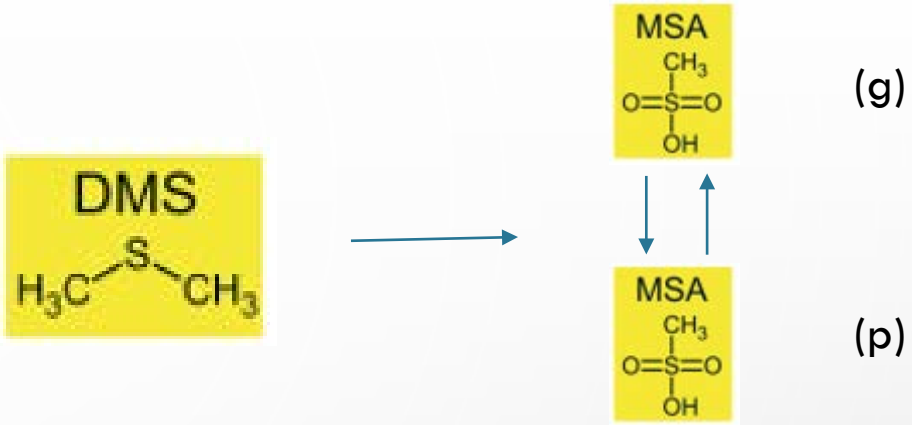

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DETERMINING THE RIE OF MSA

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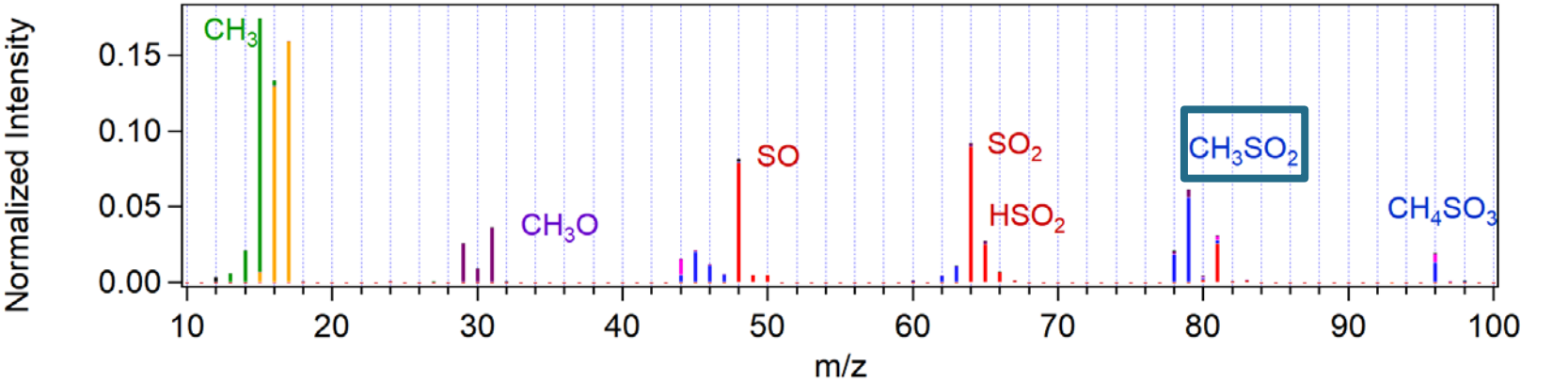
Hodshire et al, sub to ACPD

SOME BASICS

- MSA has been measured by AMS many times before
- Most studies use calibrated ratio of the very specific marker ion $CH_3SO_2^+$ to total ion counts to quantify MSA
- This ratio is pretty variable in the literature
- Importantly, the RIE of MSA was often not determined, just inferred
- MSA is semivolatile (P_{vap}= 6*10^{-4} Torr at 25°C), NH_4MSA is as semi-volatile as ammonium nitrate (T_{vap}=200°C)



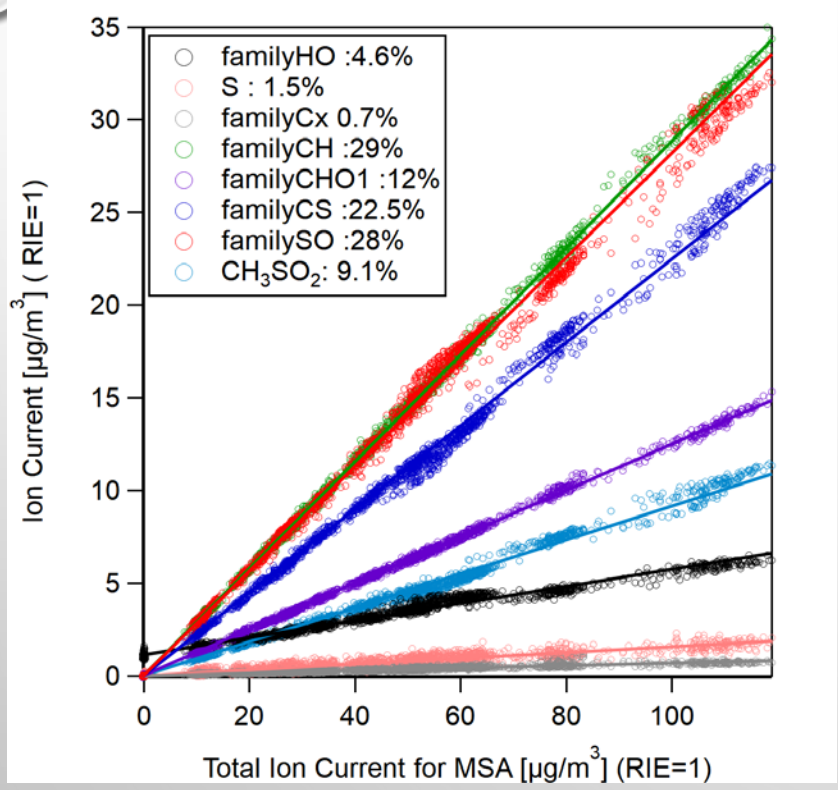
$$[MSA] = \frac{C}{CE}\frac{MW_{MSA}}{IE_{MSA}}\sum I_{MSA} = \frac{C}{CE}\frac{MW_{NO3}}{RIE_{MSA}\,IE_{NO3}}\frac{I_{CH3SO2}}{f(CH_3SO_2)}$$

