) times can lead to build up of OM on the vaporizer.

- On a hot surface the accumulation of OM can lead to slow response in open-closed cycles and provide carbon for the oxidation mechanism.

2b. Influence of vaporizer surface

Charring: *removes hydrogen and oxygen* from the solid, char is composed primarily of carbon.

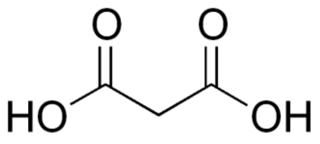
- AMS vaporizers that have been exposed to high levels of oxidized organic aerosol may have an accumulation of char.

- Char may also build up on the ion formation chamber.
- History of vaporizer is important

Lab generated aerosol used to Investigate *f*44

Acids with high O:C

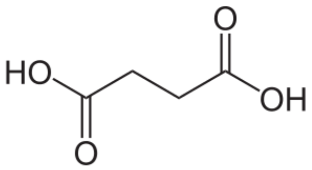
Malonic Acid $CH_2(COOH)_2$

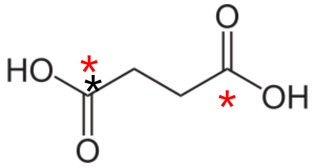


Succinic acid $(CH_2)_2(COOH)_2$

And

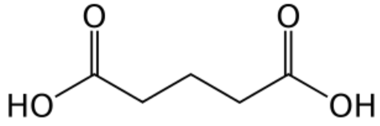
$(CH_2)_2(^{13}COOH)_2$





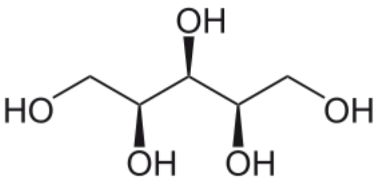
^{13}C labeled Succinic

Glutaric Acid $(CH_2)_3(COOH)_2$

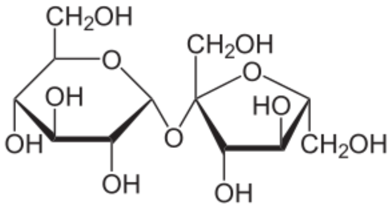


Non-Acids with high O:C

Xylitol $CH_2OH(CHOH)_3CH_2OH$

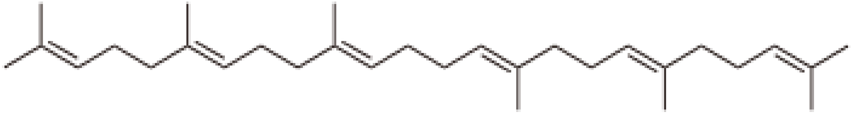


Sucrose $C_{12}H_{22}O_{11}$



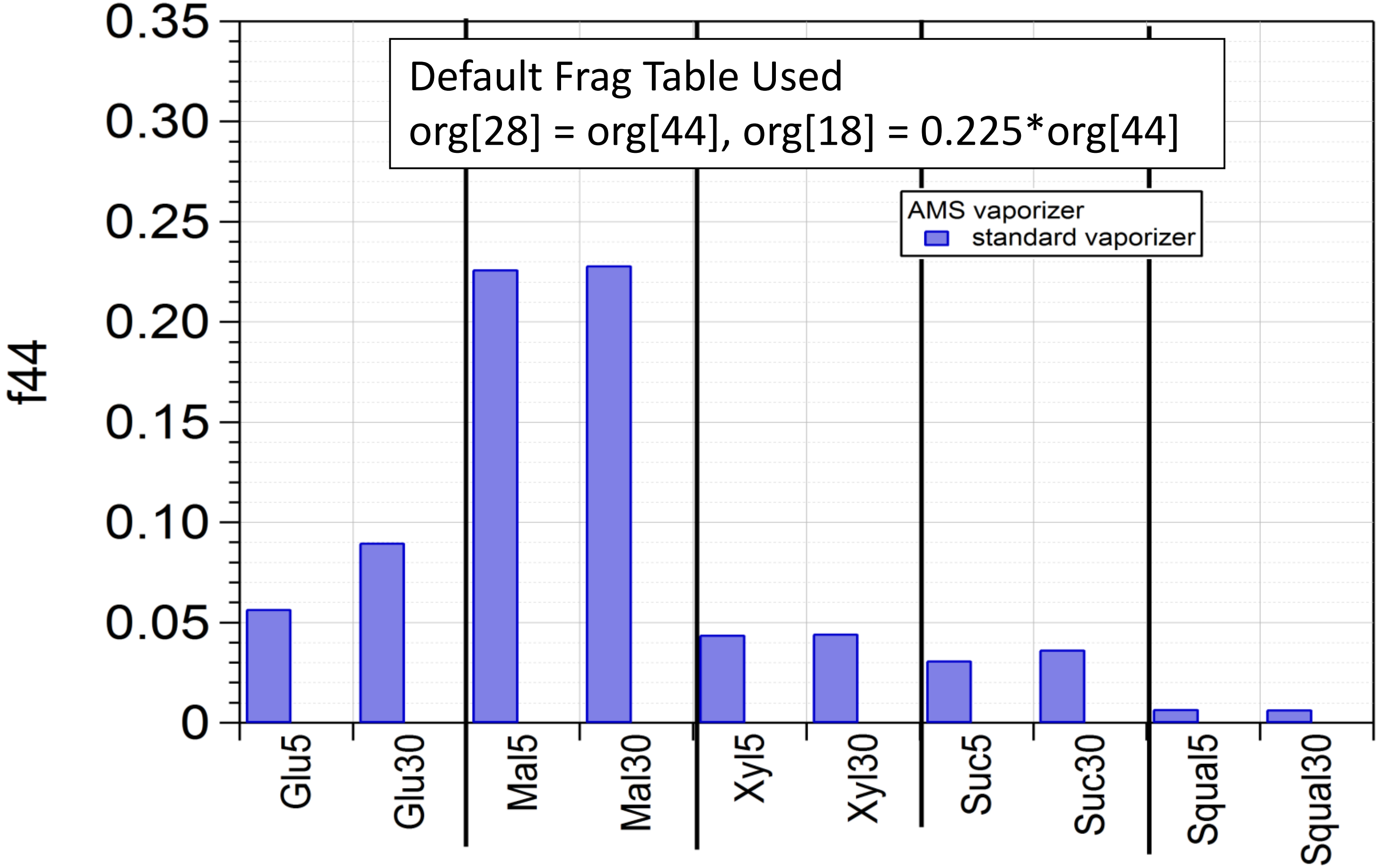
Hydrocarbon with no O

Squalane $C_{30}H_{50}$



PAM generated SOA (a-pinene oxidation)

