How the damn thing works …

Aerosol Mass Spectrometry: Morphology and Chemistry of Particles in the Lab and the Atmosphere

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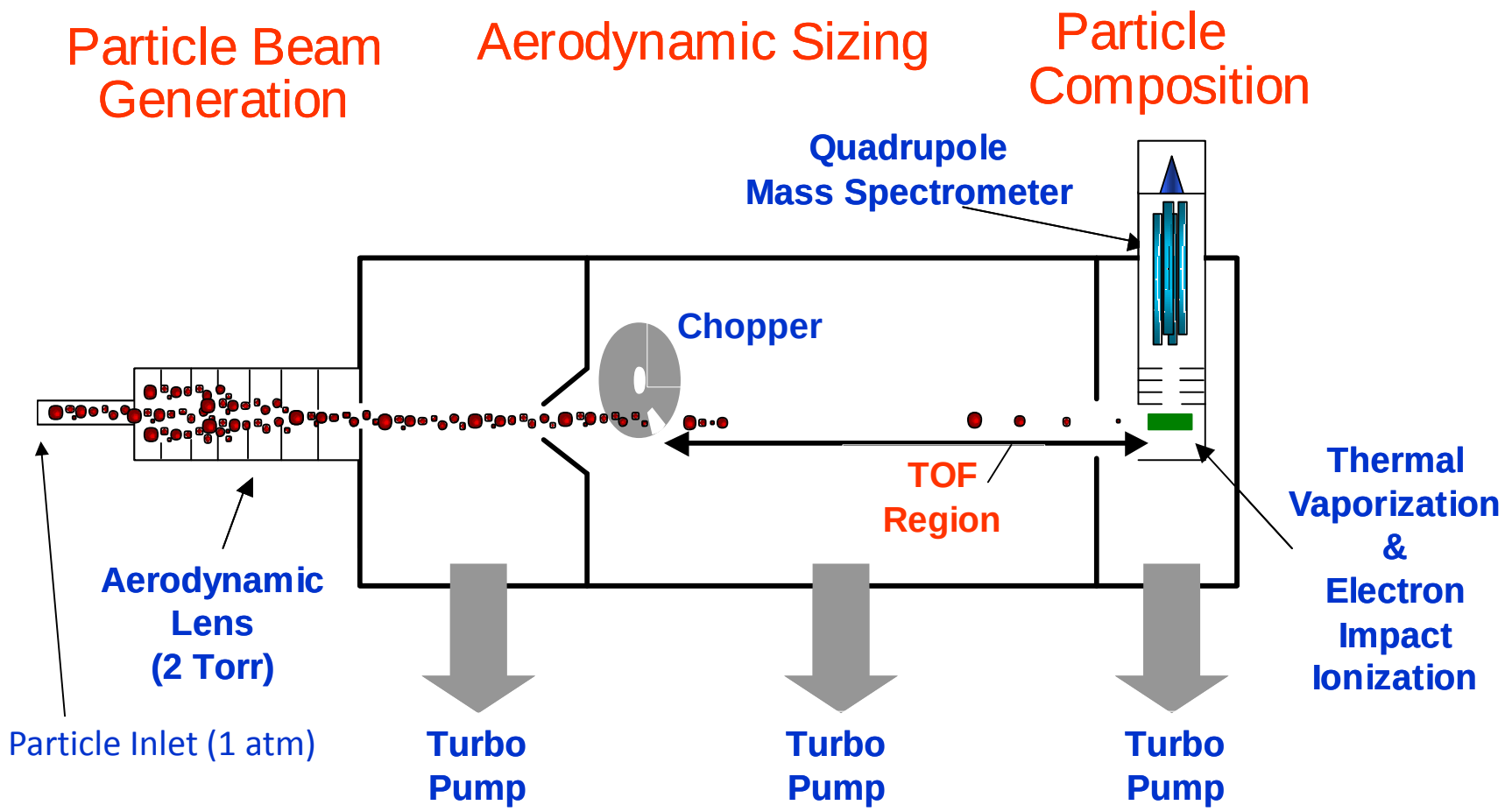
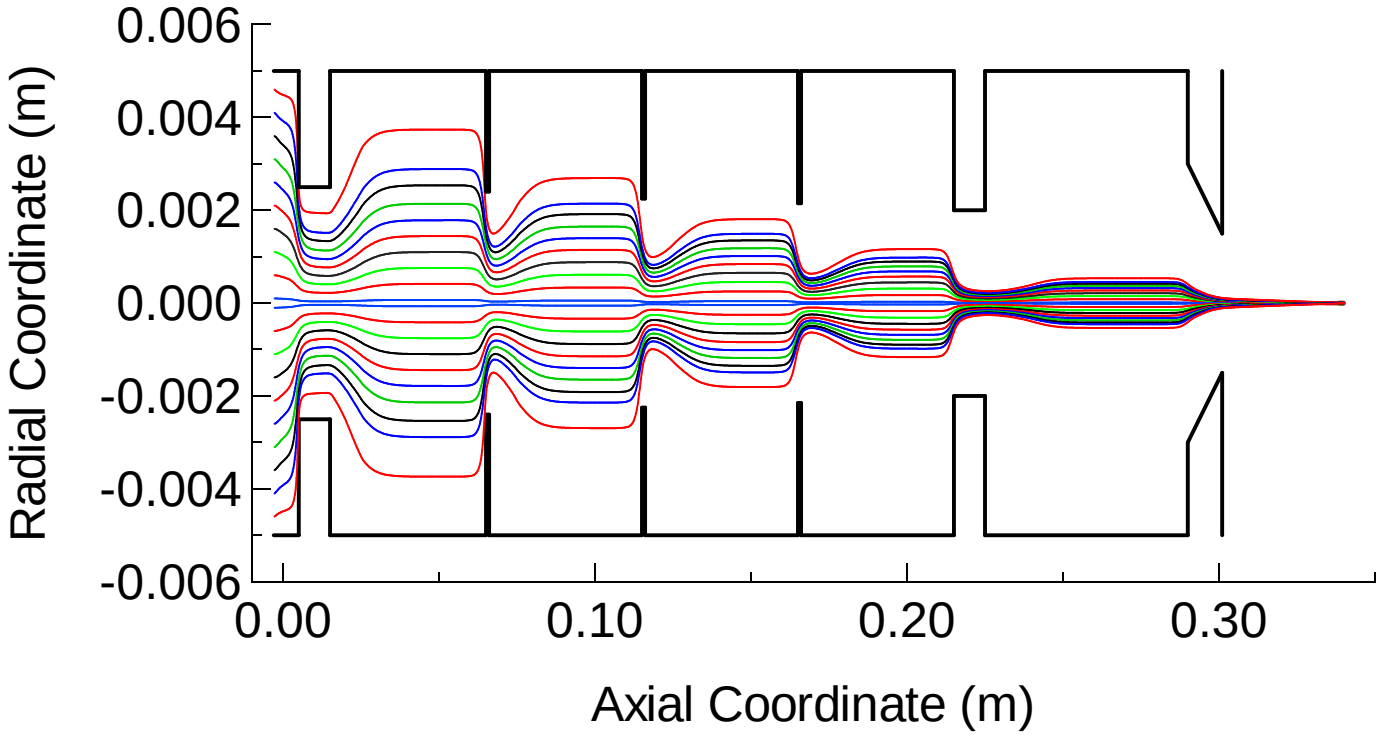
Minneapolis *Monday, 11 September 2006*

Aerosol Mass Spectrometer (AMS)



- Efficient transmission (40-1000 nm), aerodynamic sizing, linear mass signal
- Non-refractory PM1.0 mass loadings and chemically-speciated mass distributions