Needed:

1. Total ion response for MSA (including sulfur, CO_2 and water)
2. Fraction of the marker ion, f(CH_3SO_2)
3. RIE of MSA

Phinney et al, 2006, Zorn et al, 2008, Ge et al, 2012, Schmale et al 2013, Huang et al, 2015, Huang et al, 2017

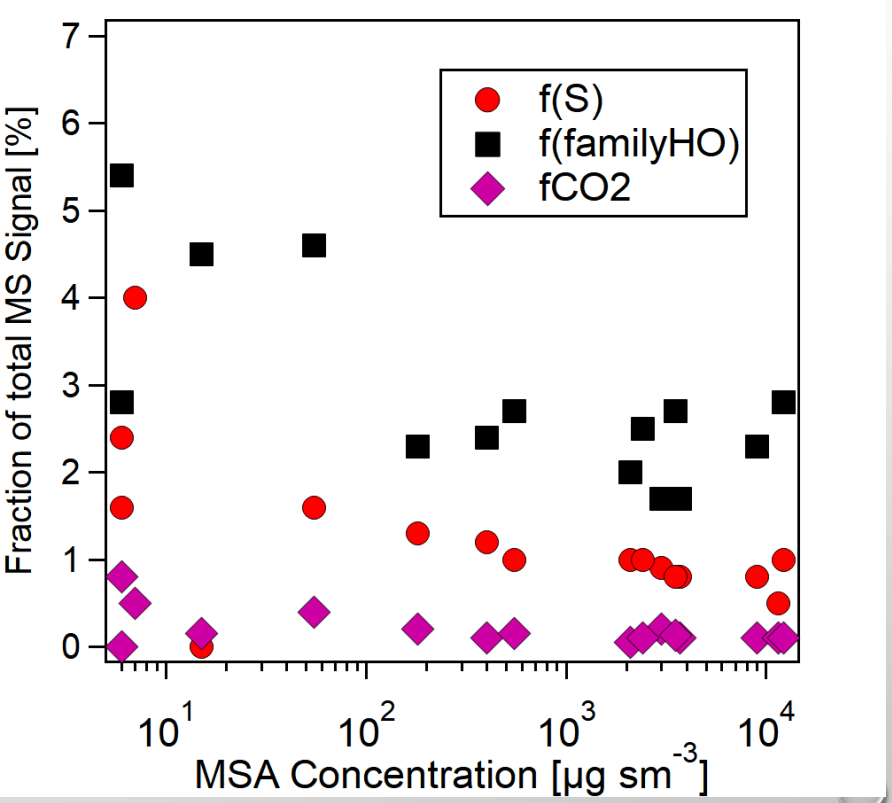
I. TOTAL MSA ION INTENSITY



Add up families with no background

Special cases:

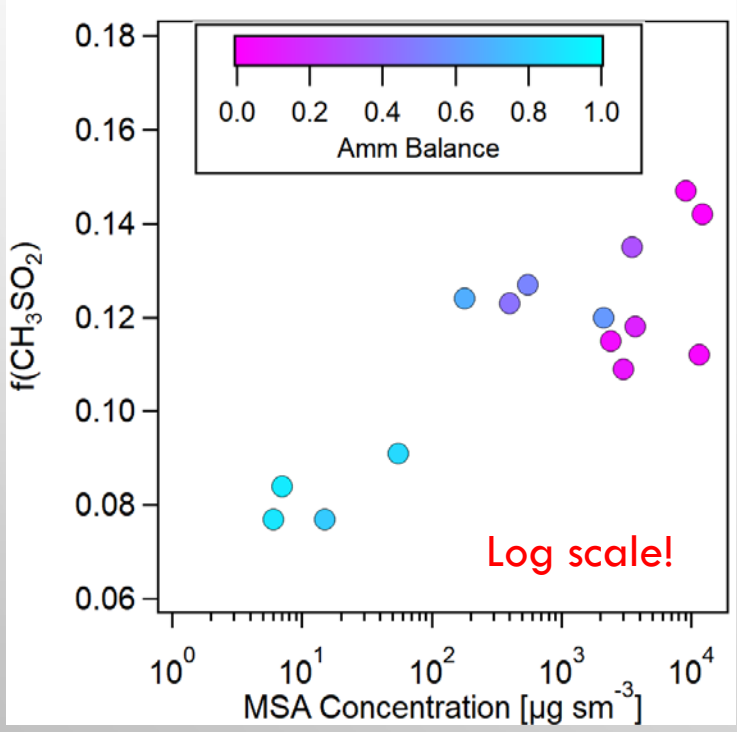
- Sulfur from fitting ^{34}S (or ^{32}S for >1 mg sm^3)
- Water and CO_2 from unconstrained regressions

