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SP-AMS rBC calibration: Bulk vs. Event Trigger

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SP-AMS quantification and calibration uncertainties

Quantification

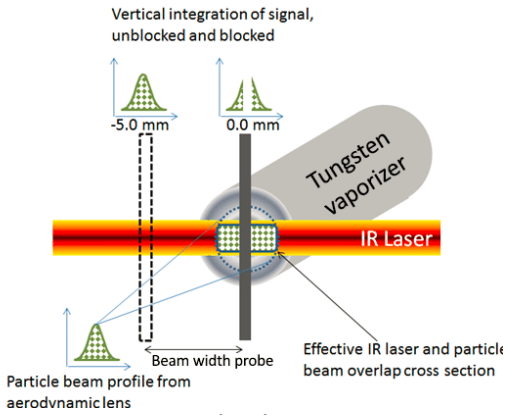
- Dual vaporizers
  - $CE_{Tungsten} = E_{Lens} \cdot \mathbf{E_{Bounce}} \cdot E_{shape}$
  - $CE_{Laser} = E_{Lens} \cdot E_{Bounce} \cdot \mathbf{E_{shape}}$
- Laser-only vaporizer
  - CE_{Laser} (no bouncing)
  - **No quantification of coating**
- Dual and laser-only vaporizer
  - Particle beam – laser beam overlap
  - Are IE/RIE comparable after removal of tungsten vaporizer?

Calibration approach

- Mass-based
  - Relies on CPC mass measurement
  - DMA, doubly charged particles, laser alignment, etc…
- Single particle-based
  - Relies on ions detected in single particle
  - No CE or CPC biases

➔ Explore the use of single particle for laser-only calibration

Beam width probe



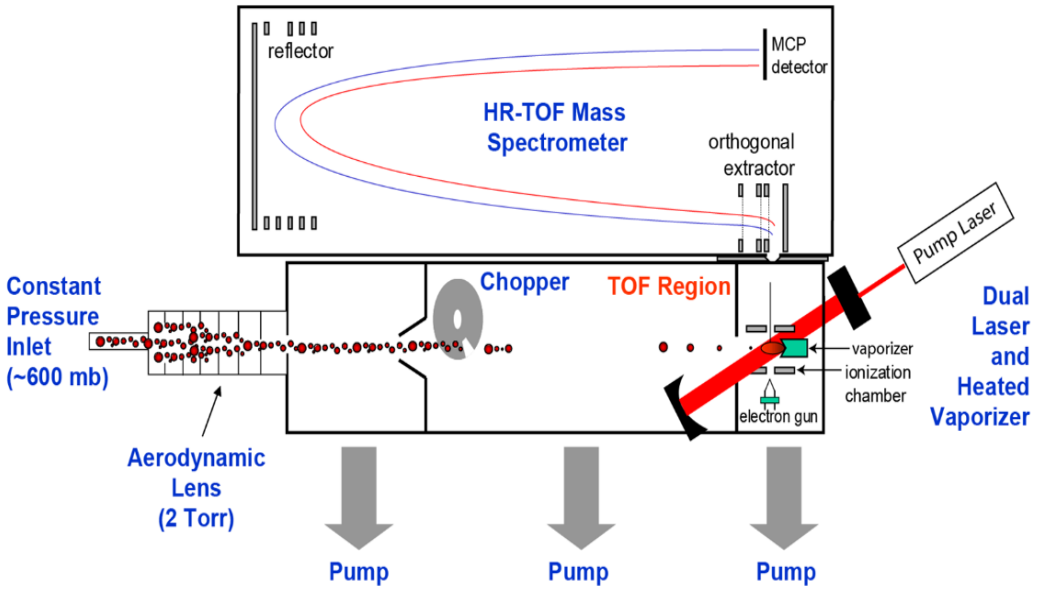
Adam et al. AMT, 2016

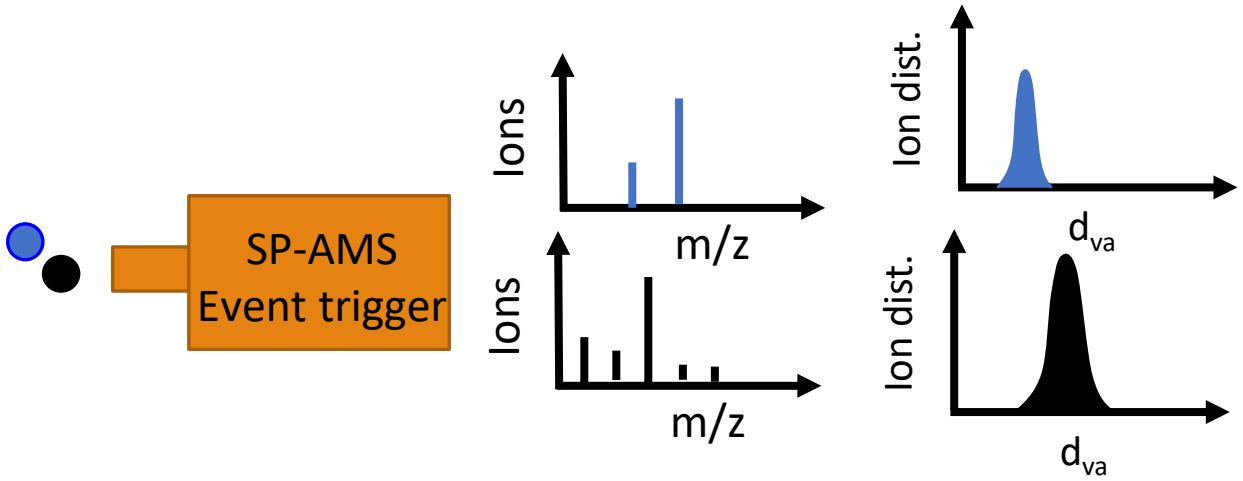
Objectives of this experiment

1. Investigate the differences between mass-based (bulk) and single particle-based calibrations

2. Toward the quantification of BC coating with laser vaporizer

SP-AMS vaporization & detection scheme





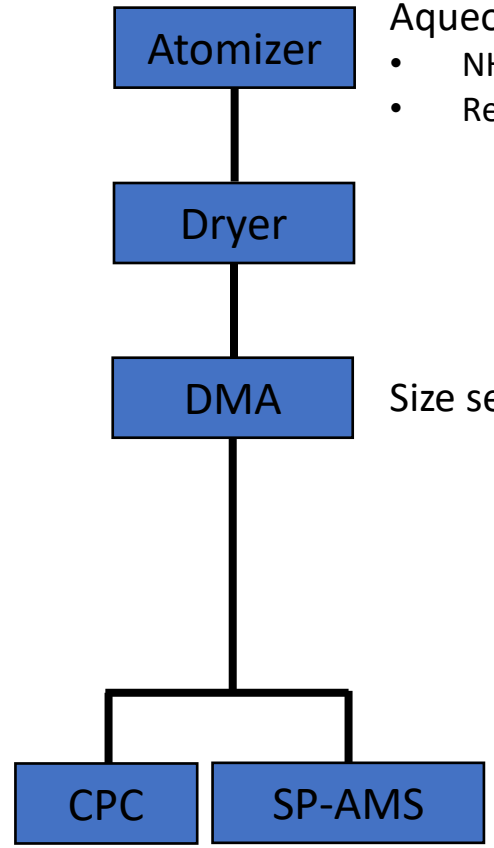
Dual vaporizer : Laser + Tungsten vaporizers