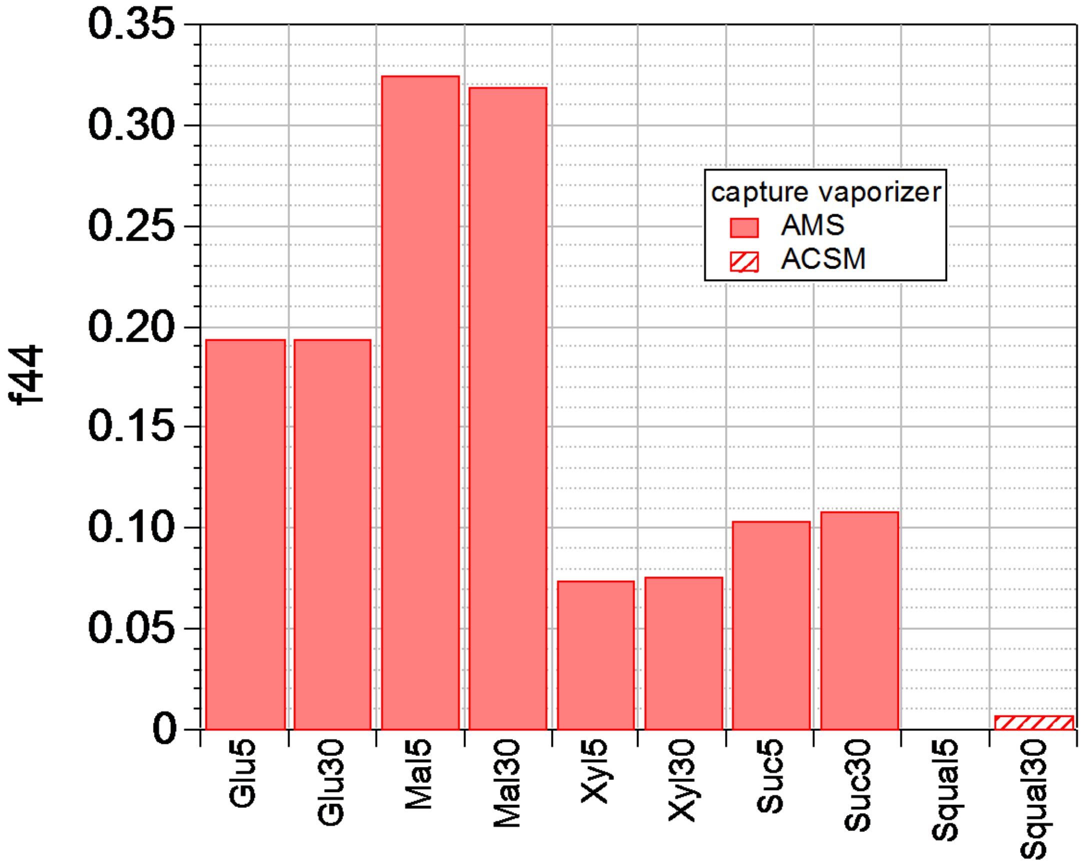
1a. Effect of measurement timescales on f44 (AMS - standard vaporizer)



Only glutaric acid shows variability in f44 for 5 and 30 s switching times.