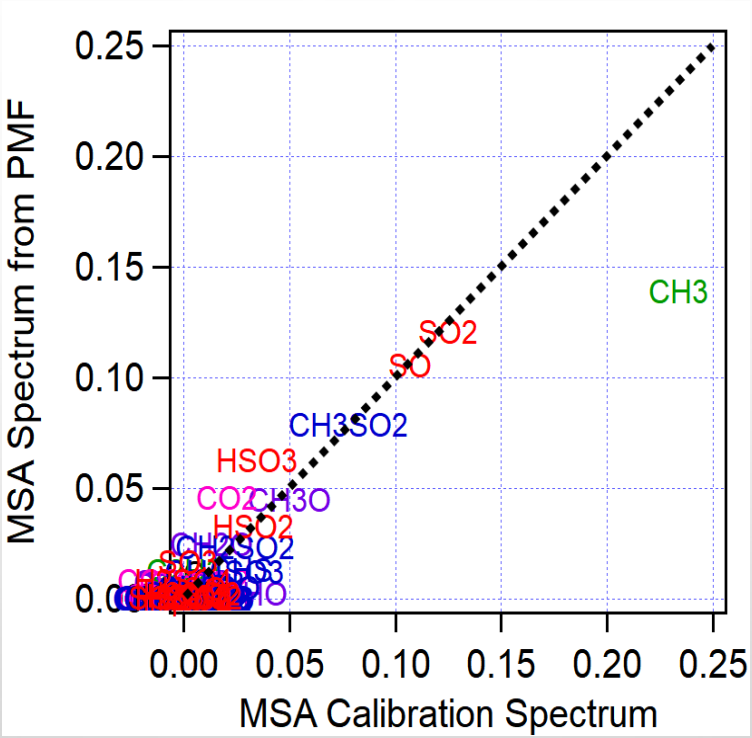


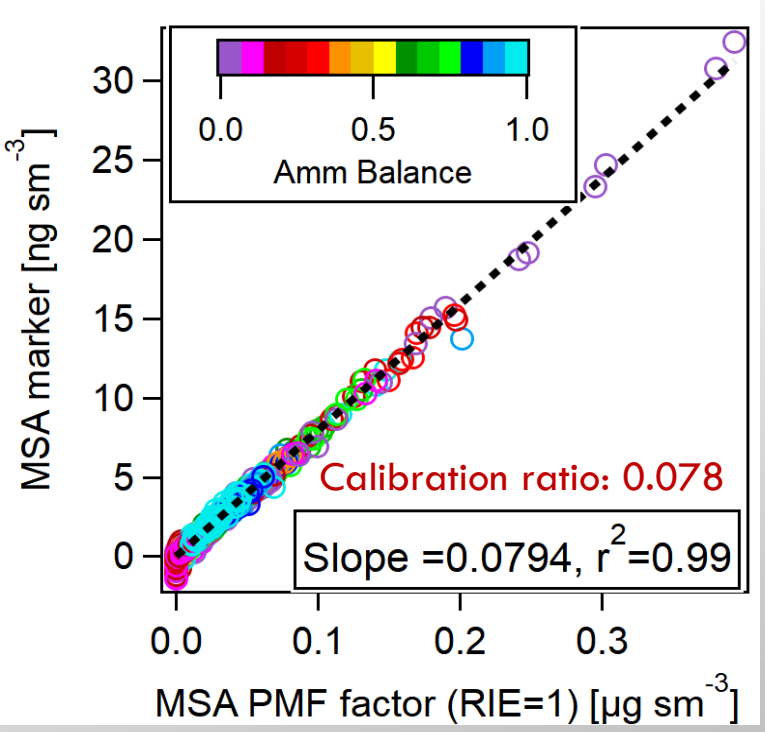
- Sulfur and Water account for 1+3~4% (Sulfate: 8+31~39%)!
- CO_2 is negligible (CO likely as well)

II. FRACTION OF $CH_3SO_2^+$

Ambient data PMF (OA + SO_x, ATom-1) to the rescue !!





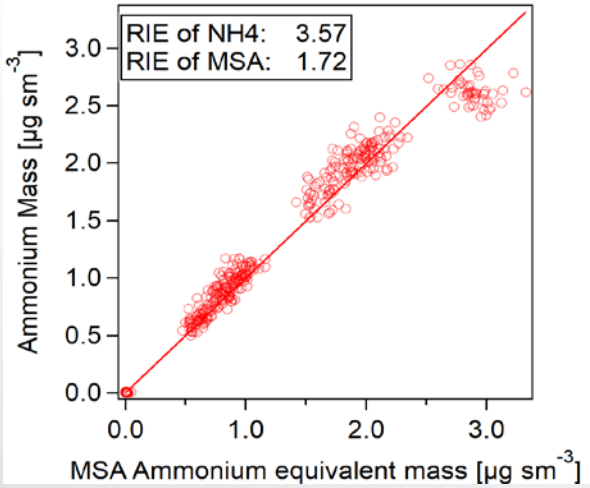


- Low concentration calibration of AMSA agrees with PMF
- No evidence for $f(CH_3SO_2)$ being a function of particle acidity