- Laser off ➔ NR-PM_1 $CE_{Tungsten}$
- Laser on ➔ NR-PM_1& rBC+coating $CE_{Tungsten} + CE_{Laser}$

Event Trigger (E.T)

- Single particle composition + size

Calibration set-up & dual mode mIE estimation



Aqueous mixtures:
- NH_4NO_3 (AN)
- Regal black (RB)

Size selected: 300 nm

~300#/cc

- Dual vaporizer
- Bulk and Single Particle

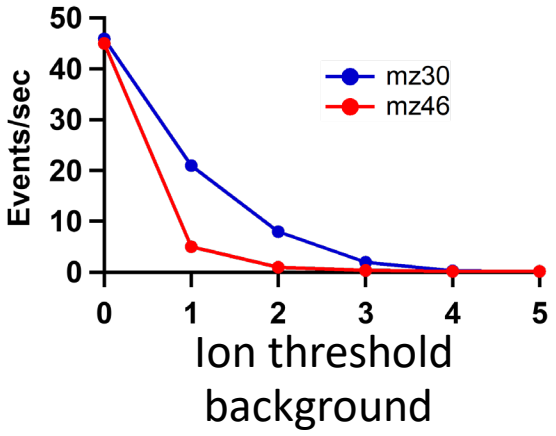
Effect of E.T settings on mIEs estimation

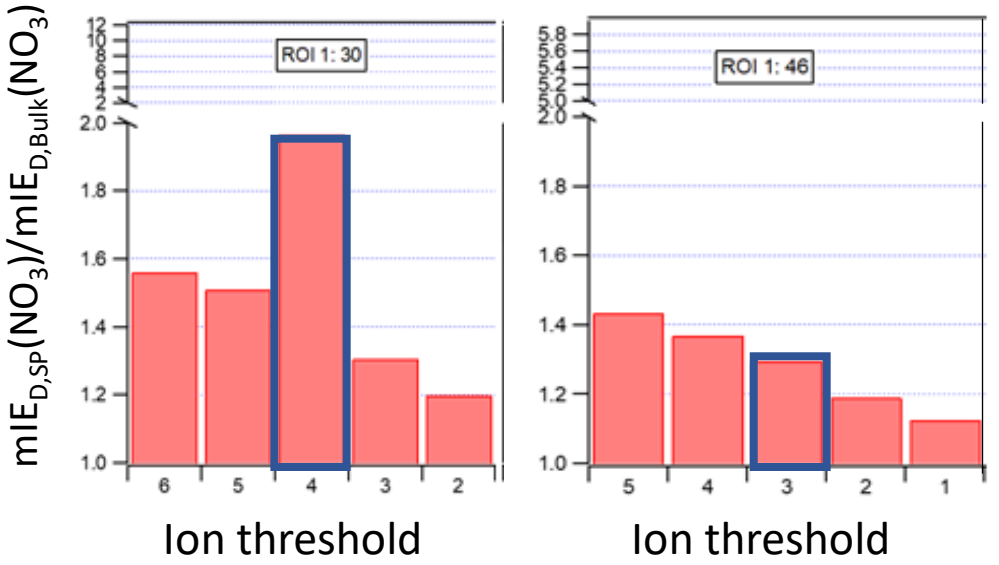
Species	Vap.	Calibration method	Parameter meas.
AN pure RB pure	Dual (D)	Total mass based (Bulk)	$mIE_{D,Bulk}(NO_3)$, $mIE_{D,Bulk}(RB)$,
		Single particle (SP)	$mIE_{D,SP}(NO_3)$, $mIE_{D,SP}(RB)$,