Aerodynamic Particle Focusing

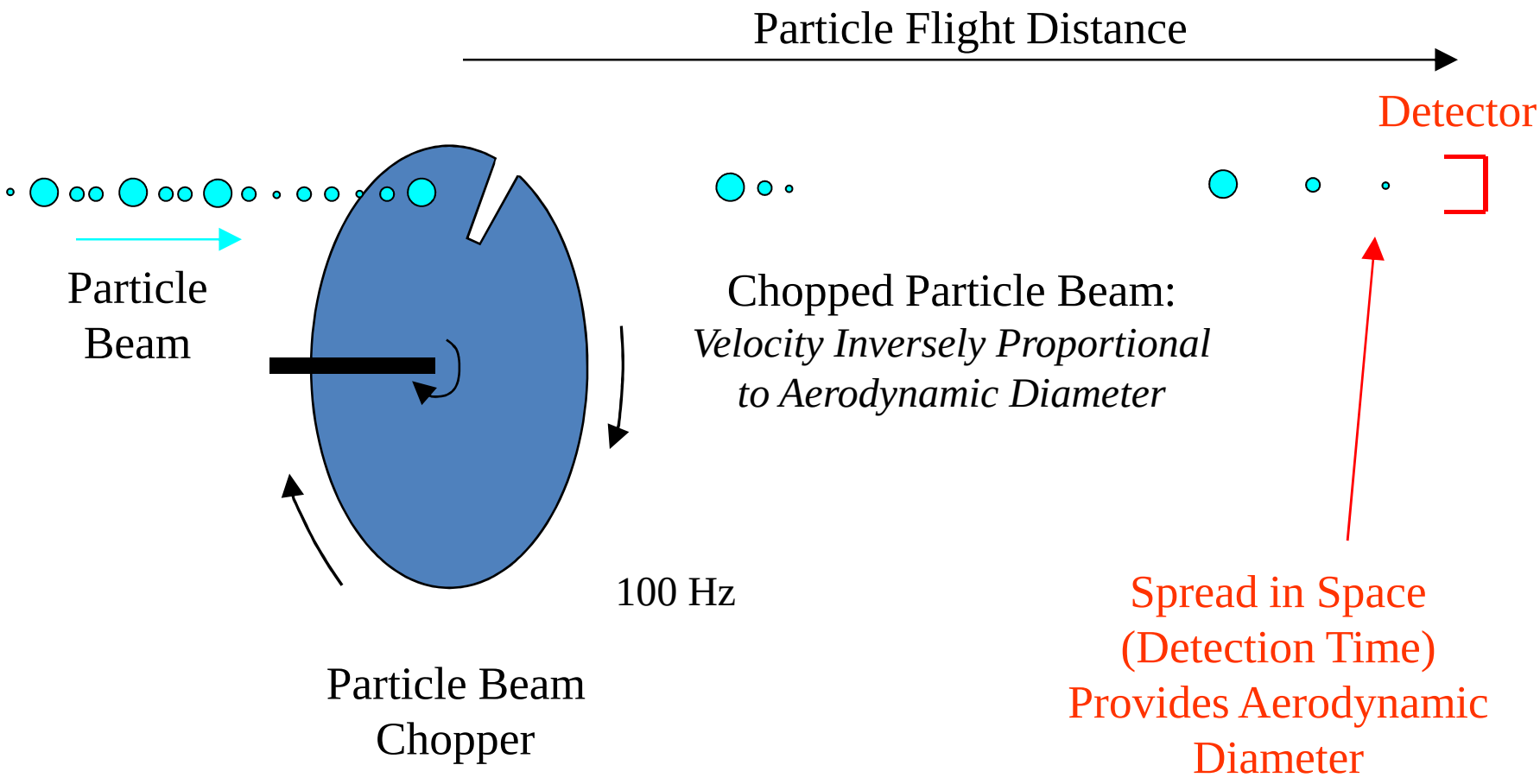


2.4 Torr inlet

10^{-3} torr Exit

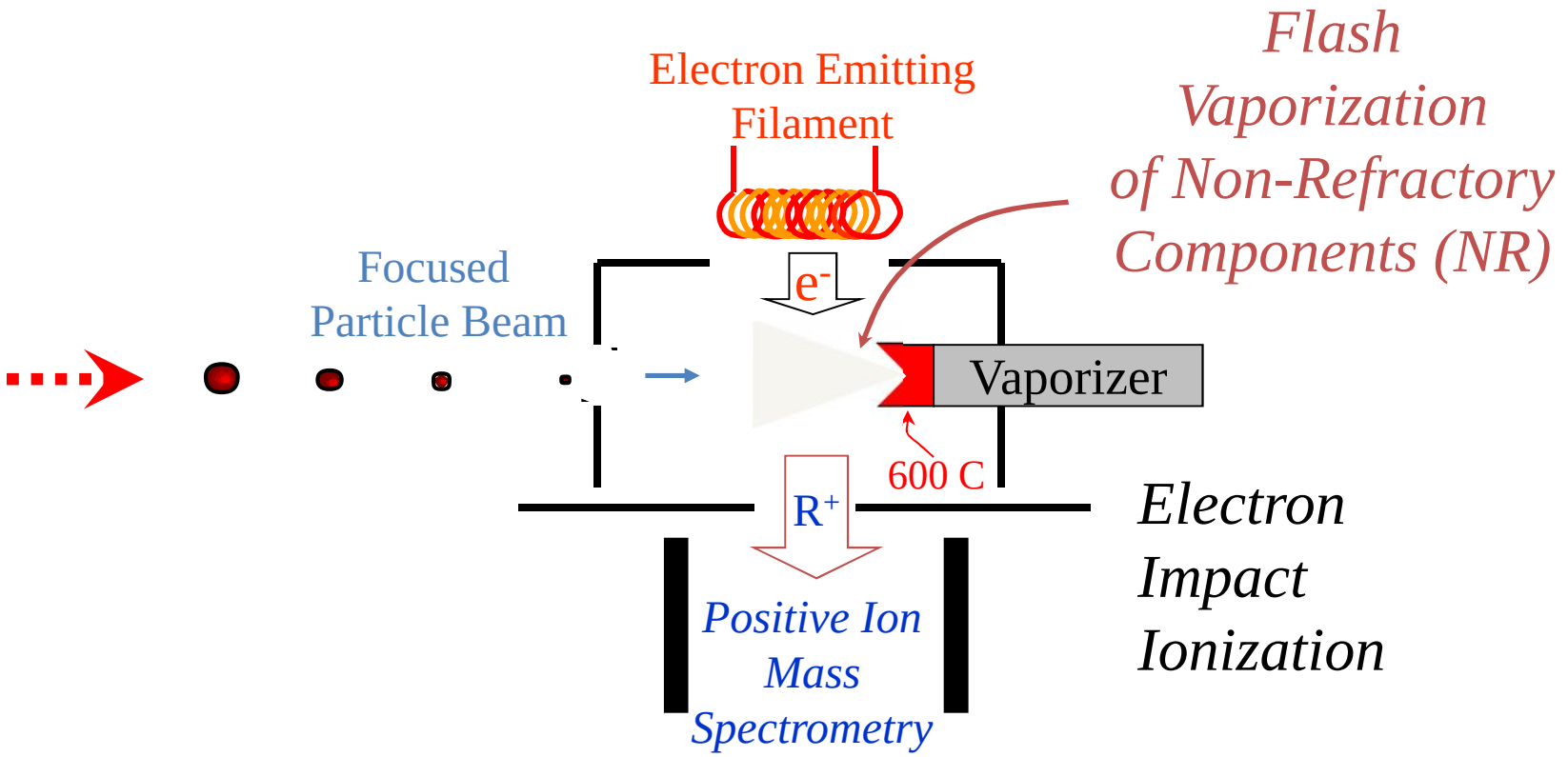
Calculated Particle Trajectories
100 nm Diameter Unit Density Spheres
(Fluent ver 4.47)

Aerosol Size Measurement



"Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles"
Jayne et al., Aerosol Science and Technology 33:1-2(49-70), 2000.

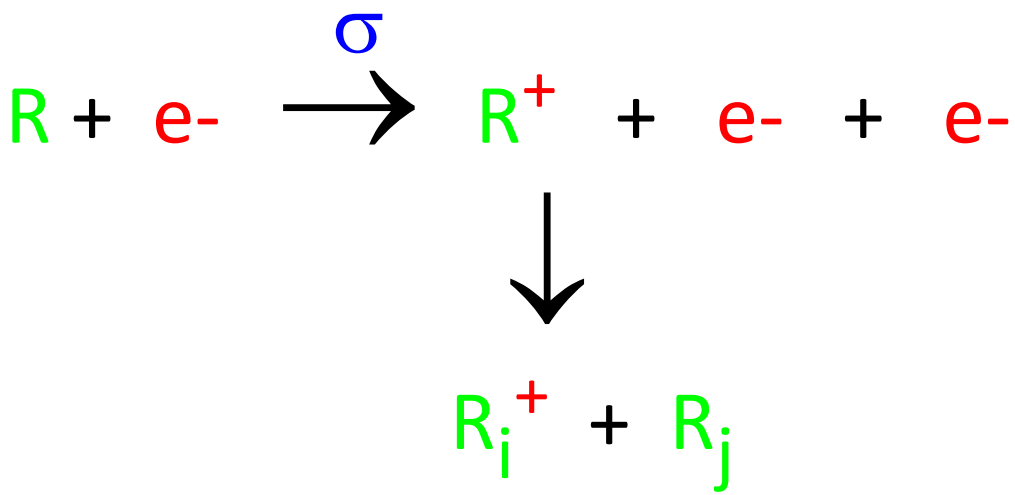
AMS Particle Detection Process



Universal and quantitative chemical analysis: 0.01 μg/m³ sensitivity.

Vaporization and analysis of most aerosol chemical constituents
- *with primary exception of crustal oxides and elemental carbon.*

ELECTRON IMPACT (EI) IONIZATION



Measure all ions:

Ion Rate = $\sum R_i^+$

EI Cross Section (σ) $\propto$ electrons/molecule

$\propto$ mass/molecule

Ion Rate = *2ndary* electrons/sec $\propto$ $\sigma \cdot$ molecules/sec

Ion Rate = $\sum R_i^+$ $\propto$ total mass/sec

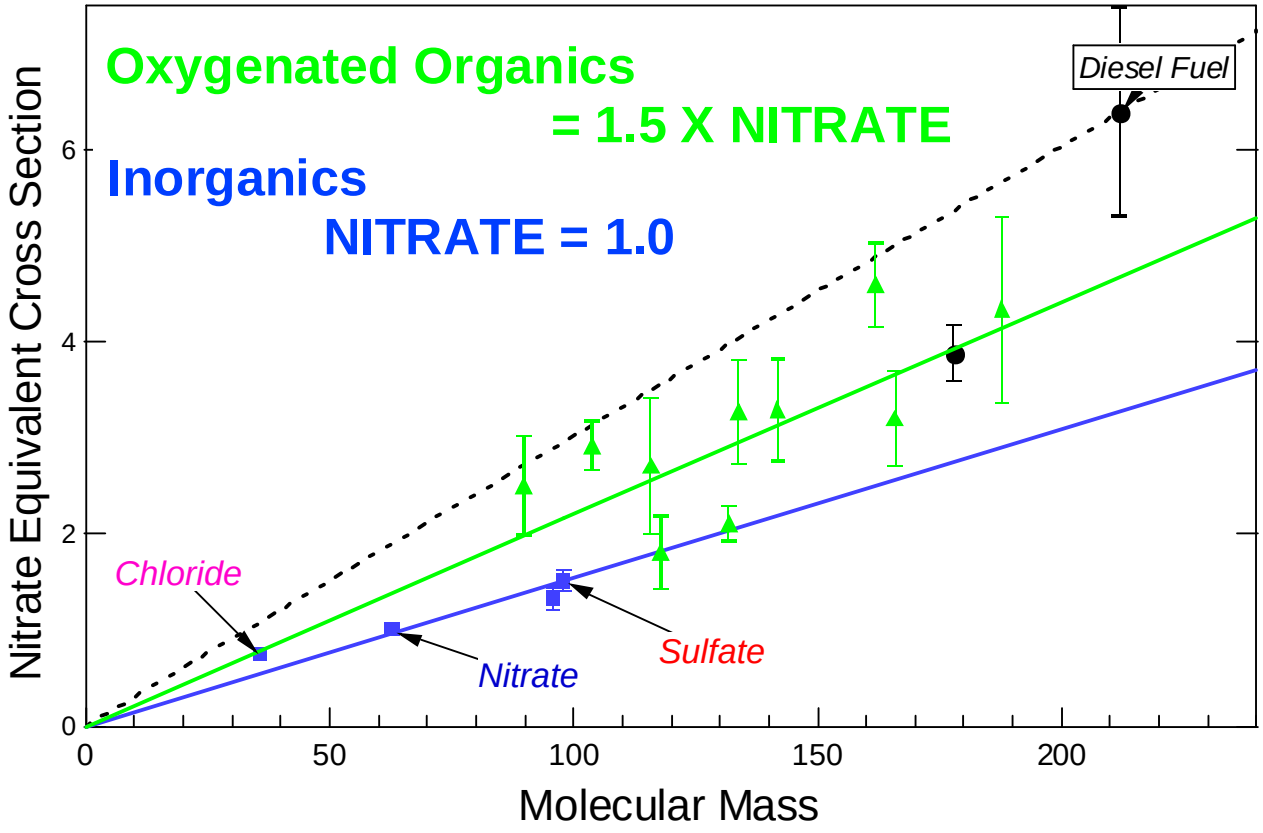
independent of parent or fragment (neutral or ion) molecular mass

EI Ionization: $A + e^- \dashrightarrow A^+ \dashrightarrow a_i^+$

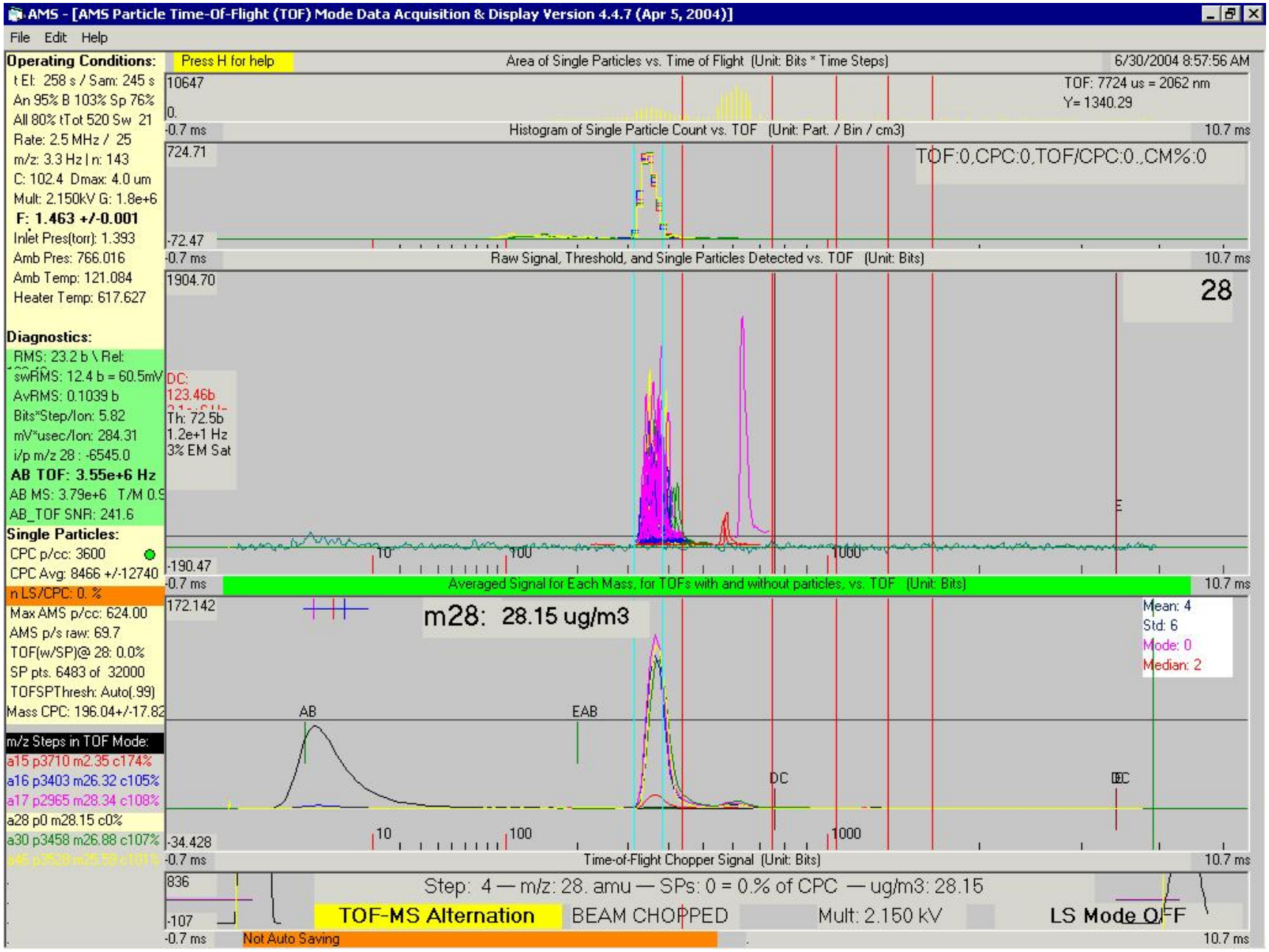
Mass Loading A $\propto$ $(MW_A/IE_A) \sum$ Ion Signal

Calibration Factor * (MW_{NO3}/IE_{NO3})

EI Ionization Cross Sections



AMS Calibration: 300nm NH_4NO_3 Particles *size elected with DMA*



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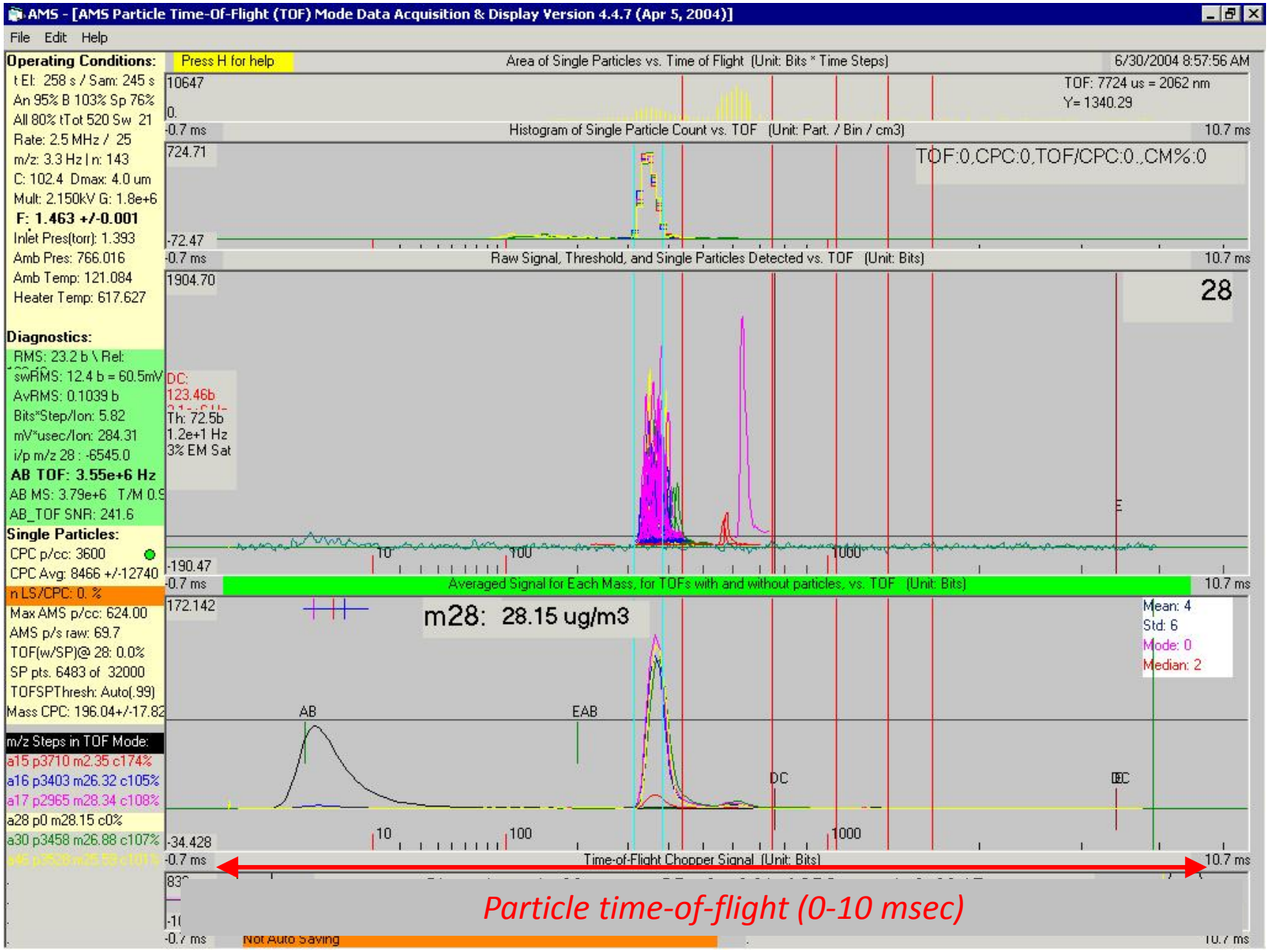