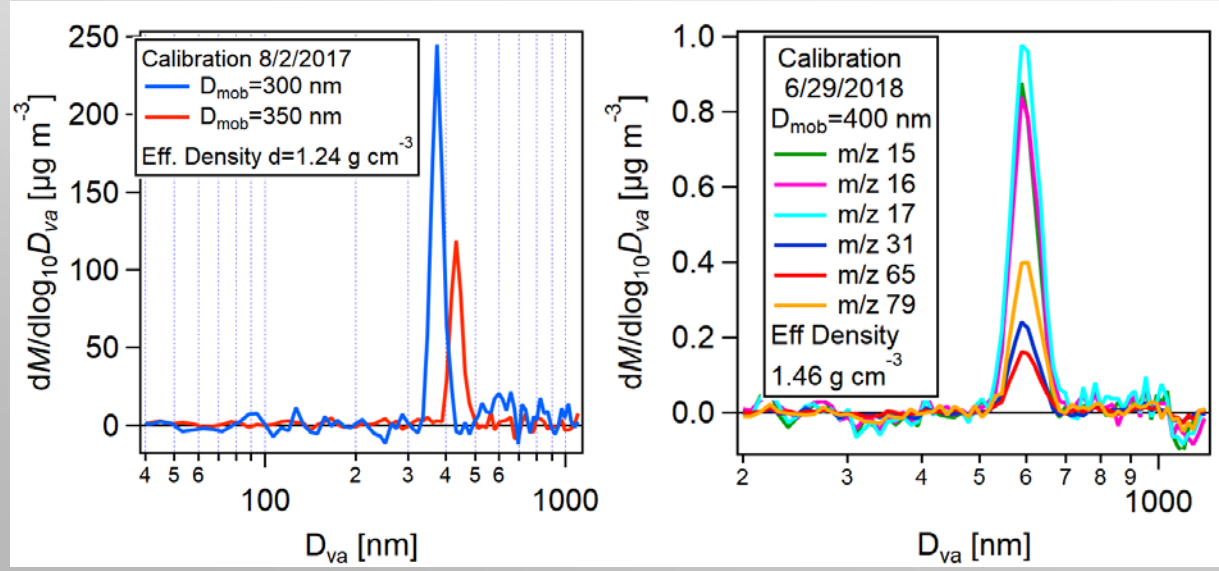
Zorn et al, 2008

III. RIE OF MSA

1. RIE from Ammonium Balance

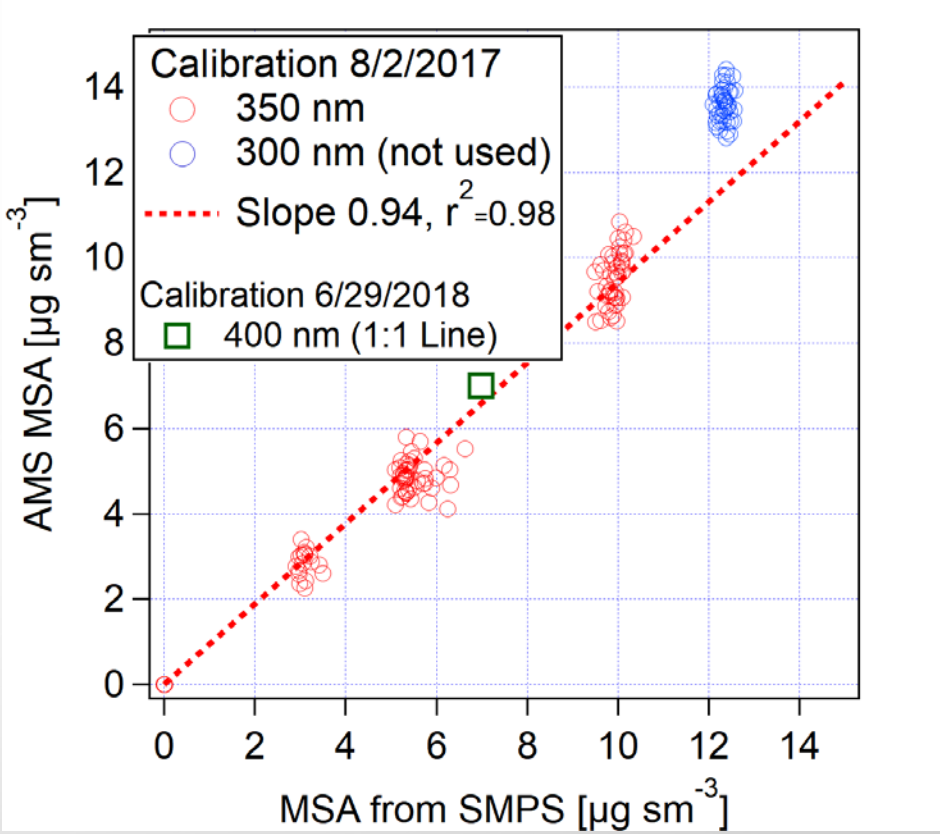


2. Monodispersity and Density from ePToF



3. CE of 1 determined from ET

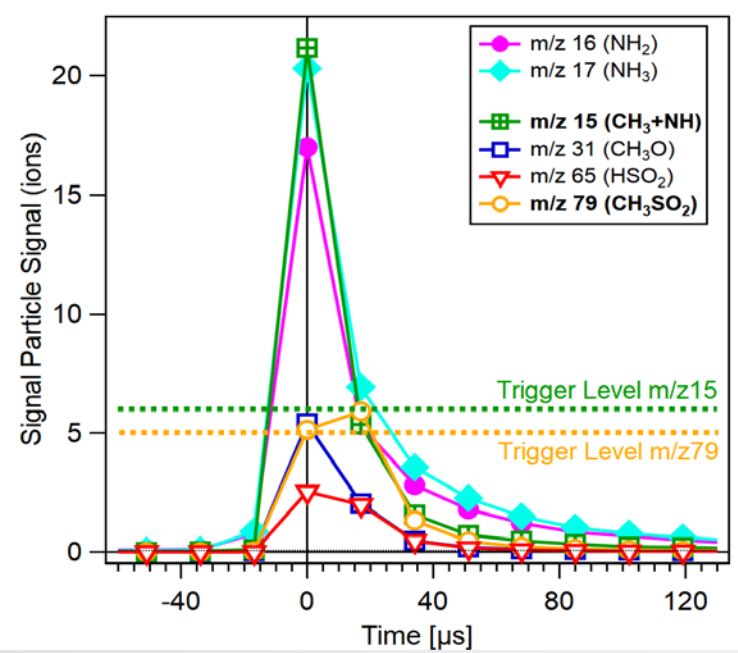
4. Sanity Check

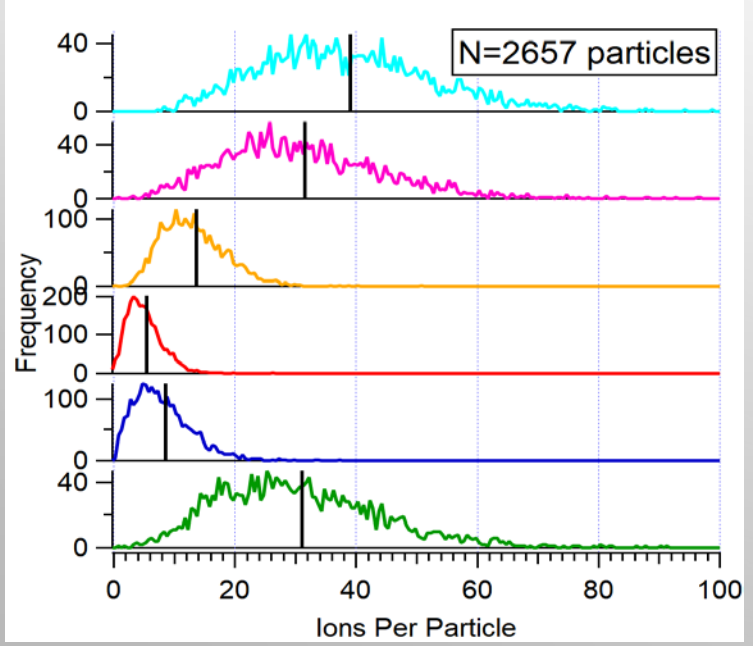


RIE(MSA)=1.70± 0.08

- Despite the very different water and sulfur contributions, RIE is very similar to sulfate
- On the high end of previous values

RIE OF MSA FROM ET





ET experiments with 400 nm AMSA particles (triggering on CH_3 and CH_3SO_2) showed CE=1

An RIE can be calculated from the ratio of Ions Per Particle for MSA vs Nitrate in back-to-back ET Calibrations:

$$RIE_{MSA} = \frac{IE_{MSA}}{IE_{NO3}}\frac{MW_{NO3}}{MW_{MSA}} = \frac{IPP_{CH3SO2*}{}^{1}/_{f(CH3SO2)}}{IPP_{NO3}}\frac{\rho_{ANO3}}{\rho_{AMSA}}\frac{MW_{AMSA}}{MW_{ANO3}}\left(\frac{D_{ANO3}}{D_{AMSA}}\right)^{3}\frac{MW_{NO3}}{MW_{MSA}}$$

However, the results were less than impressive (RIE in previous experiments was 1.70!)

Ion	IPP	f(Ion) [%]	Calc RIE
CH_3SO_2	13.05	7.8	1.42
CH_3O	8.5	5.0	1.45
HSO_2	5.5	3.3	1.36
CH_3	31.05	23.2	1.02
SO_2	5.71	5.2	0.87
Sum(NH_x)	72.4	100	1.7

RIEs calculated this way are 25% to 60% too low!

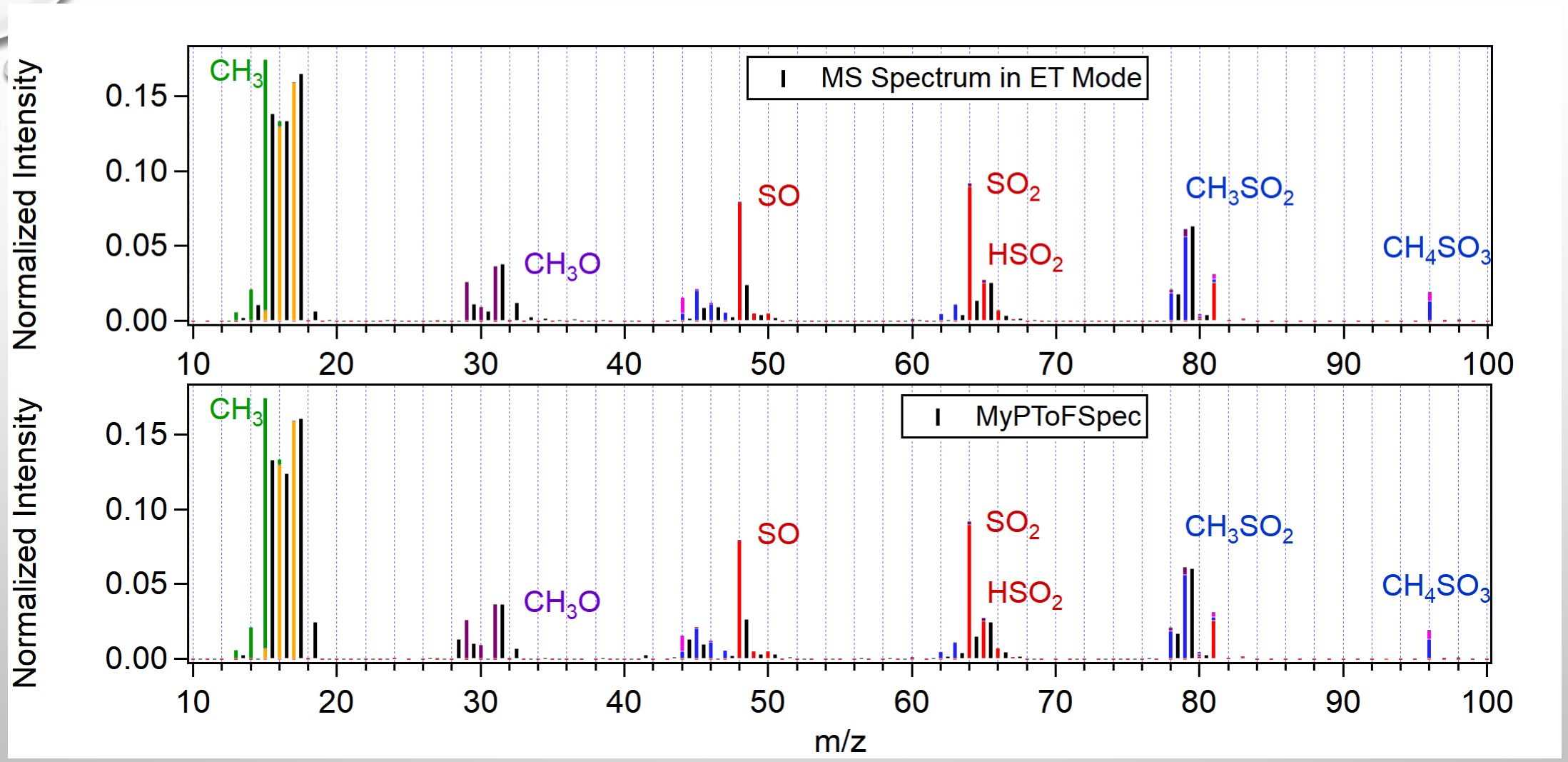
However, using:

$$RIE_{MSA} = \frac{RIE_{NH4}}{RIE_{NO3}}\frac{IPP_{NH4}}{IPP_{MSA}}\frac{MW_{MSA}}{MW_{NH4}}$$

works IF we use the RIE_{NH4} from ET (not squirrel)

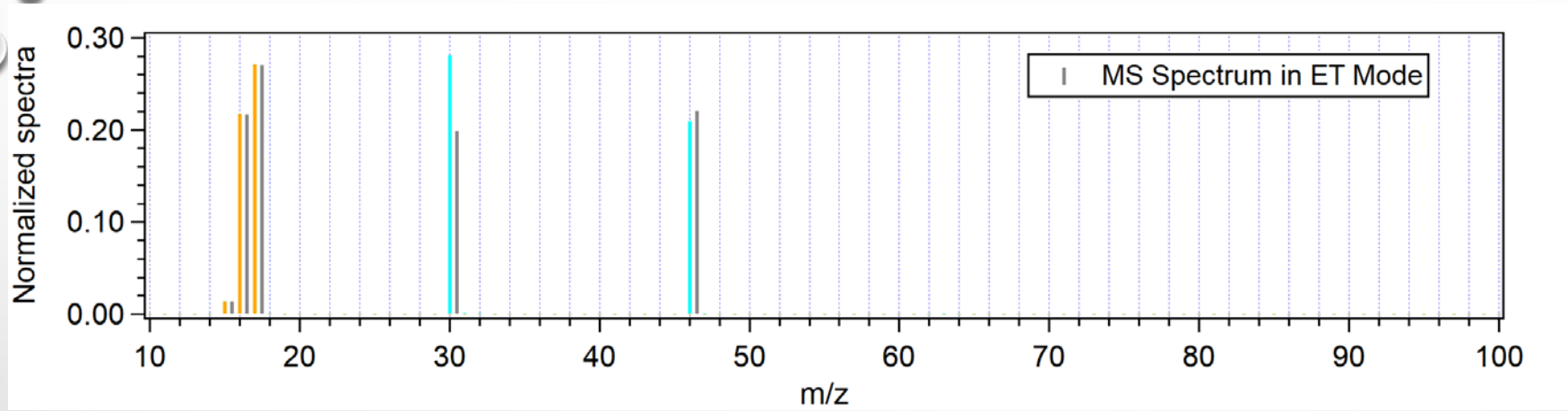
???

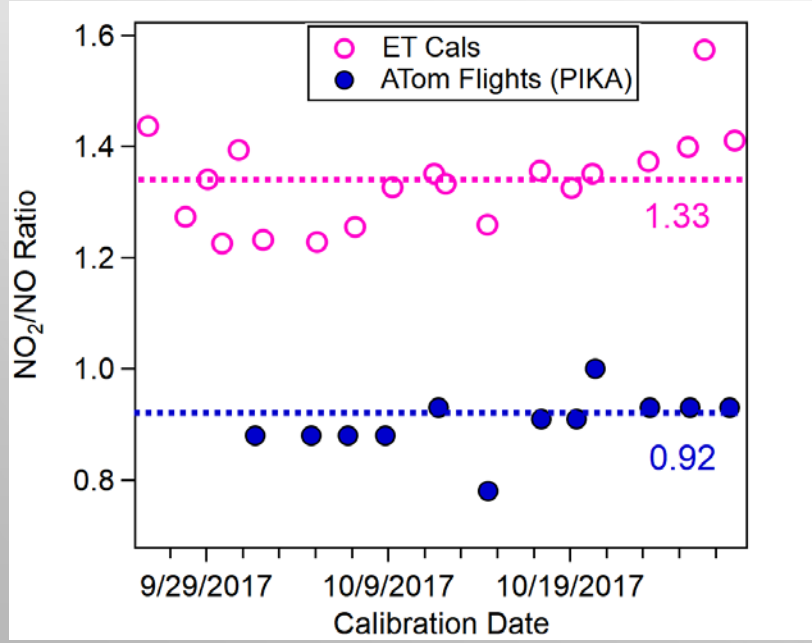
1.SO WHY ARE THE RIES FOR SOME IONS SO LOW?