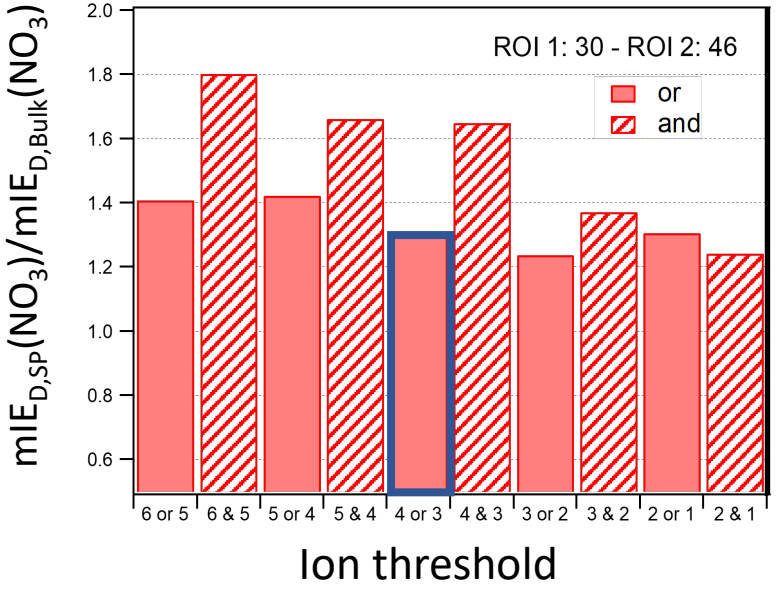
Parameters tested for NO_3 and RB

- Number of ROIs
- Ion Threshold for each m/z
- "And" or "Or" condition

E.T settings: effects of ROI and IT on $mIE_{D,SP}(NO_3)$ estimation



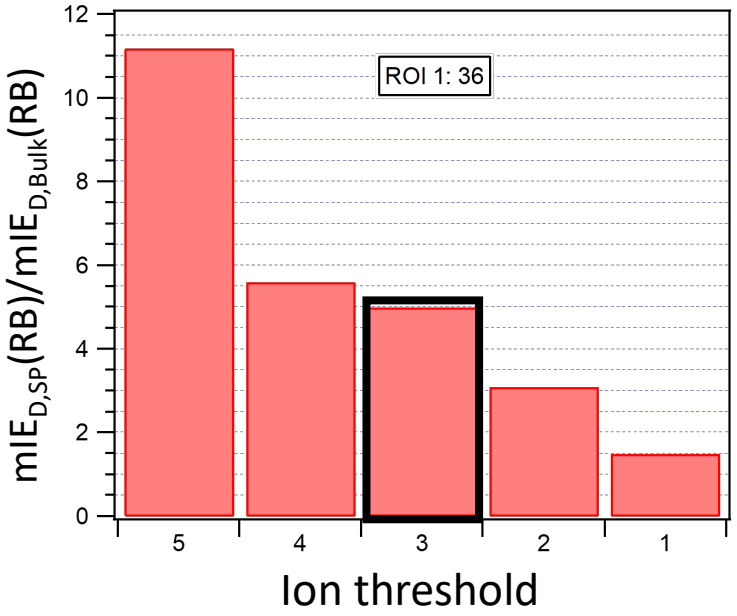


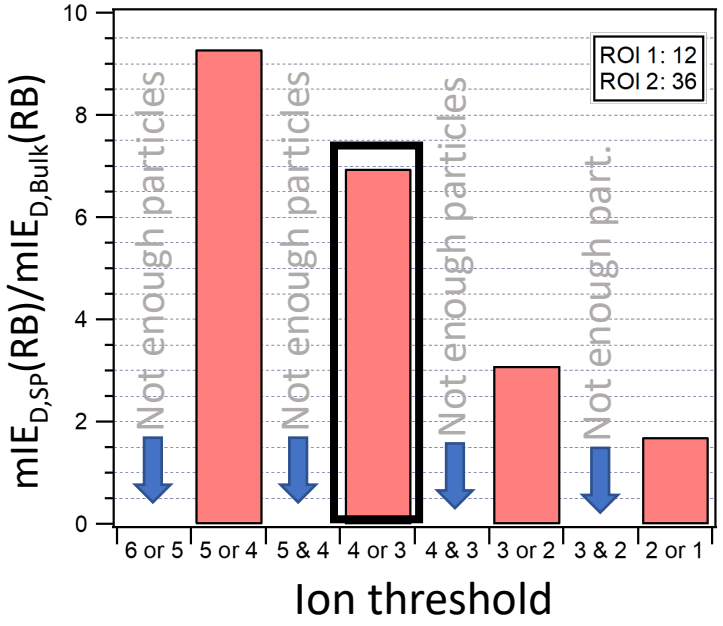


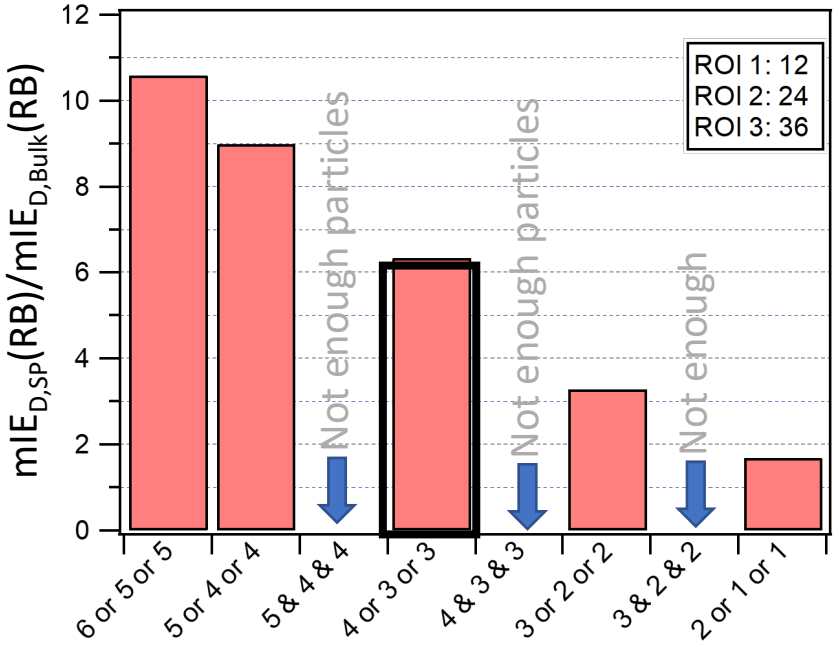
- Higher ratios for ROI m/z 30 compare to m/z 46 ➔ NO_3 fragmentation?
- Overall increase of mIE with higher IT ➔ less false particles?
- "And" condition too sensitive to IT ~20-30% ➔ "or" more comparable with bulk
- At 300nm ~20% higher by using single particle $mIE(NO_3)$

E.T settings: effects of ROI and IT on $mIE_{D,SP}(RB)$ estimation

- High IT and “and” conditions – “too” selective again
- Our instrument settings: ROI using m/z 36 drive the particle detection
  - ➢ mIE NO_3 only 20-30% difference
  - ➢ mIE RB factor 6-10 ➔ CE alone can’t explain such differences

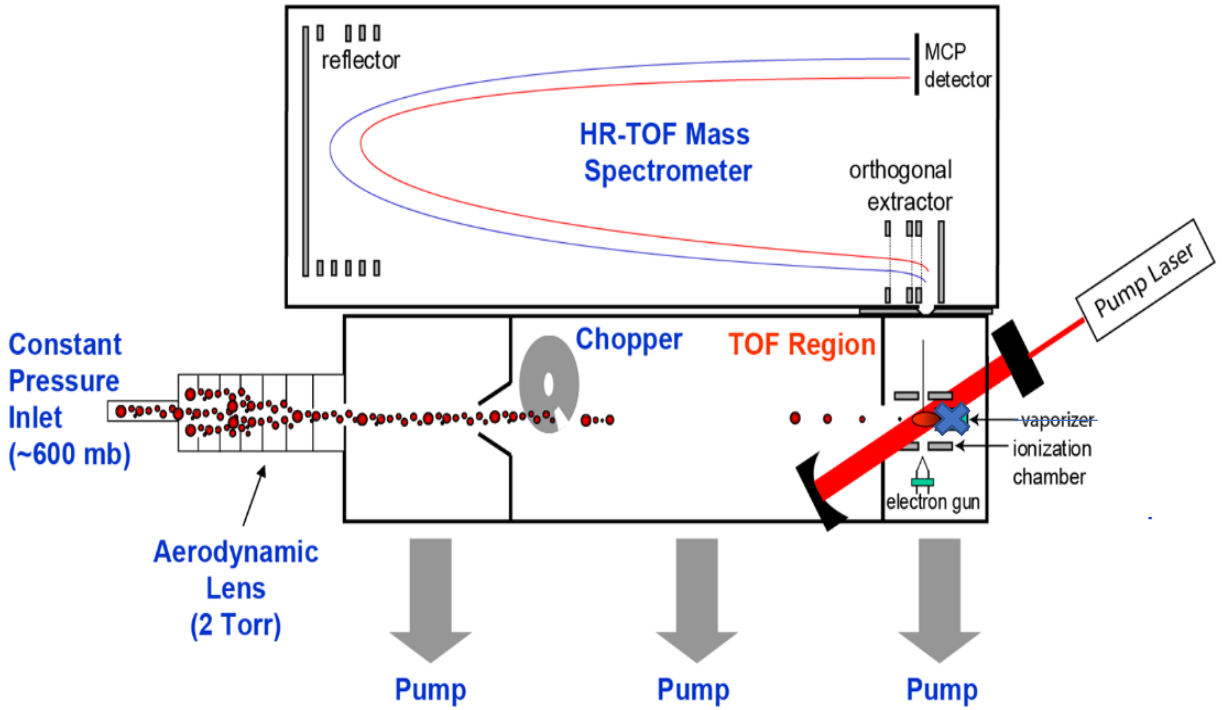






m/z 36 background Ion Threshold = 4
m/z 24 background Ion Threshold = 3
m/z 12 background Ion Threshold = 3

SP-AMS vaporization & detection scheme



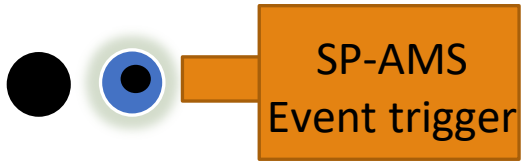
Laser-only : removal of Tungsten vaporizer