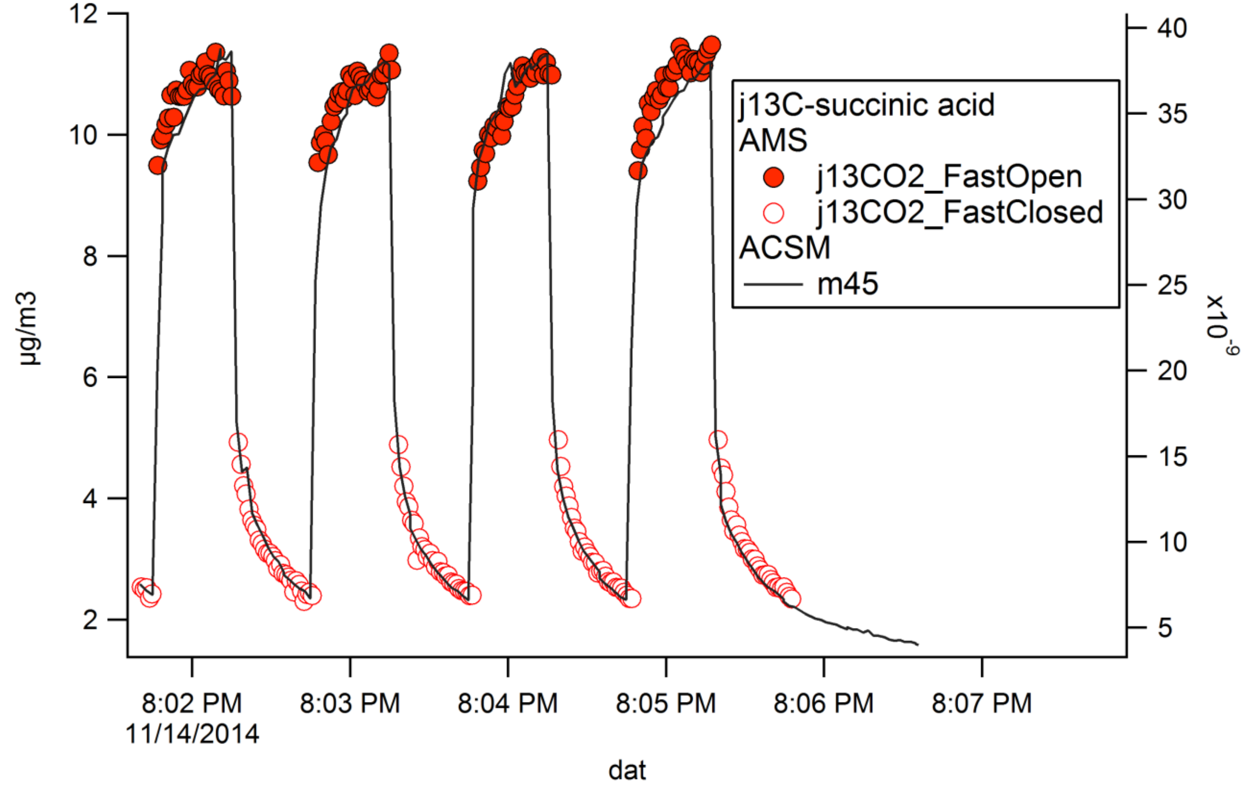
Xyl, Suc, and Squal do not have acid groups. Similar results between 5 and 30 s suggests minimal contribution of Ox mechanism for these species on these timescales