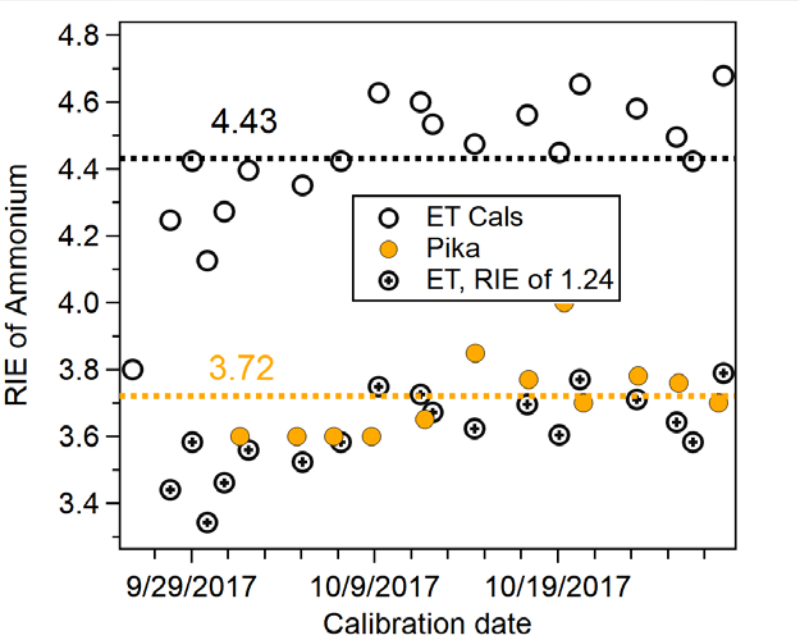


- About 30% of the total MSA mass is not present in the ET Spectrum, especially in SO_x
- This is NOT PARTICLE BOUNCE (CE=1!!), but slow evaporation from vaporizer (PTOF looks like ET)
- Using the fractional contributions in the ET spectrum lines all MSA ions up
- But they are still low by ~20%