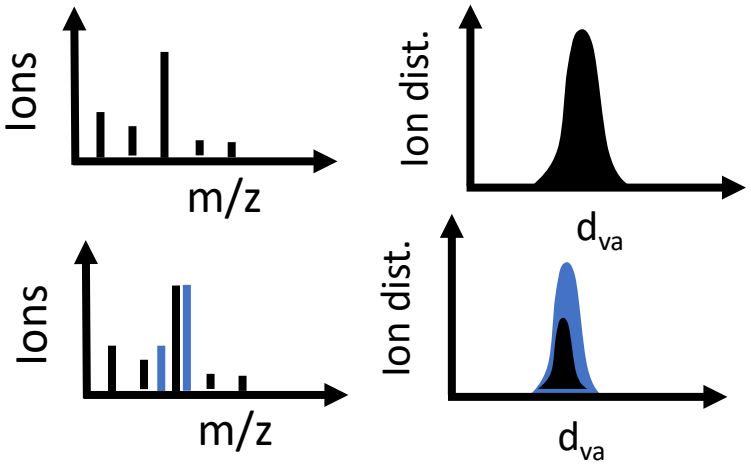
$$CE_{Laser} = E_{Lens} \cdot E_{shape}$$

- rBC+coating
- No coating quantification

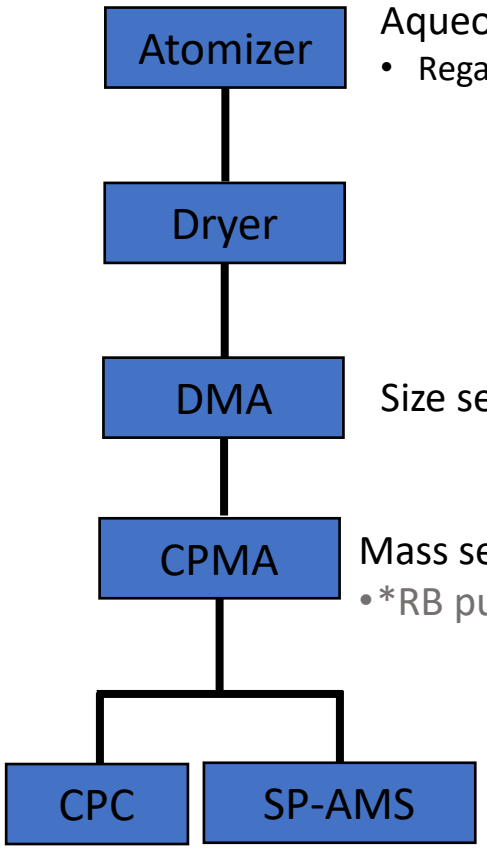
Event Trigger

- Single particle composition + size





Set-up and method for laser-only calibration



Aqueous solution:
- Regal black (RB)

Size selected: 300 nm

Mass selected:
- *RB pure ~ 12 fg

- Laser-only
- Bulk and Single Particle

Estimation of laser-only mIE(RB)

Species	Vaporizer	Calibration method	Parameter meas.
RB pure	Laser-only (L)	Total mass based (Bulk)	$mIE_{L,Bulk}$(RB)
		Single particle (SP)	$mIE_{L,SP}$(RB)

Mass based cal. – RB pure

Date	AB	SI	$mIE_{L,bulk}$(RB)	σ(mIE)
2-Jun	1.11E+05	1.77	174	3
21-Jun	9.99E+04	1.74	110	2
19-Jul	1.04E+05	1.68	118	2
Average	1.05E+05		134	

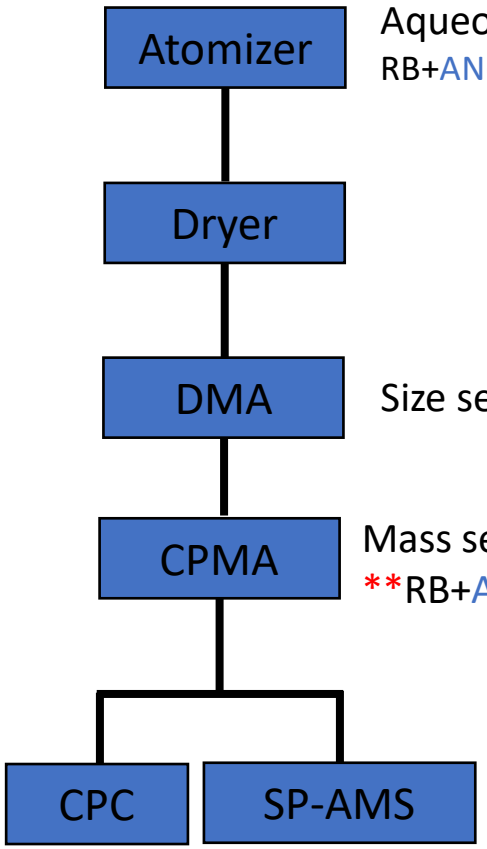
Single particle cal. (14 points) – RB pure

	mass fg	IPP	$mIE_{L,SP}$(RB)	std dev
min	12.0	11.2	901	0.17
max	12.4	20.0	1668	0.16
Avg	12.3	15.3	1247	0.16

- mIE(RB) same order of magnitude with and without Tungsten vaporizer

- mIE(RB) from single particle is still ~6-10 superior to mass-based one

Set-up and method for laser-only calibration



Aqueous mixtures:
RB+AN(1:3)

Size selected: 300 nm

Mass selected:
**RB+AN ~ 21 fg

- Laser-only
- Bulk and Single Particle

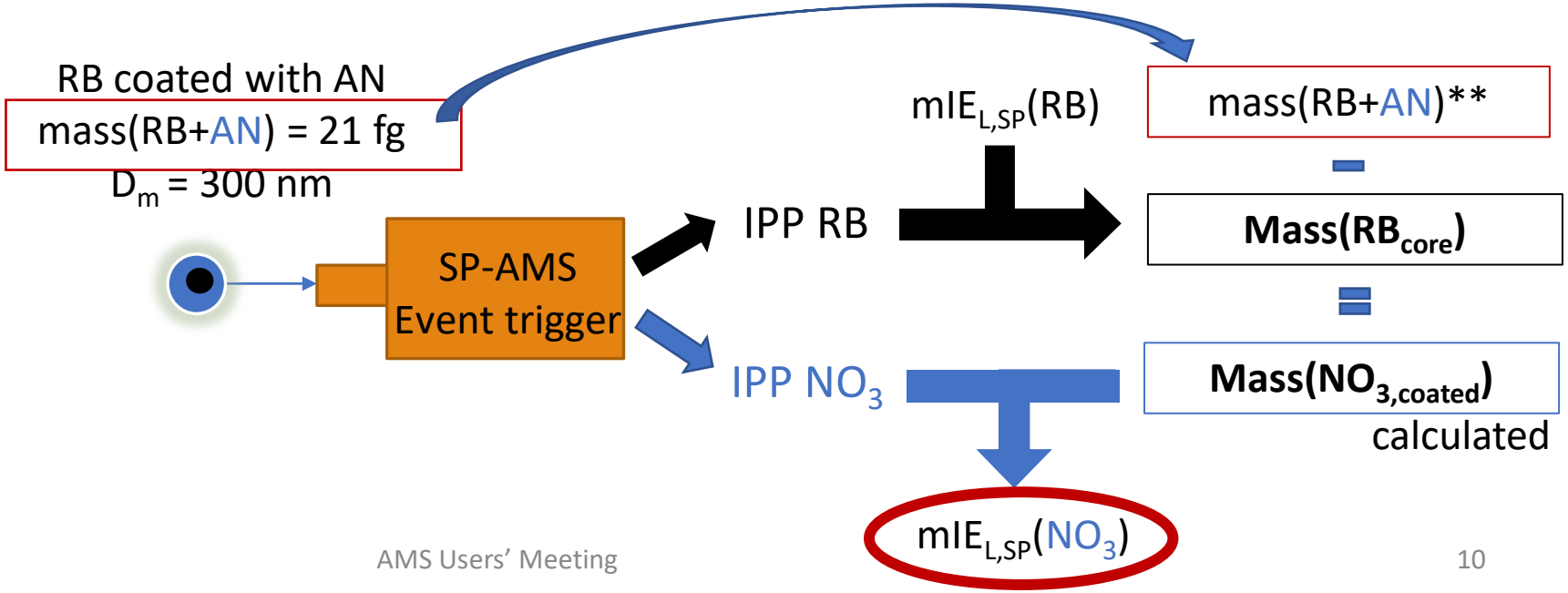
Estimation of laser-only mIE(NO_3)