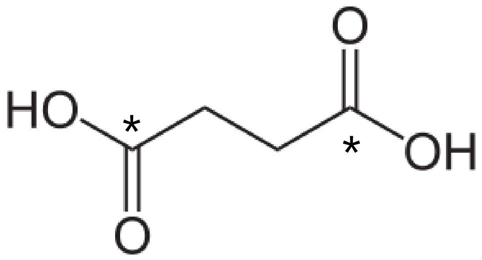
1a. Effect of measurements timescales on f44 (AMS with capture vaporizer-CV)



- Essentially no variability observed between 5 and 30 sec switching with CV.
- CV enhances f44 compared to Standard Vaporizer.
- For squalane, a hydrocarbon (C30H50), negligible 44 signal is observed (f44 < 0.01)…CO2 comes from acid group in particle.

1b. Case Study :13C Labelled Succinic Acid





- Slow time profiles observed for $^{13}CO_2$ formation
- The CO2 comes from the particle

2a. Variability in *f*44 From Vaporizer Bias Tuning

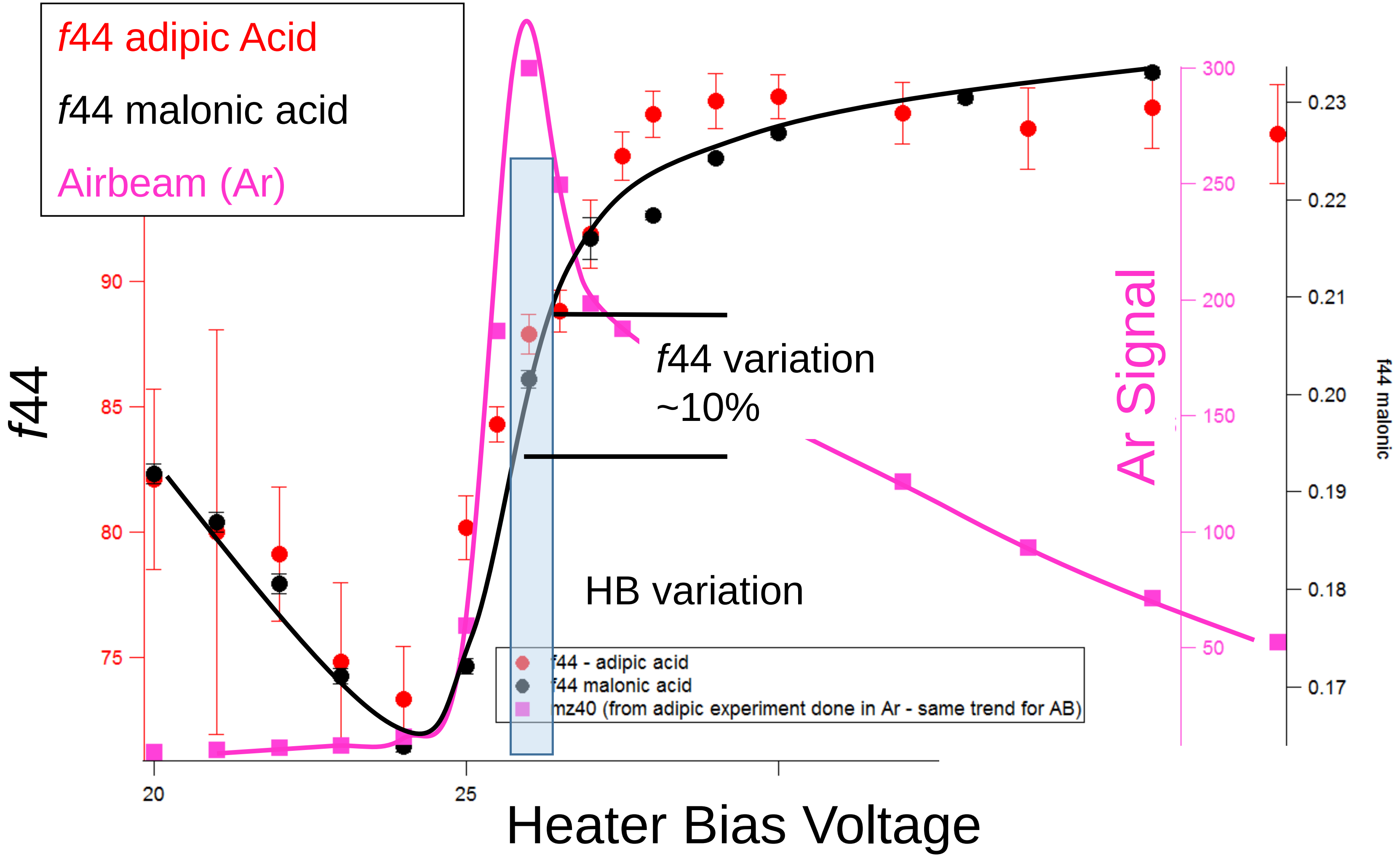
HB tuning can preferentially sample ions produced in different regions of the ionizer (i.e vaporizer vs. ionizer cage).

This effect can influence *f*44 ratios and 30/46 (others?)