LET'S LOOK AT ANOTHER SV AEROSOL WITH CE=1: AMMONIUM NITRATE



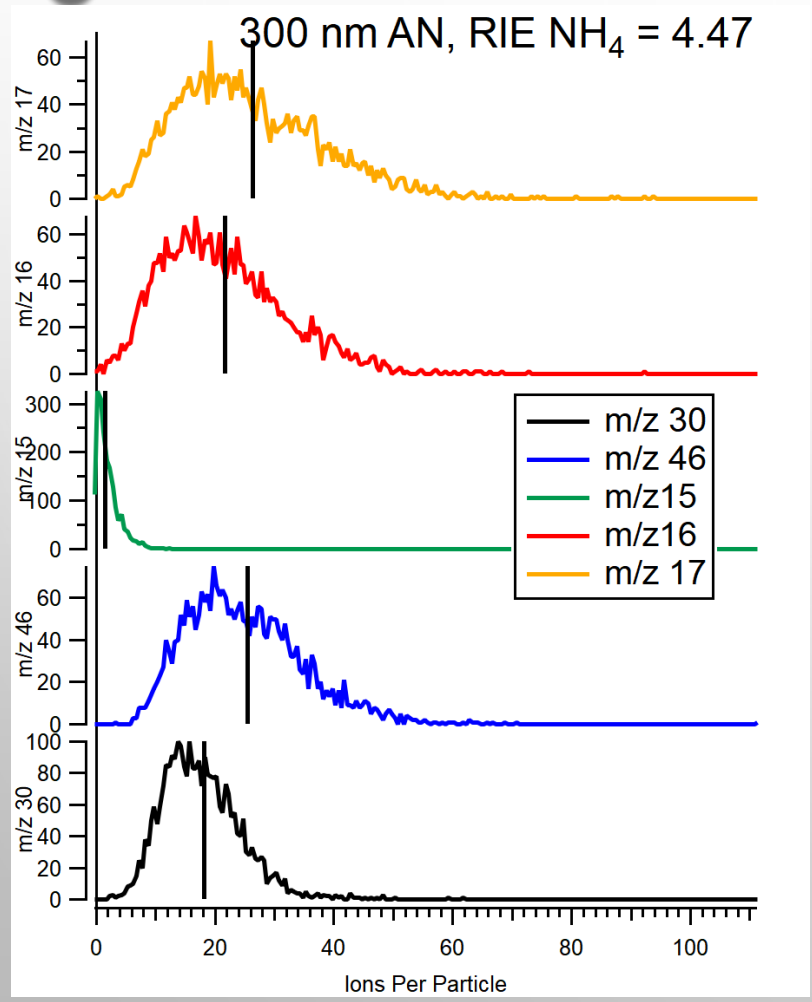


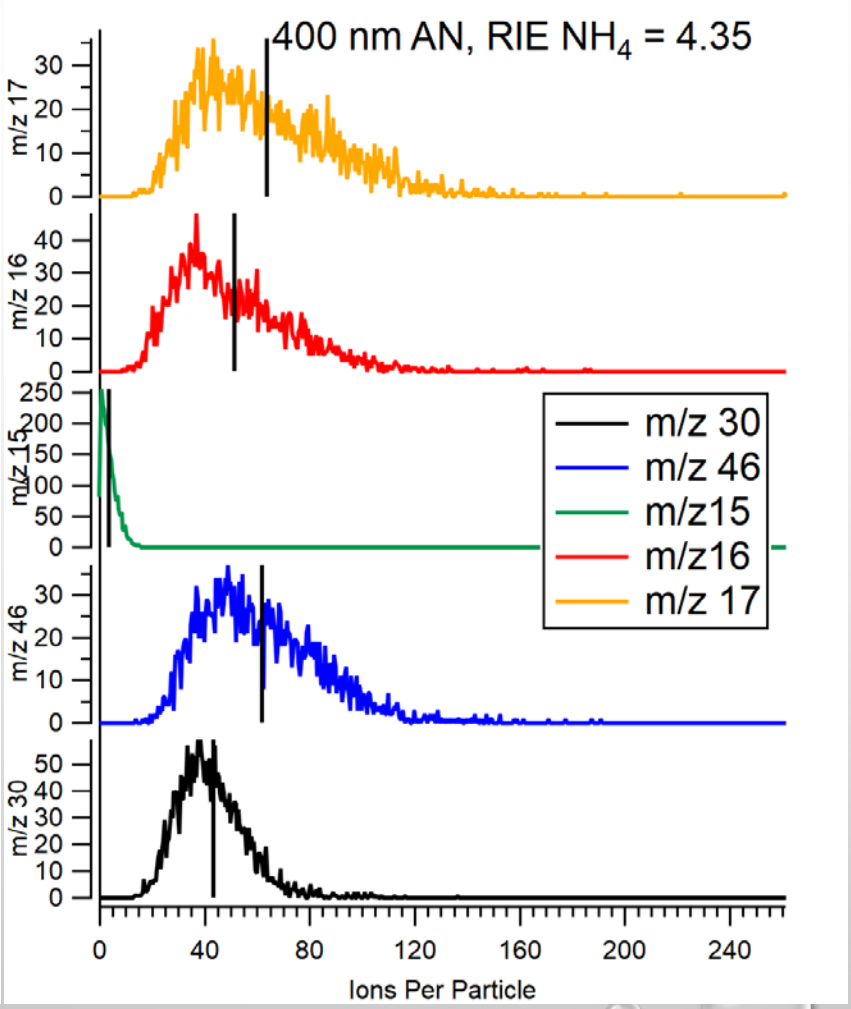


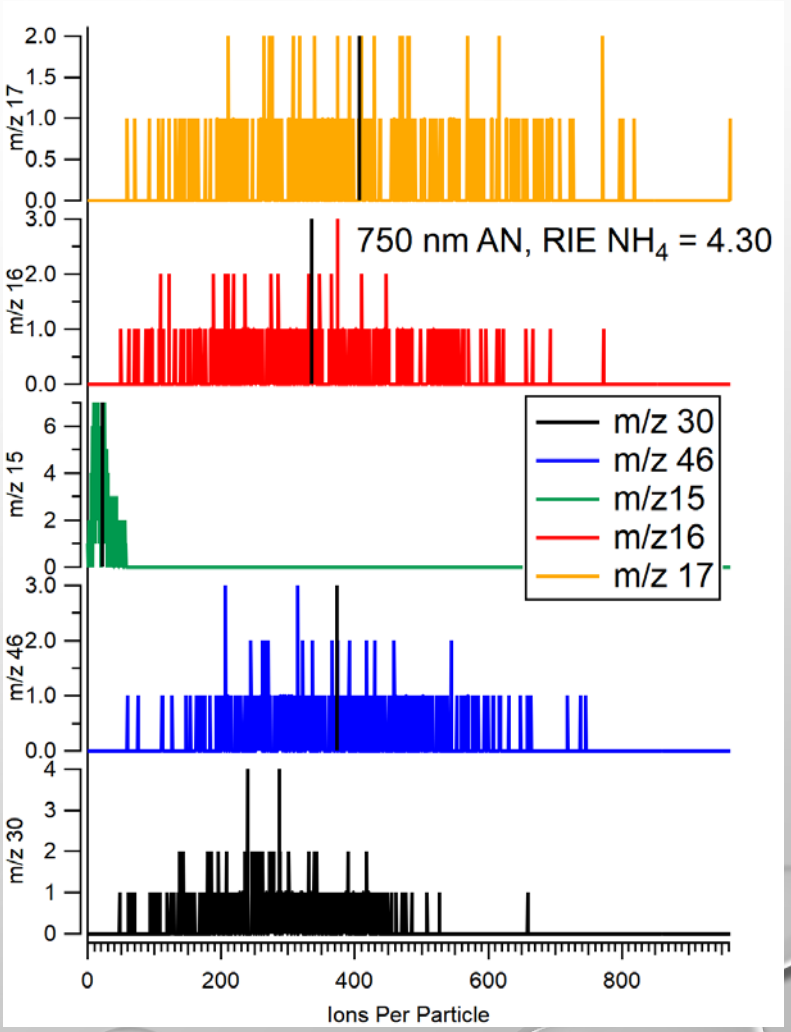
- Signal from NO^+ is missing in ET (vs squirrel) due to slow evaporation
- Hence the IE of NO3 needs to be corrected for the missing mass
- For ATom-3, that would suggest an RIE of NO_3 of 1.19 (+0.05 or +0.1 to account for N and HNO_3)
- With this correction, RIE of NH_4 (and of MSA) matches up!

ADDITIONAL SLIDES

SOME AN DATA


300 nm AN, RIE NH_4 = 4.47
m/z 17
m/z 16
m/z 15
m/z 46
m/z 30
m/z 30
m/z 46
m/z15
m/z16
m/z 17
Ions Per Particle


400 nm AN, RIE NH_4 = 4.35
m/z 17
m/z 16
m/z 15
m/z 46
m/z 30
m/z 30
m/z 46
m/z15
m/z16
m/z 17
Ions Per Particle


750 nm AN, RIE NH_4 = 4.30
m/z 17
m/z 16
m/z 15
m/z 46
m/z 30
m/z 30
m/z 46
m/z15
m/z16
m/z 17
Ions Per Particle