Species	Vaporizer	Calibration method	Parameter meas.
RB pure	Laser-only (L)	Single particle (SP)	$mIE_{L,SP}(RB)$
AN+RB		Single particle (SP)	$mIE_{L,SP}(NO_3)$

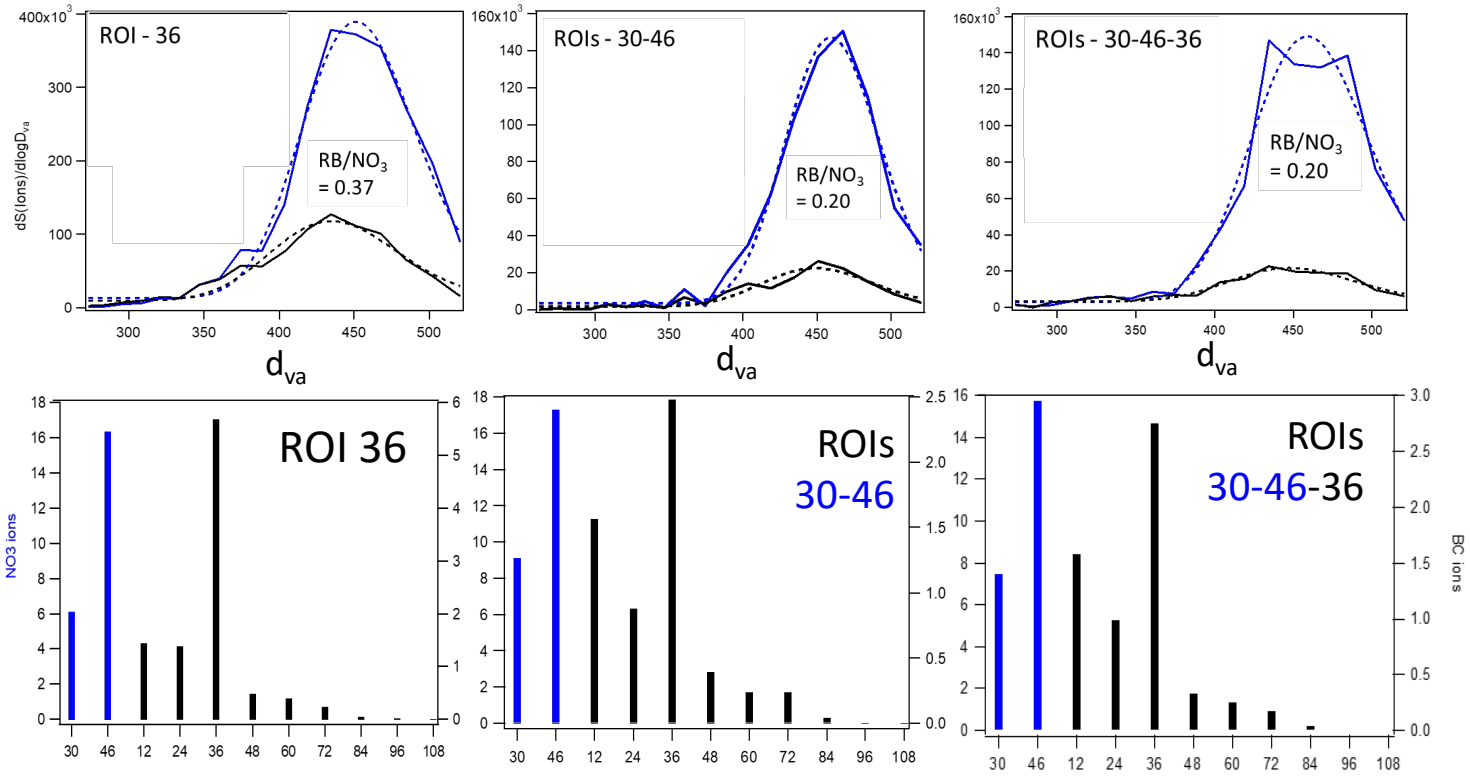
[1] $mIE_{L,SP}(RB) = IPP(RB)/mass(RB_{pure})$*

[2] $mass(RB_{core}) = IPP(RB)/mIE_{L,SP}(RB)$

[3] $mIE_{L,SP}(NO3) = IPP(NO_3)/(mass(RB+AN)^{**} - mass(RB_{core}))$



Laser vaporizer only – estimation of Laser only mIE(NO_3)



➔ depending on ROIs - different type of particles are targeted

Single particle based cal. (26 points) – AN+RB										
ROI(s)	IT(s)	*$mIE_{L,SP}$ (RB)	mass RB-core	IPP RB	mass $NO_{3\text{-coated}}$	IPP NO3	$mIE_{L,SP}$ (NO_3)	IE NO3	#event	AB
Average		1183	6.4	7	14.5	28	2388	2.46E-07	1272	1.0E+05
std		133	2.3	3	2.3	2	503	5.20E-08	1507	3.23E+03