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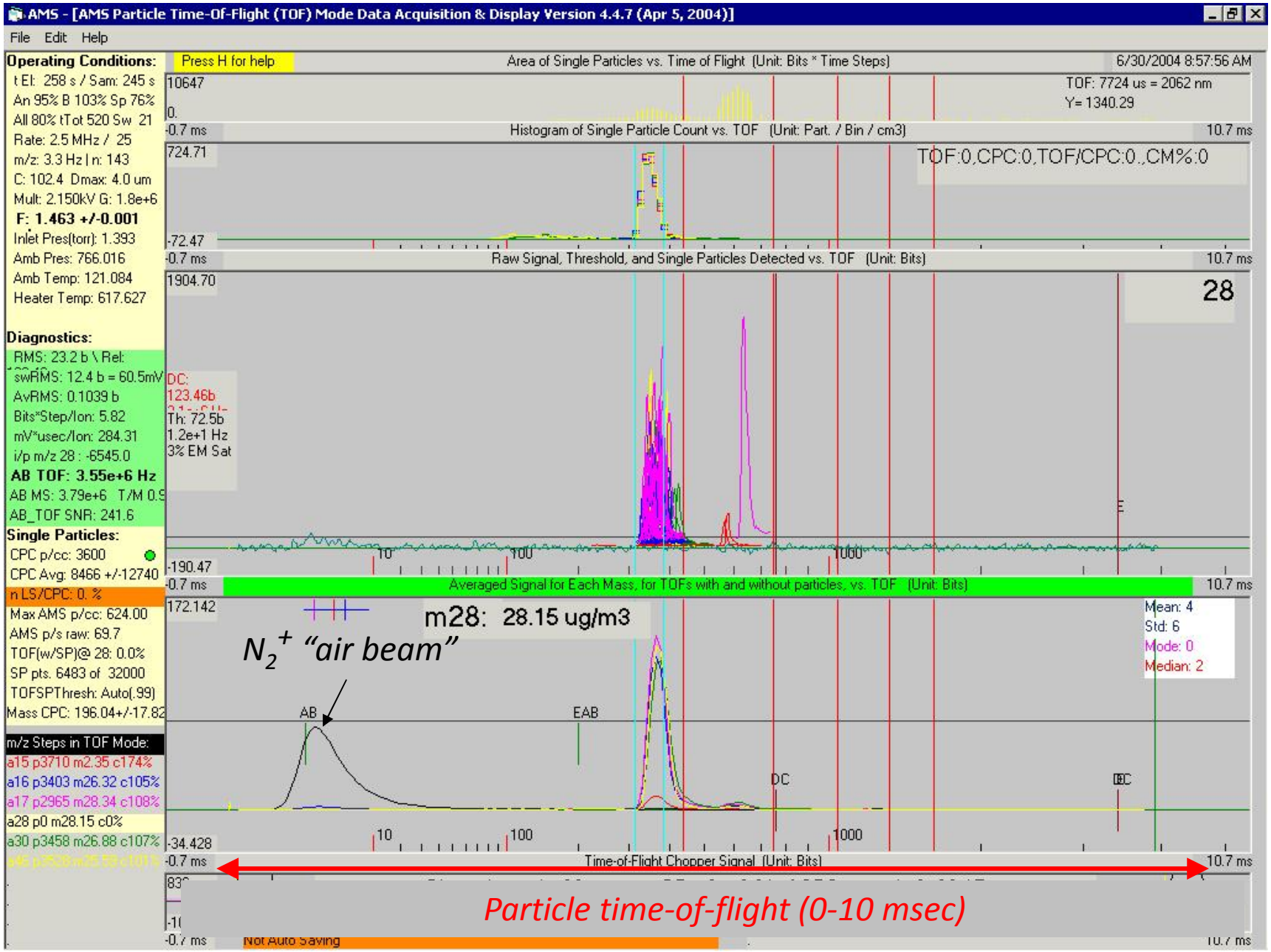

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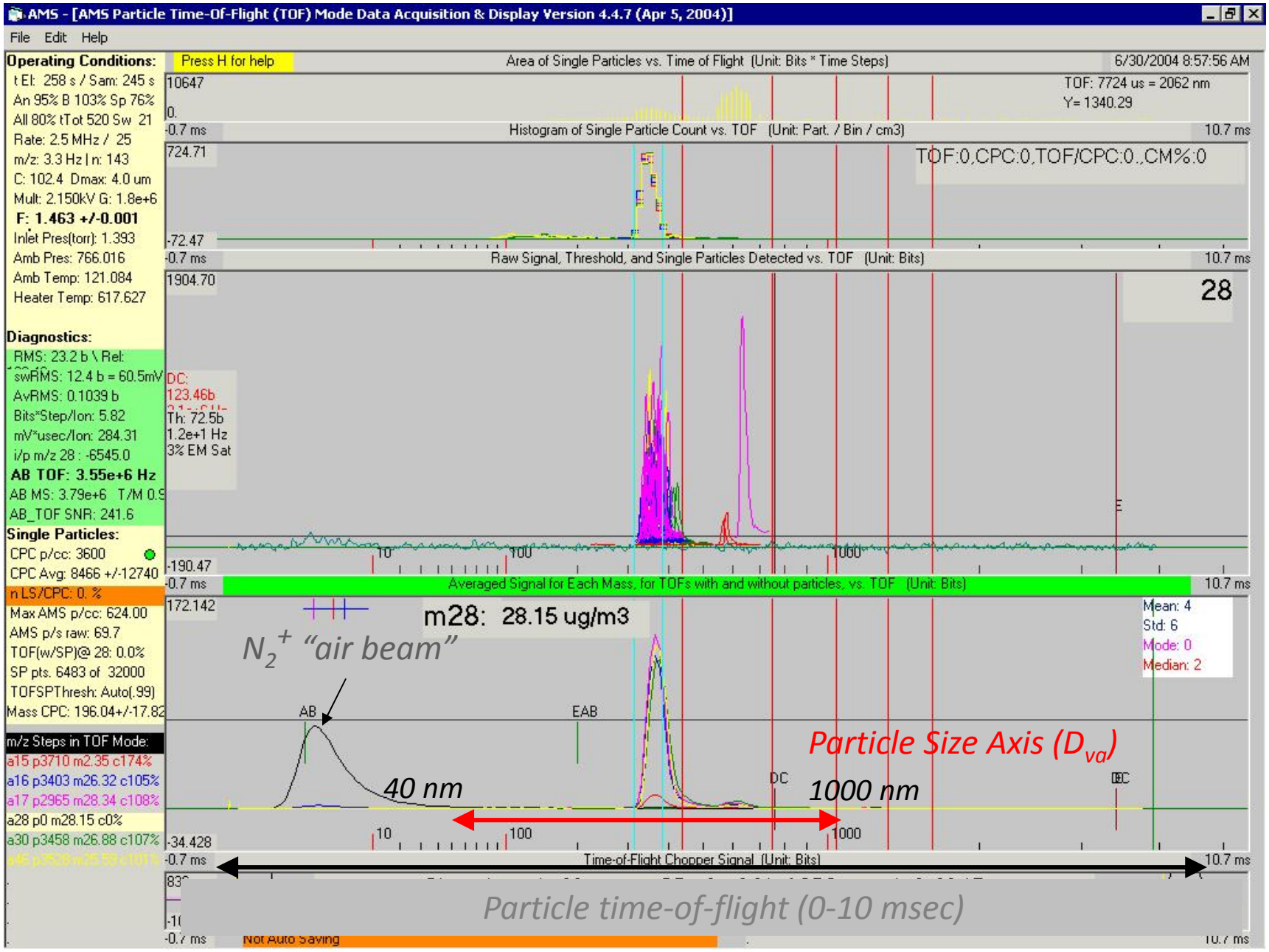