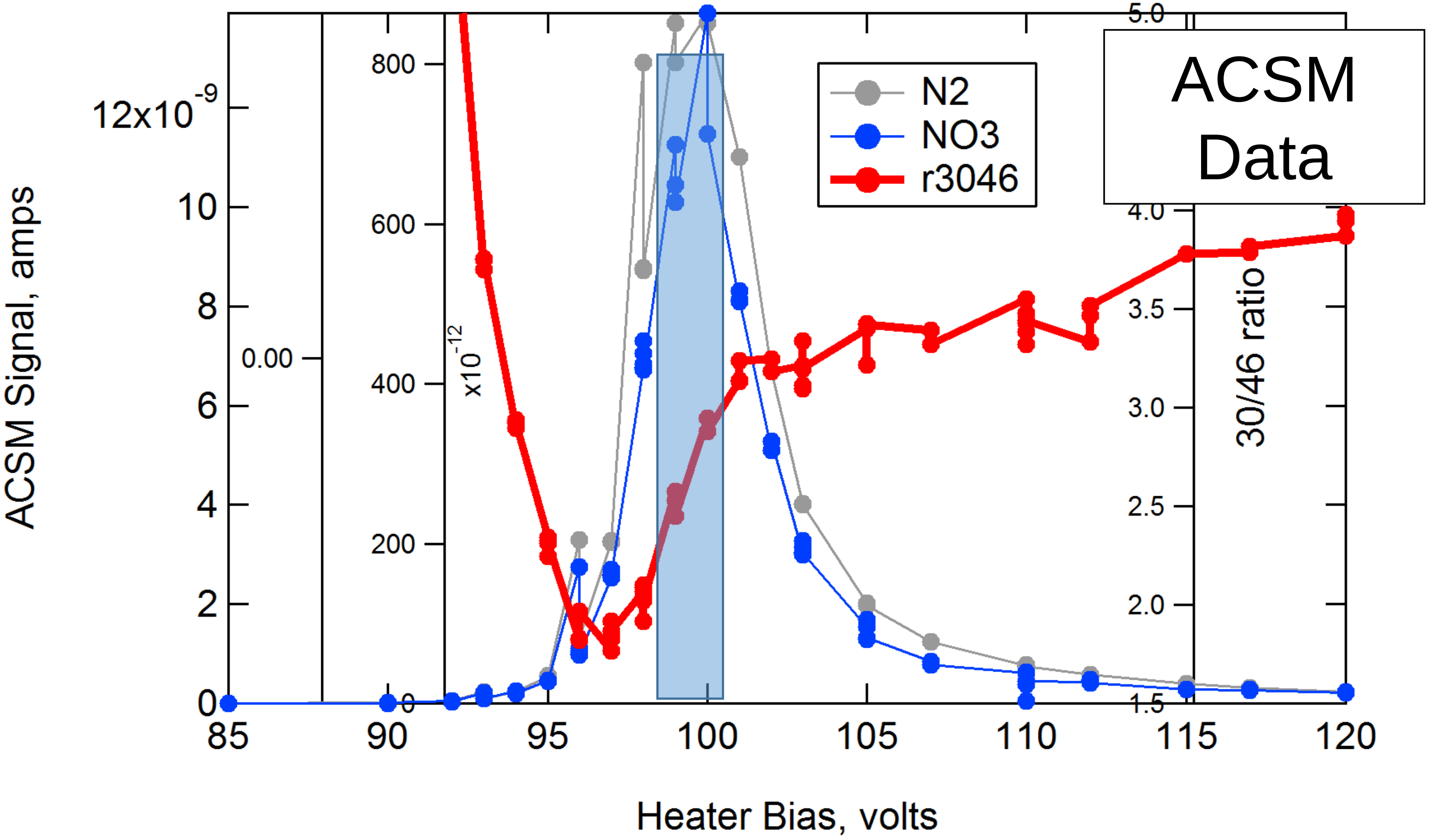
Variability in 30/46 and *f*44 ratios among instruments (AMS or ACSM) could be attributed to subtle changes in HB voltage?

2a. Trends in Ion signals with Heater Bias (AMS)