*$mIE_{L,SP}$(RB) from laser-only RB pure cal.
** mass(RB+AN) = 21.3 fg

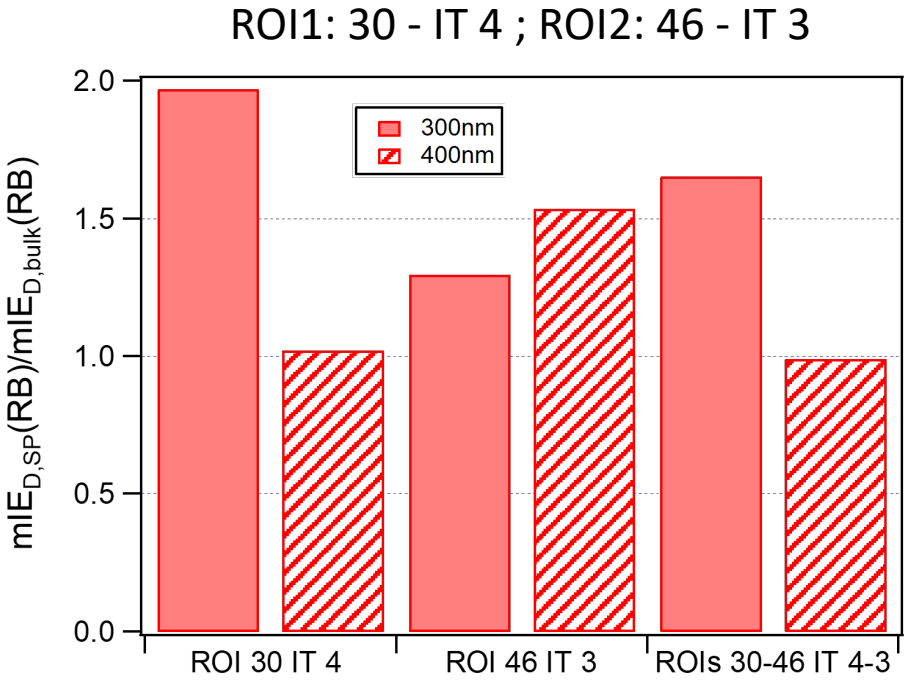
➔ Laser-only mIE(NO_3) **~2-3 times higher** than dual vaporizer one

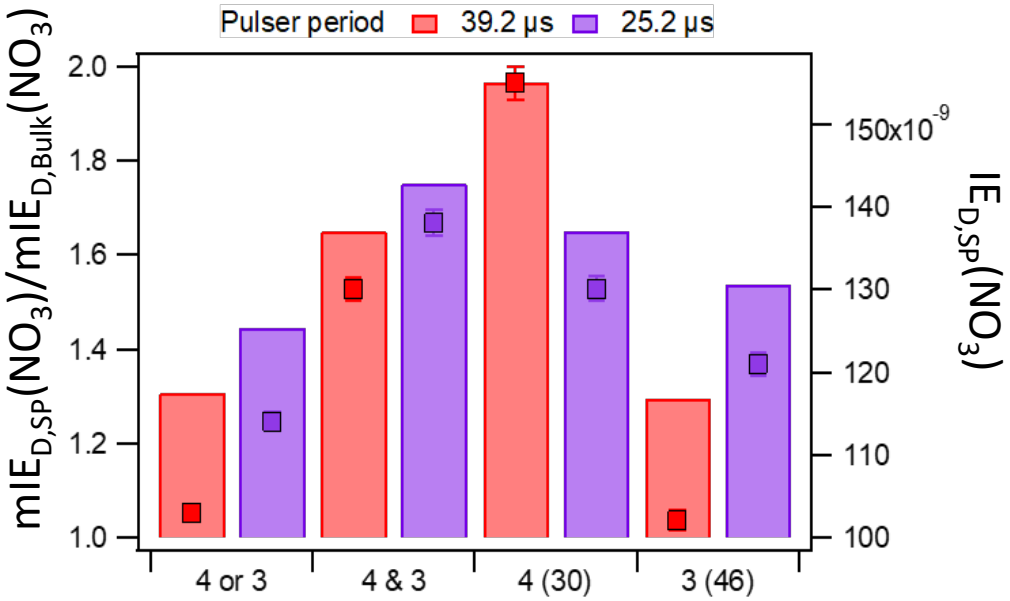
What still needs to be addressed

1. Best practice for E.T calibration ➔ size selection **400nm**, 150-200#/cc (Benjamin Nault's presentation)
2. Investigate the effect of CE and laser alignment on our estimations ➔ beam width probe/light scattering
3. Improve our set-up to generate more homogeneous RB-coated particles

Thank You!

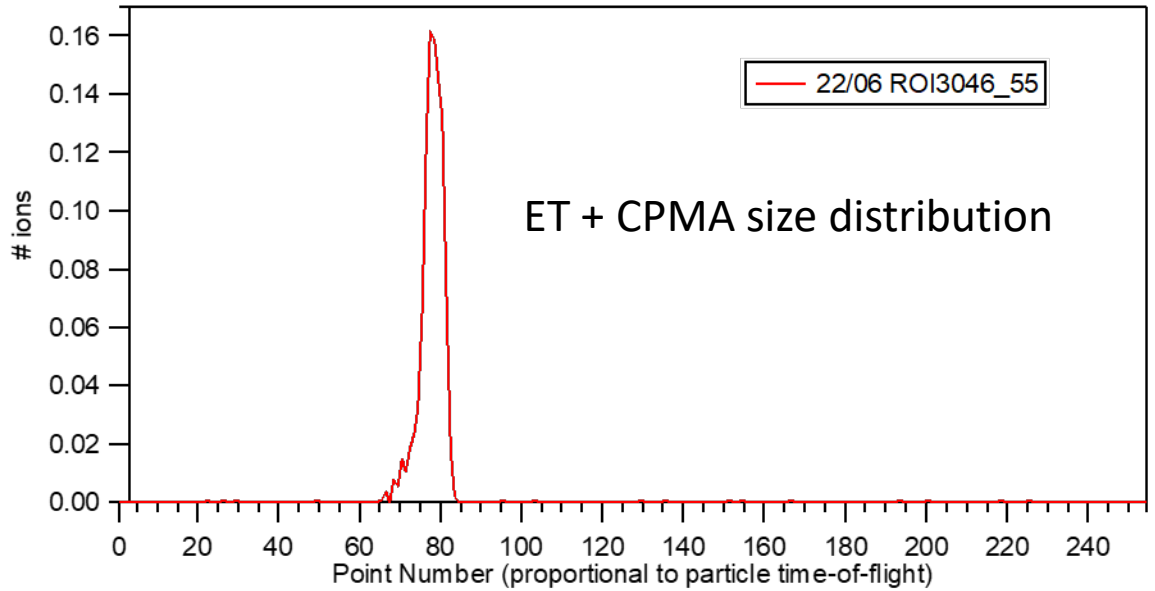
Size and pulser period effect on $IE_{D,SP}(NO_3)$ estimation