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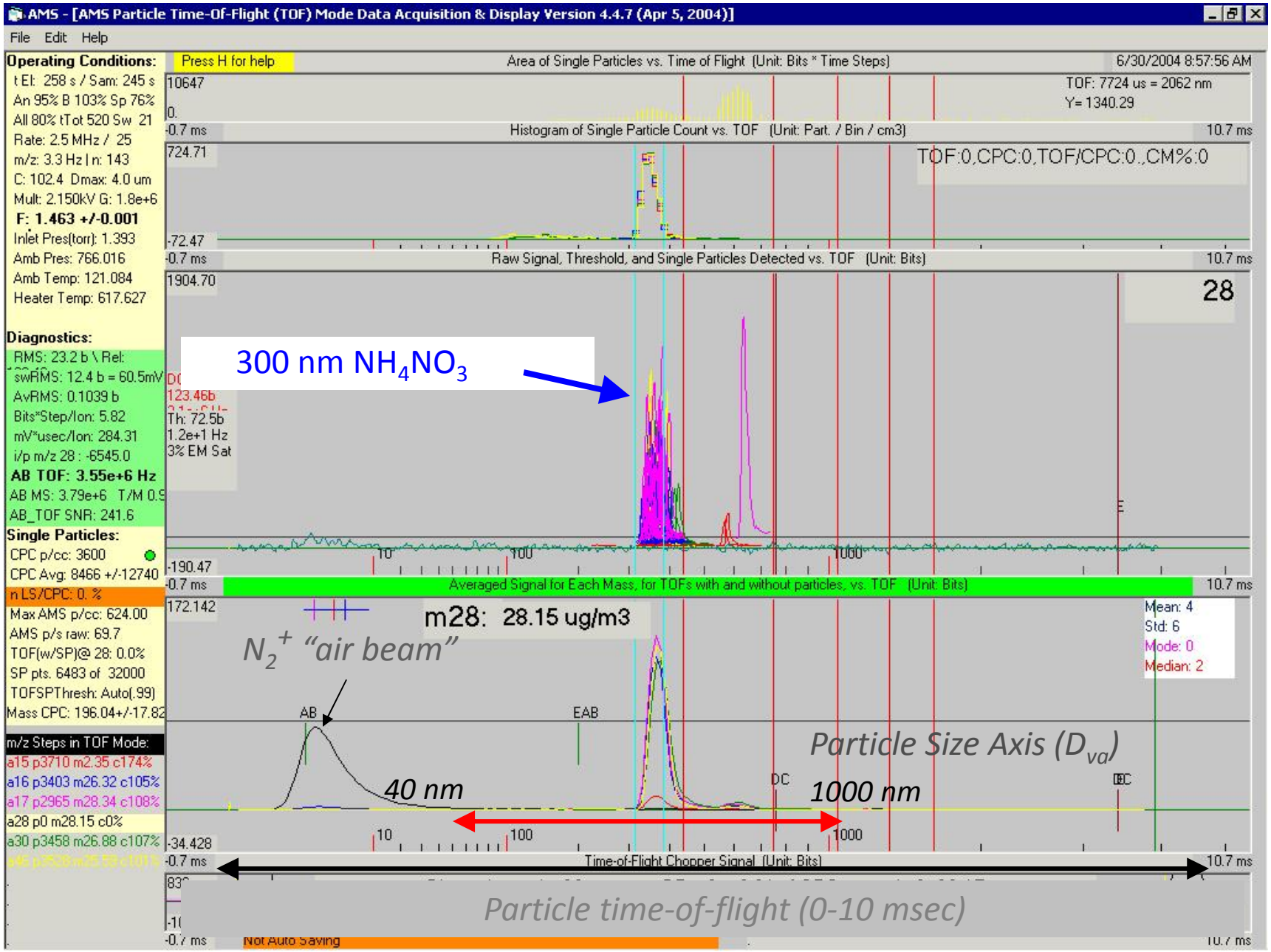

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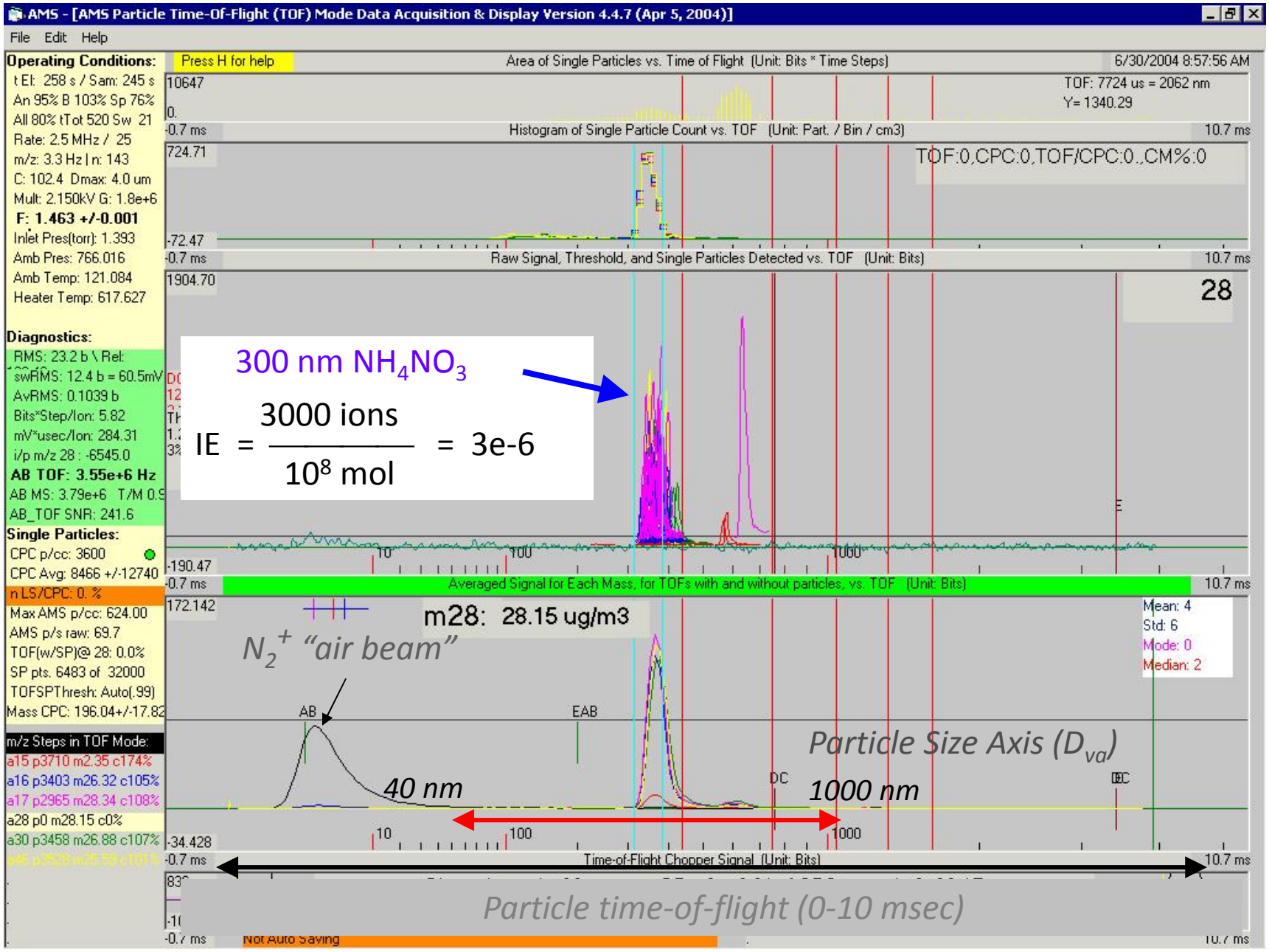