*f*44 ratio can depend on heater bias voltage



2a. Trends in Ion signals with Heater Bias



Ratio of m30/m46 can depends on HB

Similar trends observed in AMS

3. Can we correct for *f*44 variability?

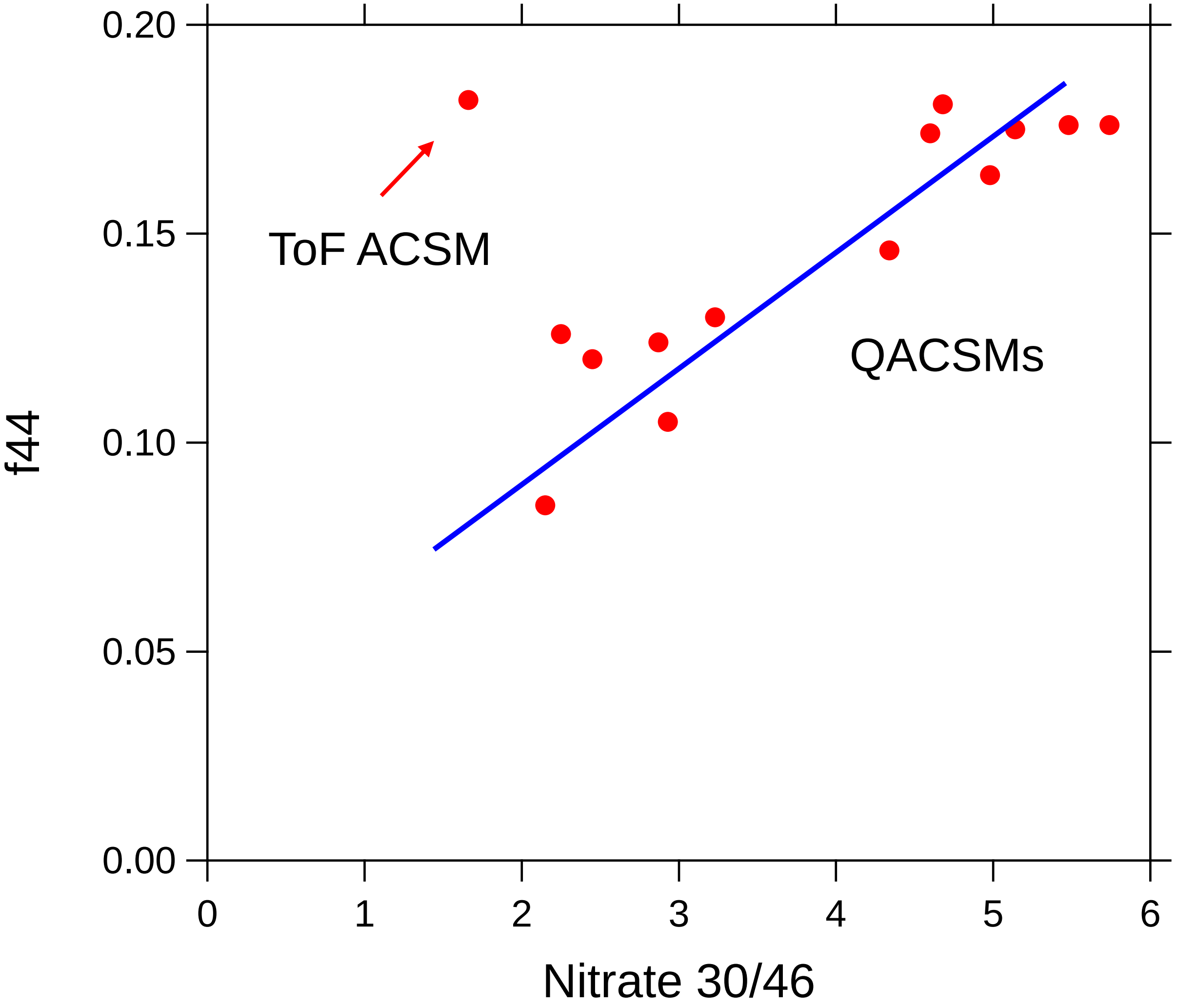
For ACSMs

A metric that correlates with f44 variability is 30/46 nitrate ratio. Looking into using this to derive a correction.