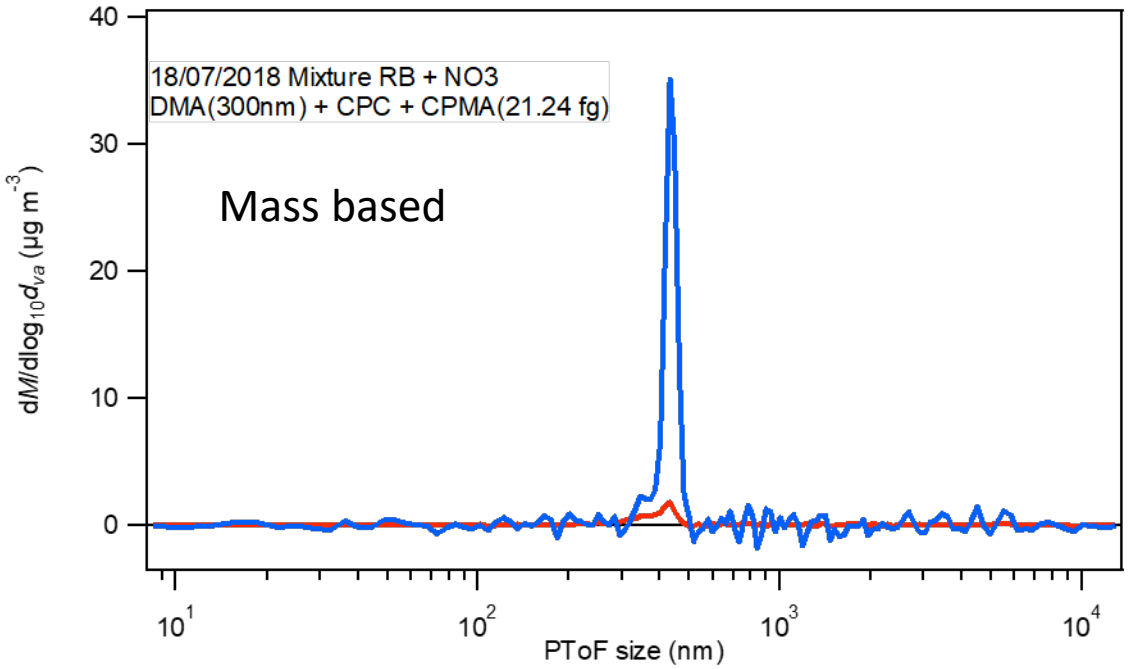


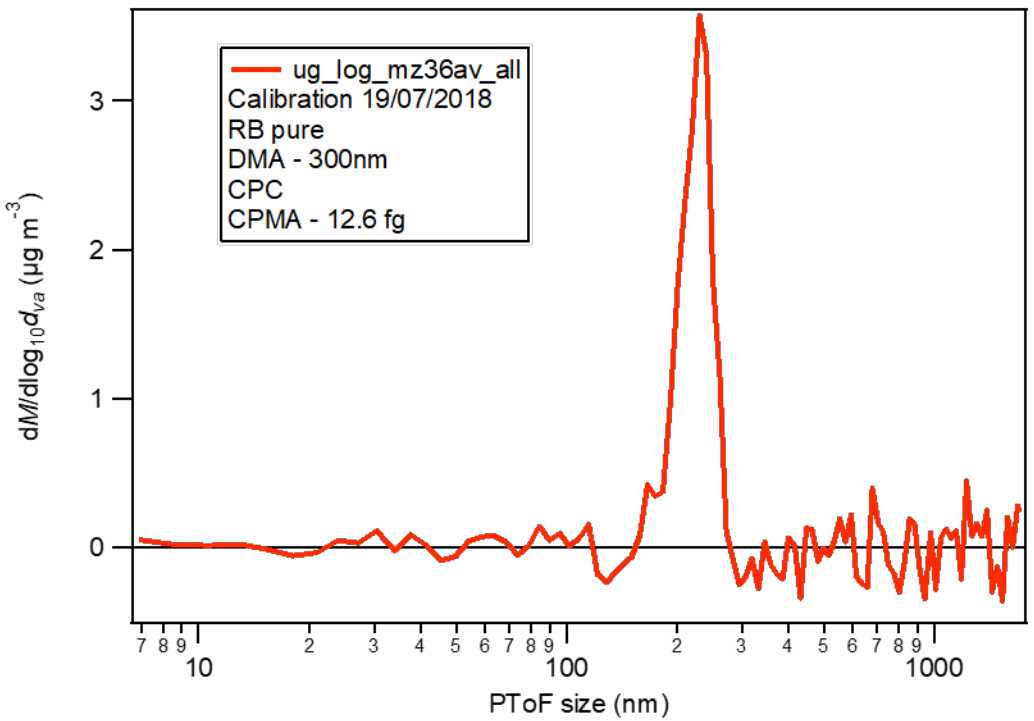


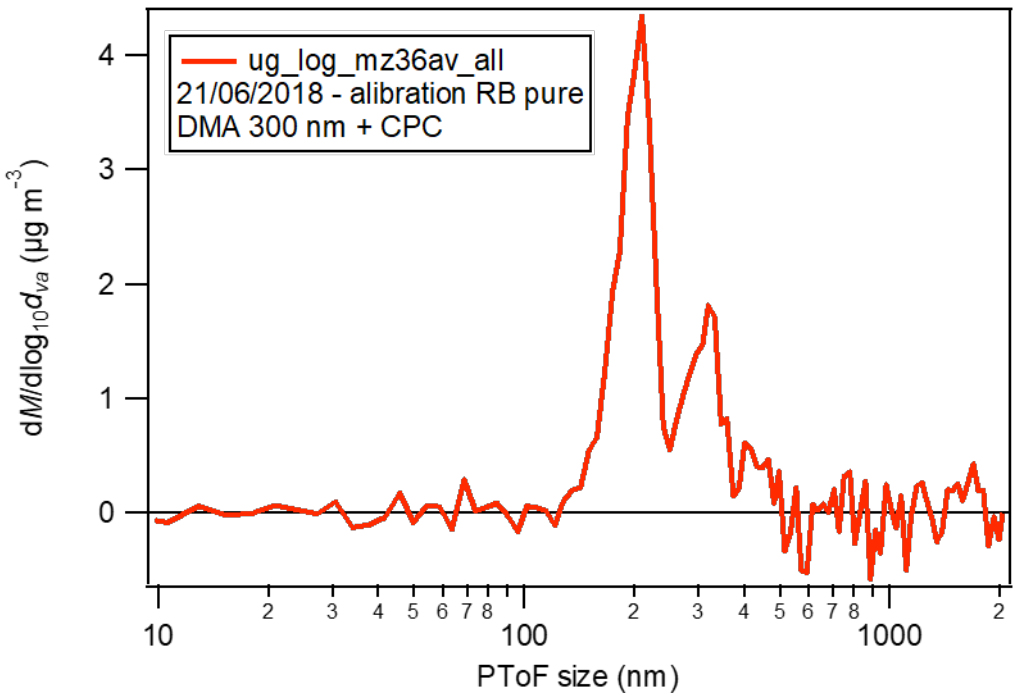
➔ 400 nm seems closer to the mass based mIE at 300nm

➔ Is shorter pulse necessary


22/06 ROI3046_55
ET + CPMA size distribution
ions
Point Number (proportional to particle time-of-flight)


18/07/2018 Mixture RB + NO3
DMA(300nm) + CPC + CPMA(21.24 fg)
Mass based
dM/dlog10dva (µg m-3)
PToF size (nm)


ug_log_mz36av_all
Calibration 19/07/2018
RB pure
DMA - 300nm
CPC
CPMA - 12.6 fg
dM/dlog10dva (µg m-3)
PToF size (nm)


ug_log_mz36av_all
21/06/2018 - alibration RB pure
DMA 300 nm + CPC
dM/dlog10dva (µg m-3)
PToF size (nm)

Observation from bulk and Single particle calibrations from 2017-2018

Mass based calibration (15 values)