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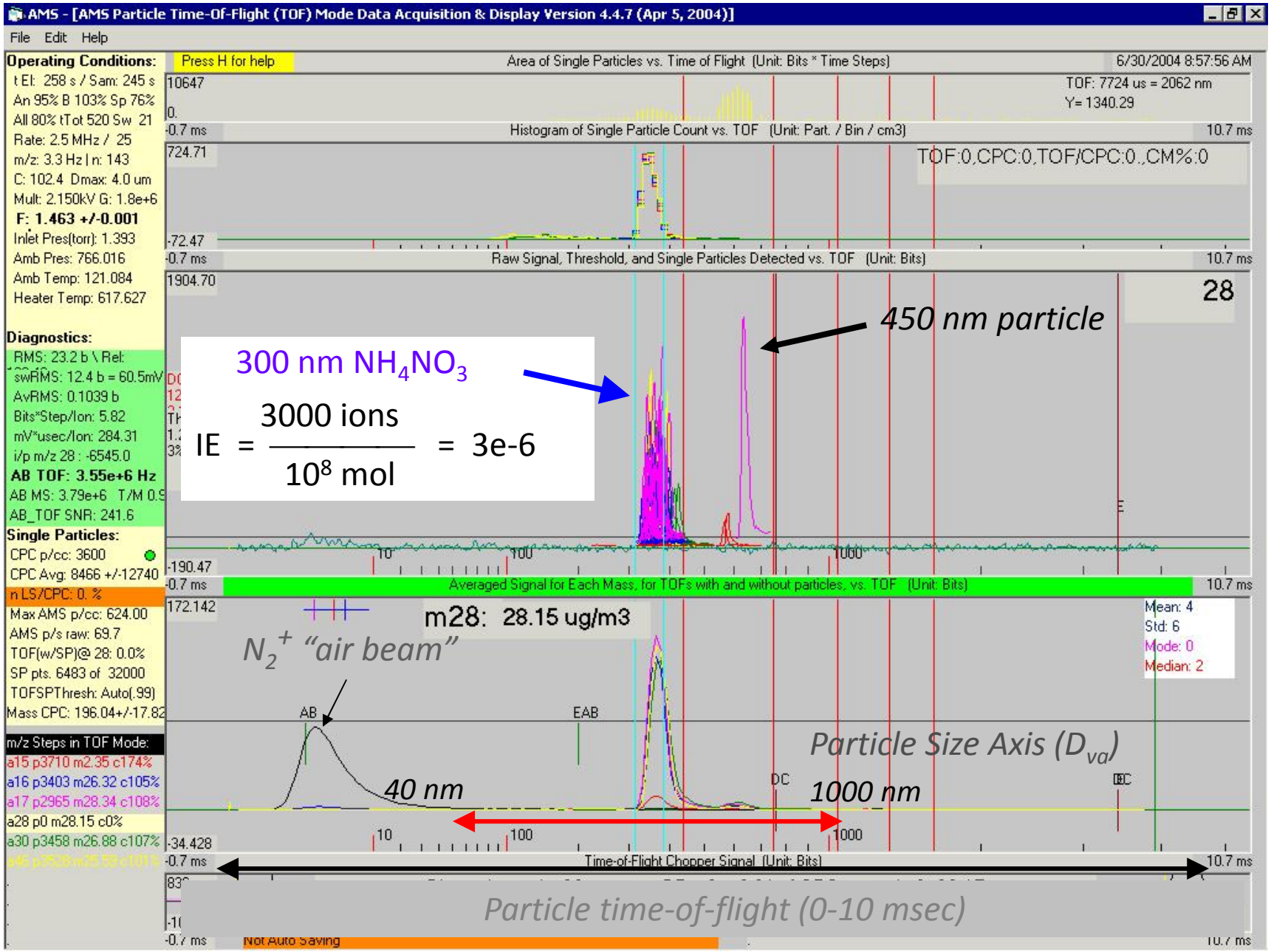
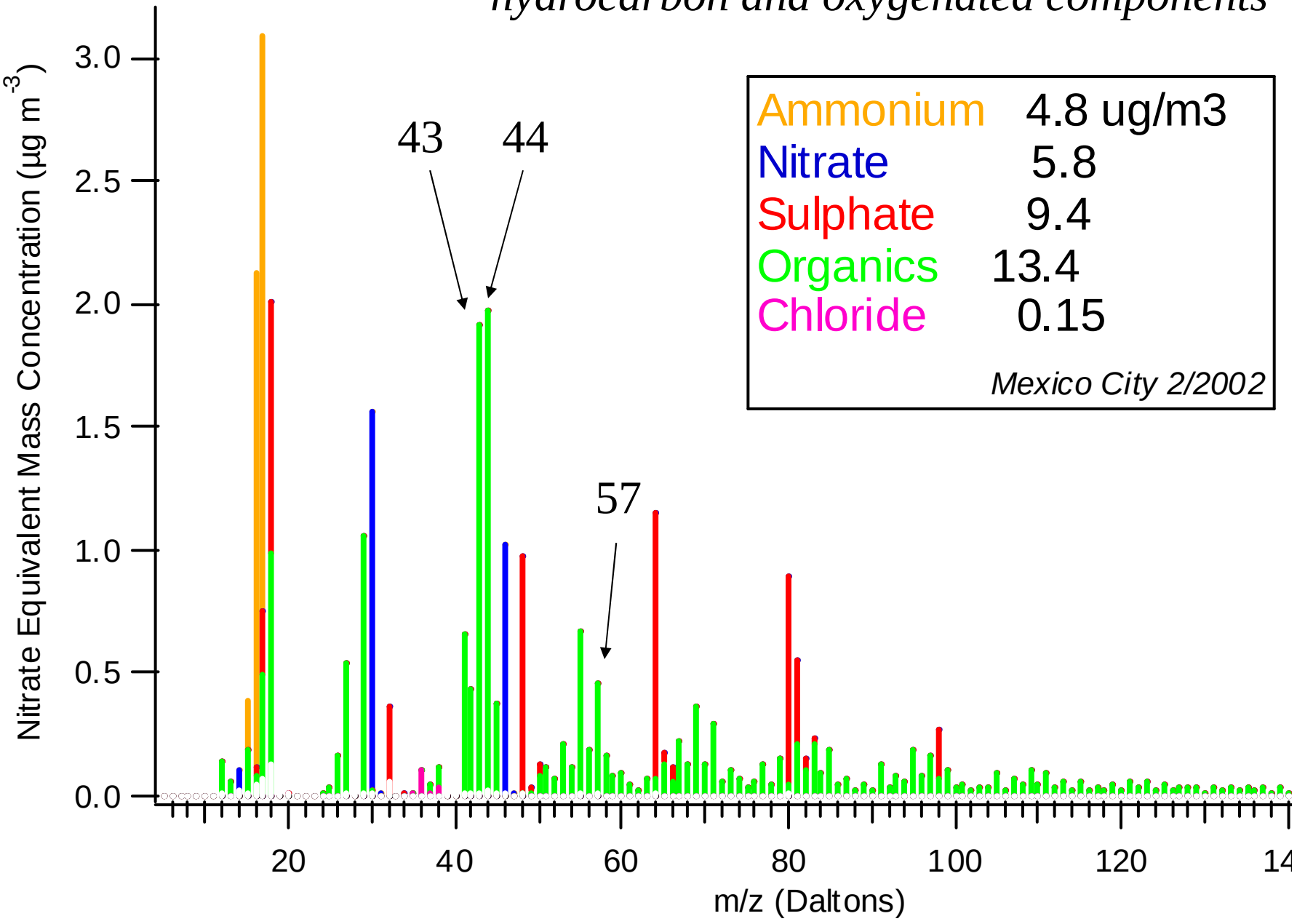


Urban organic aerosol is a mixture of hydrocarbon and oxygenated components



MS Signatures for Aerosol Species Identification

color coded to match spectra

Group	Molecule/Species		Ion Fragments	Mass Fragments
Water	H_2O	e^- →	H_2O^+ , HO^+ , O^+	18, 17, 16
Ammonium	NH_3	e^- →	NH_3^+, NH_2^+, NH^+	17, 16, 15
Nitrate	HNO_3	e^- →	HNO_3^+, NO_2^+, NO^+	63, 46, 30
Sulfate	H_2SO_4	e^- →	$H_2SO_4^+$, HSO_3^+, SO_3+	98, 81, 80
			SO_2^+, SO^+	64, 48
Organic *(Oxygenated)*	$C_nH_mO_y$	e^- →	H_2O^+, CO^+, CO_2^+	18, 28, 44
			$H_3C_2O^+$, HCO_2^+, C_n,H_m^+	43, 45, ...
Organic *(hydrocarbon)*	C_nH_m	e^- →	$C_n,H_m,^+$	27,29,41,43,55,57,69,71...

Standard electron impact ionization @ 70 eV

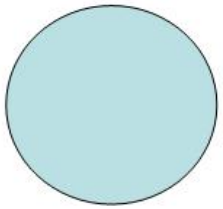
Easy to quantify: ca. NIST MS library

Easy to separate inorganic and organic components

Speciation of organic composition is challenging

ATMOSPHERIC AEROSOL

	Diameter (micron)	Molecules	Mass (gram)
Nano	**0.01**	**10^{5}**	**10^{-18}**
Ultrafine	**0.1**	**10^{8}**	**10^{-15}**
Fine	**1.0**	**10^{11}**	**10^{-12}**
Coarse	**10**	**10^{14}**	**10^{-9}**



AMS Sensitivity:

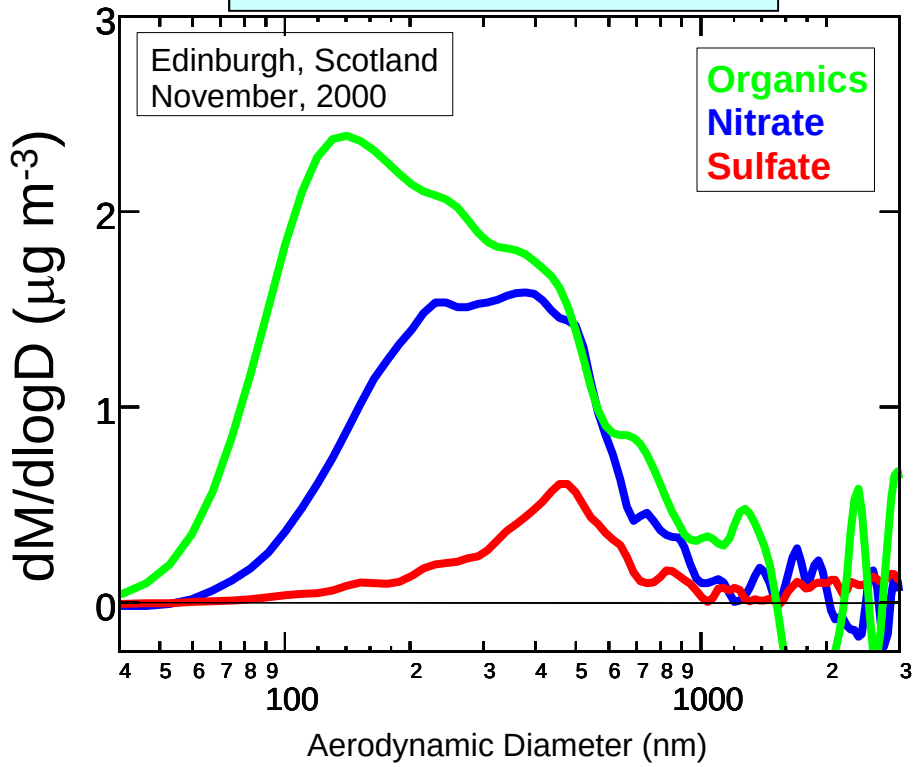
100 ions

100,000

IE = 1e-6 ions / molecule

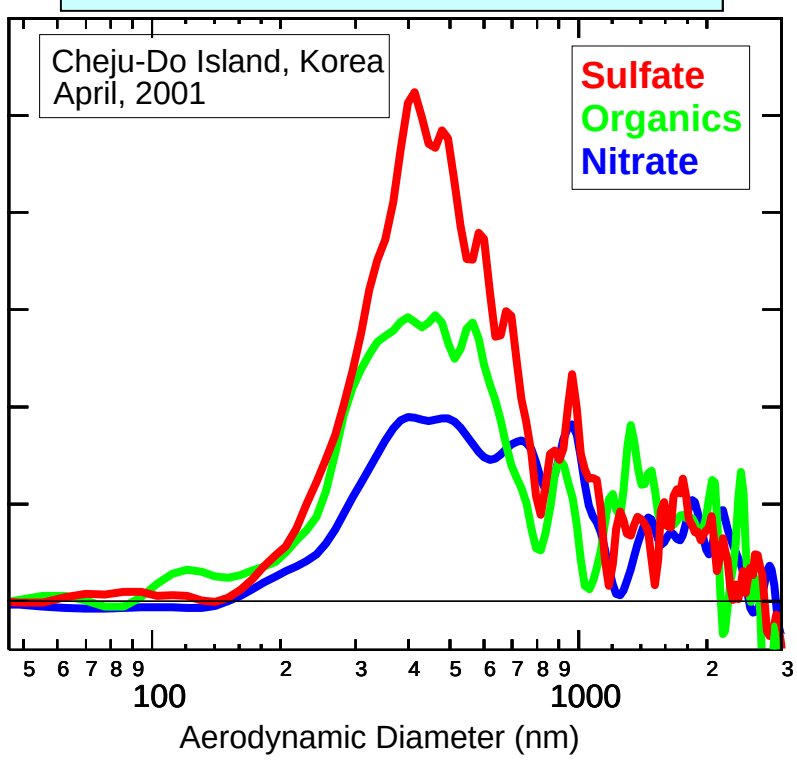
AMS Mass Distributions

Urban Site *Bi-modal*
Local Sources



Scotland *SASUA-3*

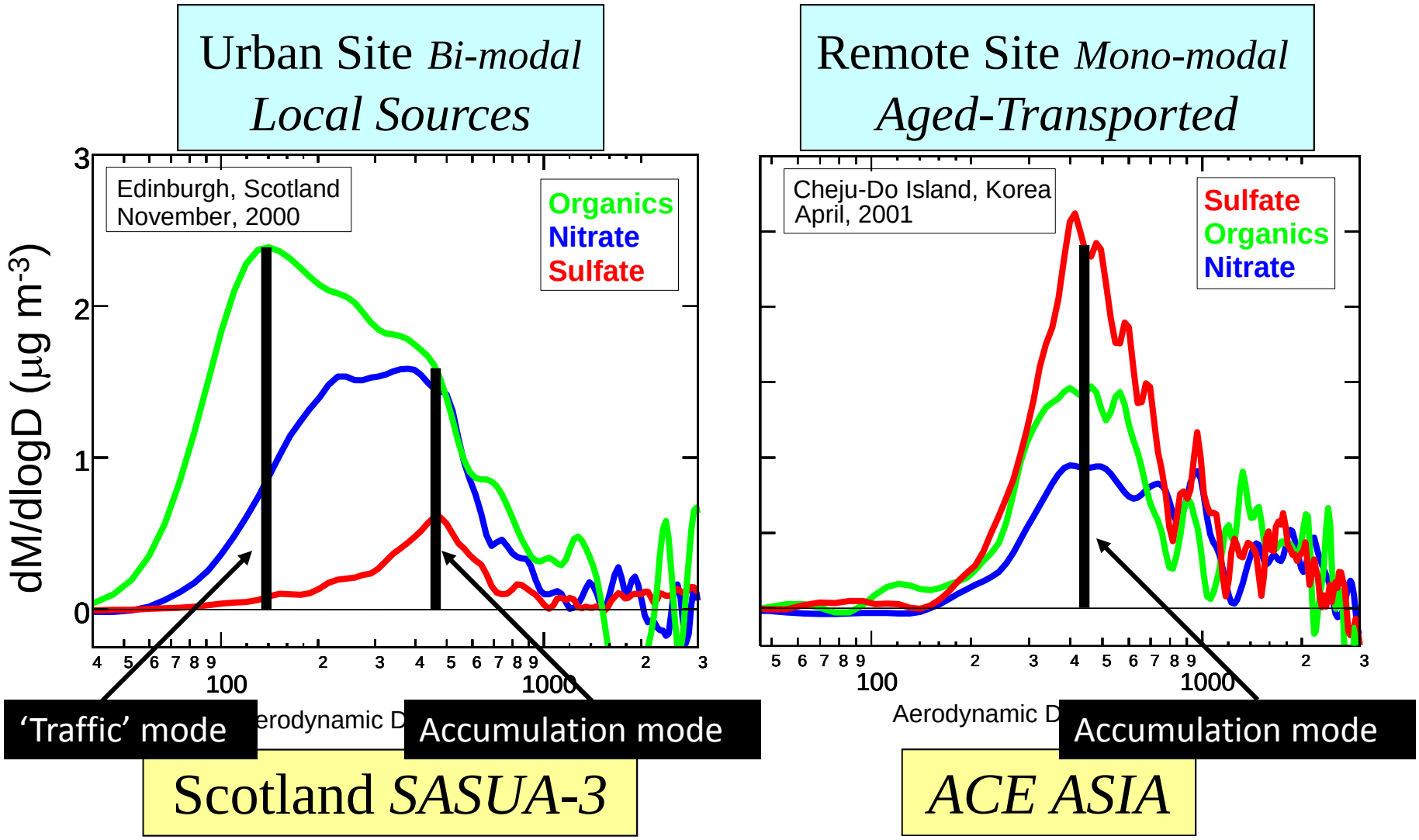
Remote Site *Mono-modal*
Aged-Transported



ACE ASIA

Allan, Alfarra et al. (U. Manchester)

Observed ‘Traffic’ Mode in Size Distributions



Allan, Alfarra et al. (U. Manchester)

Organic Mass Spectra

$C_nH_{2n+0,2} \xrightarrow{e^-} C_mH_{2m\pm1}^+$

27, 29, 41, 43, 55, 57, 69, 71, …

$C_3H_5^+$ $C_4H_7^+$ $C_5H_9^+$

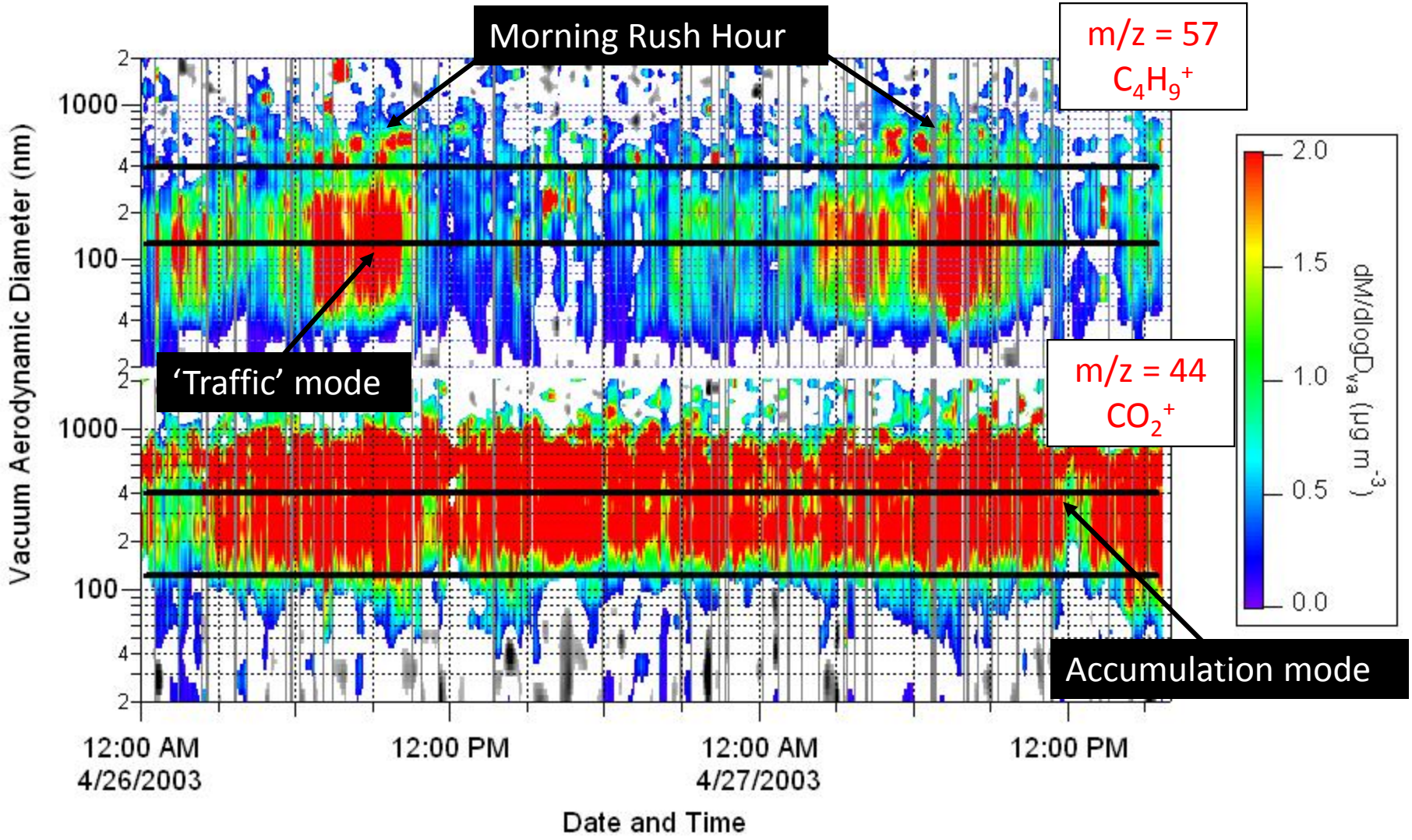
$C_nH_mO_y \xrightarrow{e^-} H_2O^+, CO^+, CO_2^+, C_2H_3O^+$

18 *28* *44* *43*

29, 55, ….