For AMSs

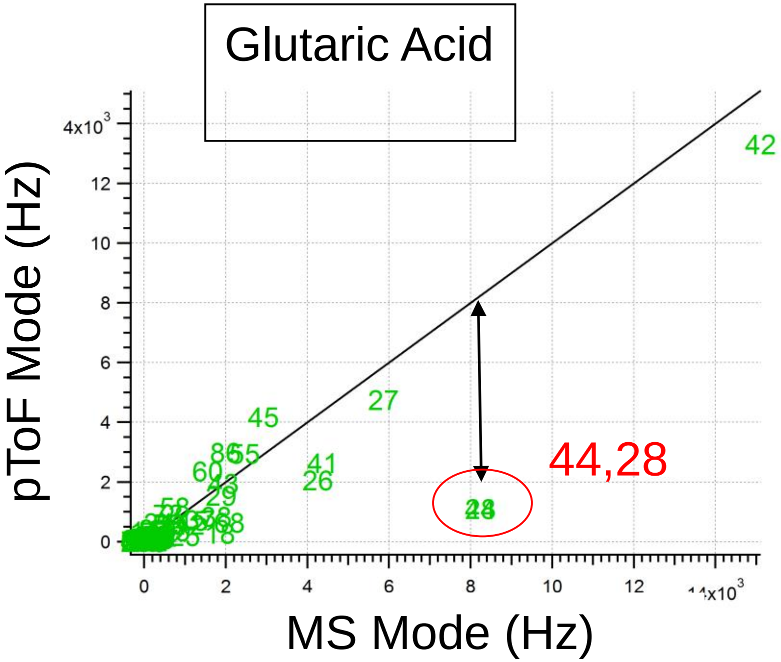
Plots of pTOF vs MS is a diagnostic for the extent of this effect and may provide a correction factor for f44. MS mode measures slowly vaporizing particles not measured in pToF mode.

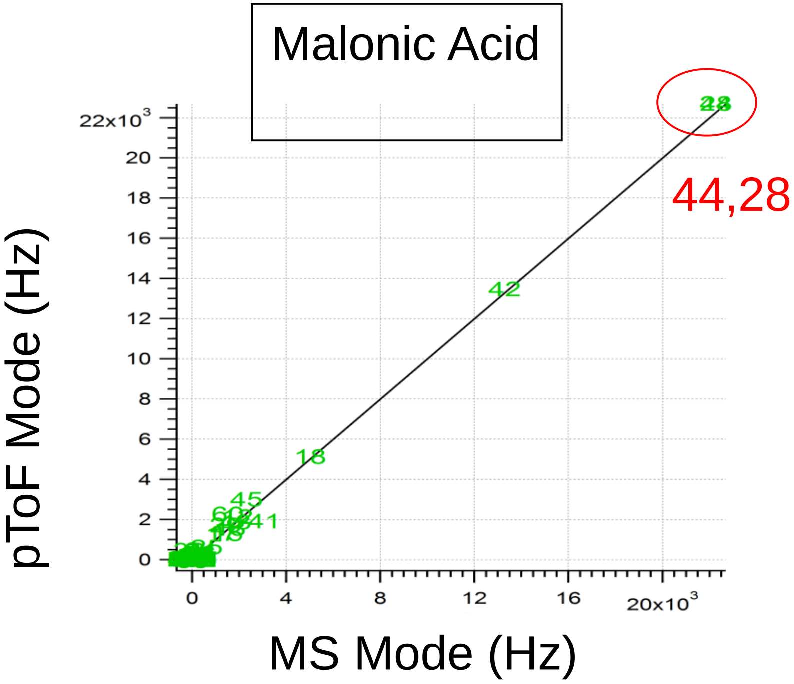
ACTRIS ACSM Intercomparison Data



ToF ACSM is outlier, it was operated with an 8min open – 2 min closed cycle

3. AMS MS/pTOF comparisons





The degree to which 44 falls off the pTOF/MS ratio of other ions is an indicator of the extent of the f44 issue.

The deviation from the line can be used to develop a correction.

This analysis can be applied on existing AMS data sets.

Summary

- The ACTRIS intercomparison has provided a unique opportunity to better understand particle vaporization and detection details in ACSM (and AMS) system.
- Mass 44 (and 18) from decarboxylation reactions can exhibit slow rise and fall (open/closed) times. Sampling this signal at different times can lead to different *f*44 ratios (difference between AMS and ACSM).
- The extent of the *f*44 variability depends on the history of the vaporizer.

Summary, continued

- Capture vaporizer enhances decaboxylation and minimizes sampling artifacts. A new *f*44 vs O:C calibration for CV will be needed.
- Heater Bias tuning can influence *f*44 and 30/46 ratios.
- Variation of *f*44 umong instruments does not impact PMF/ME2 results.

END