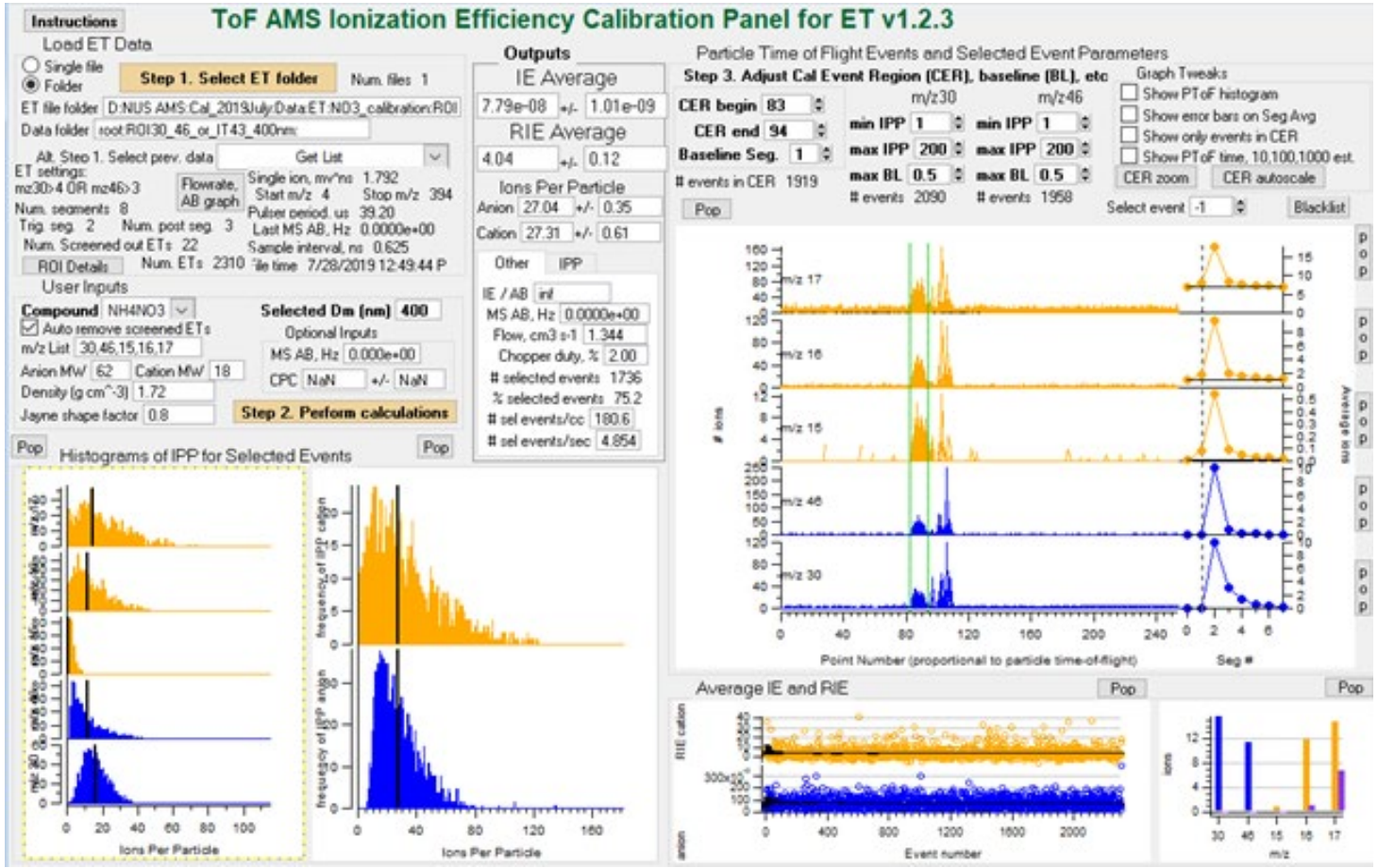
	IE	σIE	IE/AB	SI	mIE NO3	mIE NH4	mIE RB	σ(mIE-RB)	RIE(NH_4)	σRIE NH4	RIE-RB	σRIE RB
Avg	**8.13E-08**	2.39E-09	2.70E-13	1.80	788	3324	142	3	4.23	0.06	0.18	0.04
Min	**3.09E-08**	7.25E-10	2.05E-13	1.70	300	1303	64	2	3.50	0.02	0.14	0.02
Max	**1.10E-07**	1.32E-08	3.48E-13	1.84	1062	4537	179	7	5.00	0.15	0.25	0.11

Single particle calibration (33 values)

	IE NO3	mIE NO3	AB	IE/AB	mass BC	IPP BC	IPP NO3	RIE NH4	mIE BC	RIE BC
average	**1.14E-07**	**1132**	3.66E+05	**3.47E-13**	12.35	22	18	3.40	**1767**	**1.56**
min	**9.21E-08**	**1094**	2.98E+05	**2.77E-13**	12.23	20	18	3.34	**1644**	**1.27**
max	**1.44E-07**	**1179**	4.27E+05	**4.26E-13**	12.58	25	18	3.44	**1989**	**1.64**

Similar range of value for mIE NO_3

Factor 10 between mIE BC from mass based to ET-based calibrations!


Instructions
ToF AMS Ionization Efficiency Calibration Panel for ET v1.2.3
Load ET Data
Single file
Folder
Step 1. Select ET folder
Num. files 1
ET file folder D:\NUS AMS\Cal_2019\July\Data\ET\NO3_calibration\ROI
Data folder root:ROI30_46_or_IT43_400nm\
Alt. Step 1. Select prev. data
Get List
ET settings:
mz30>4 OR mz46>3
Flowrate, AB graph
Single ion, mv^ns 1.792
Start m/z 4
Stop m/z 394
Num. segments 8
Pulser period, us 39.20
Trig. seg. 2
Num. post seg. 3
Last MS AB, Hz 0.0000e+00
Num. Screened out ETs 22
Sample interval, ns 0.625
ROI Details
Num. ETs 2310
File time 7/28/2019 12:49:44 P
User Inputs
Compound NH4NO3
Selected Dm (nm) 400
Auto remove screened ETs
Optional Inputs
m/z List 30,46,15,16,17
MS AB, Hz 0.000e+00
Anion MW 62
Cation MW 18
CPC NaN +/- NaN
Density (g cm^-3) 1.72
Jayne shape factor 0.8
Step 2. Perform calculations
Pop
Histograms of IPP for Selected Events
Pop
Ions Per Particle
Ions Per Particle
Outputs
IE Average
7.79e-08 +/- 1.01e-09
RIE Average
4.04 +/- 0.12
Ions Per Particle
Anion 27.04 +/- 0.35
Cation 27.31 +/- 0.61
Other
IPP
IE / AB inf
MS AB, Hz 0.0000e+00
Flow, cm3 s-1 1.344
Chopper duty, % 2.00
selected events 1736
% selected events 75.2
# sel events/cc 180.6
# sel events/sec 4.854
Particle Time of Flight Events and Selected Event Parameters
Step 3. Adjust Cal Event Region (CER), baseline (BL), etc
CER begin 83
CER end 94
Baseline Seg. 1
events in CER 1919
m/z30
min IPP 1
max IPP 200
max BL 0.5
events 2090
m/z46
min IPP 1
max IPP 200
max BL 0.5
events 1958
Graph Tweaks
Show PToF histogram
Show error bars on Seg Avg
Show only events in CER
Show PToF time, 10,100,1000 est.
CER zoom
CER autoscale
Pop
Select event -1
Blacklist
m/z 17
m/z 16
m/z 15
m/z 46
m/z 30
ions
Average ions
Point Number (proportional to particle time-of-flight)
Seg #
Average IE and RIE
Pop
Pop
RIE cation
RIE anion
Event number
ions
m/z