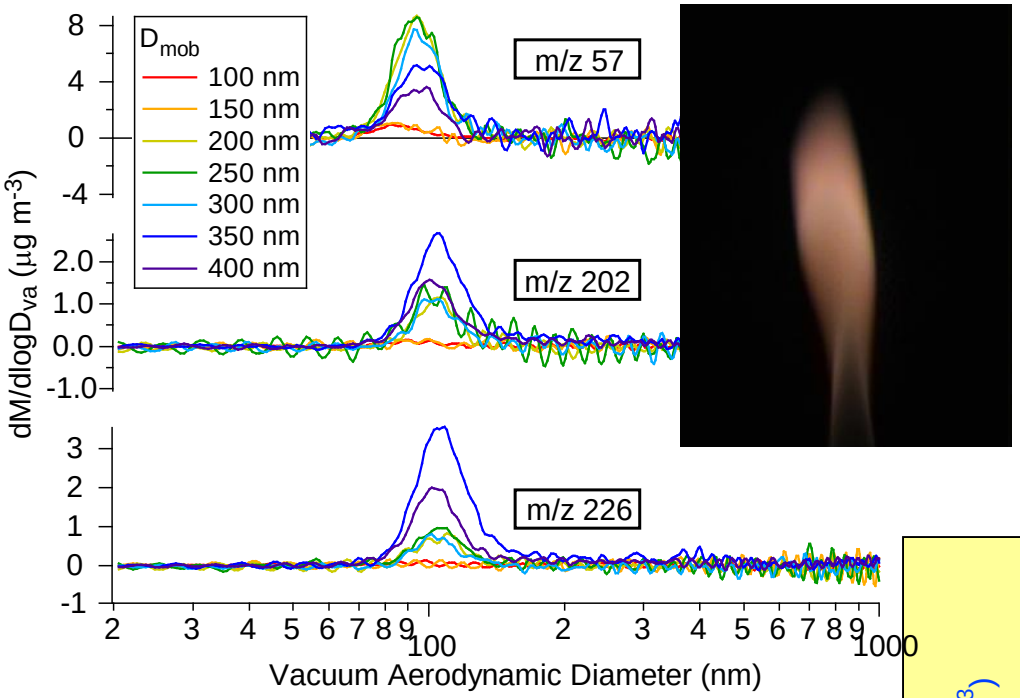
Following flash vaporization at ~600°C

Organic Mass Distributions



- Small mode, hydrocarbon-based, primary traffic organic PM
- Accumulation mode oxidized organic PM

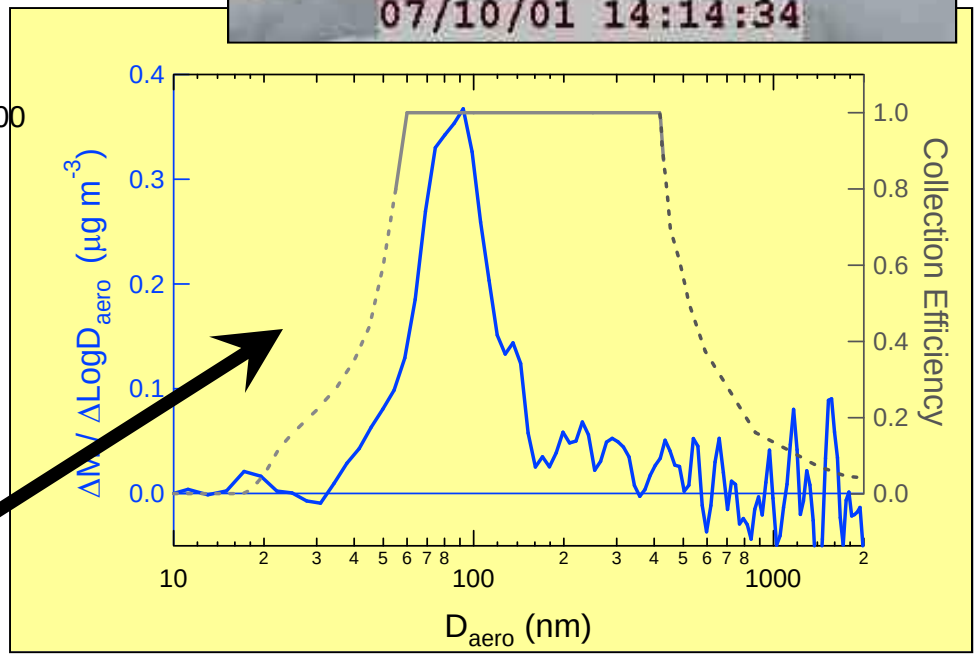
What is the nature of the small mode organics?



Flame generated soot in the lab
(Slowik et al, 2005; DeCarlo et al., 2005)

Diesel particles on the road

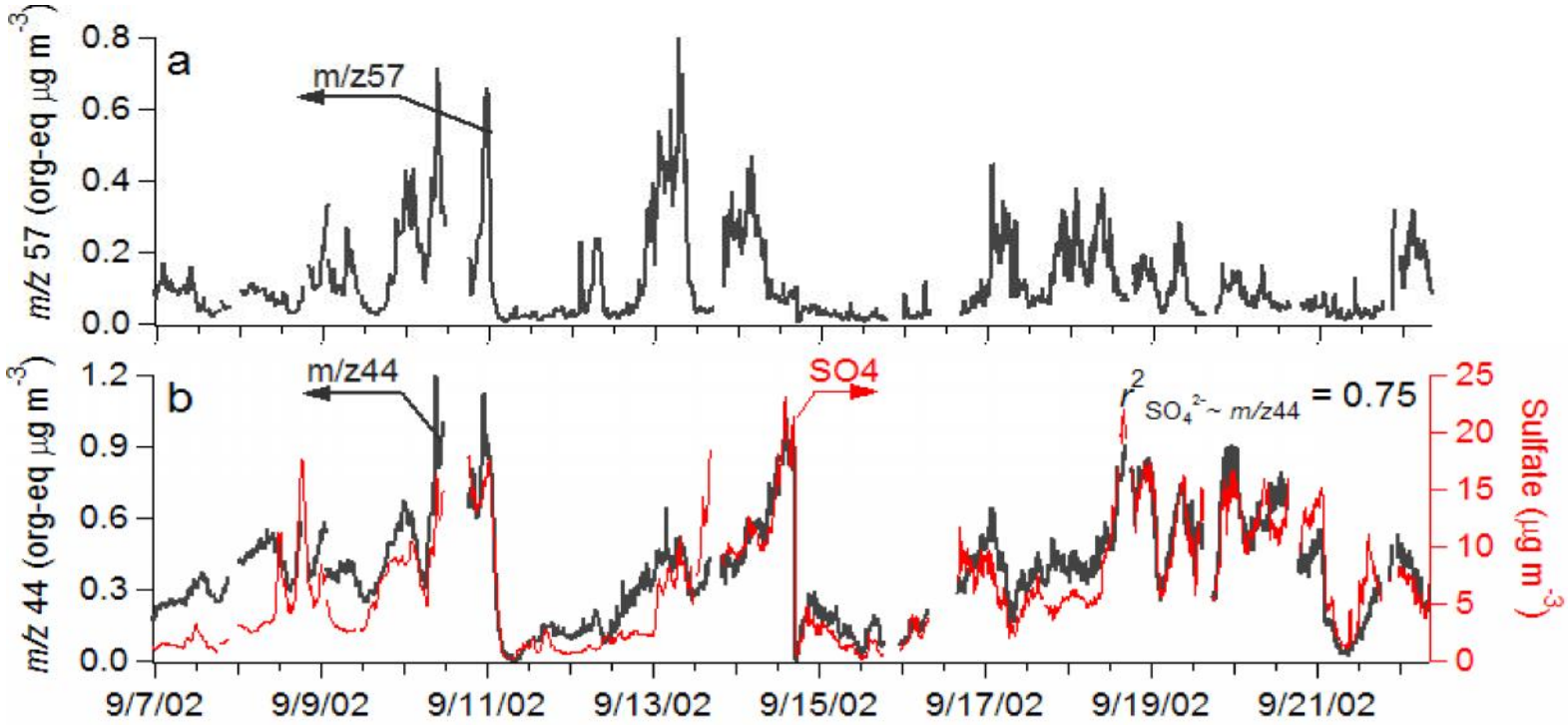
(Canagaratna et al., 2003)

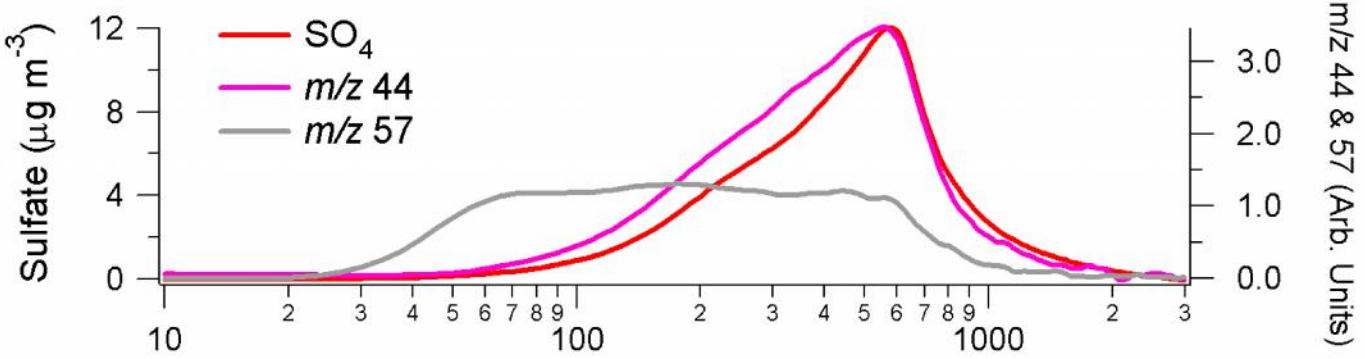


AMS Mass Spectral Tracers

m/z 57 (mostly $C_4H_9^+$): Hydrocarbon-like Organic Aerosol (HOA; likely POA)

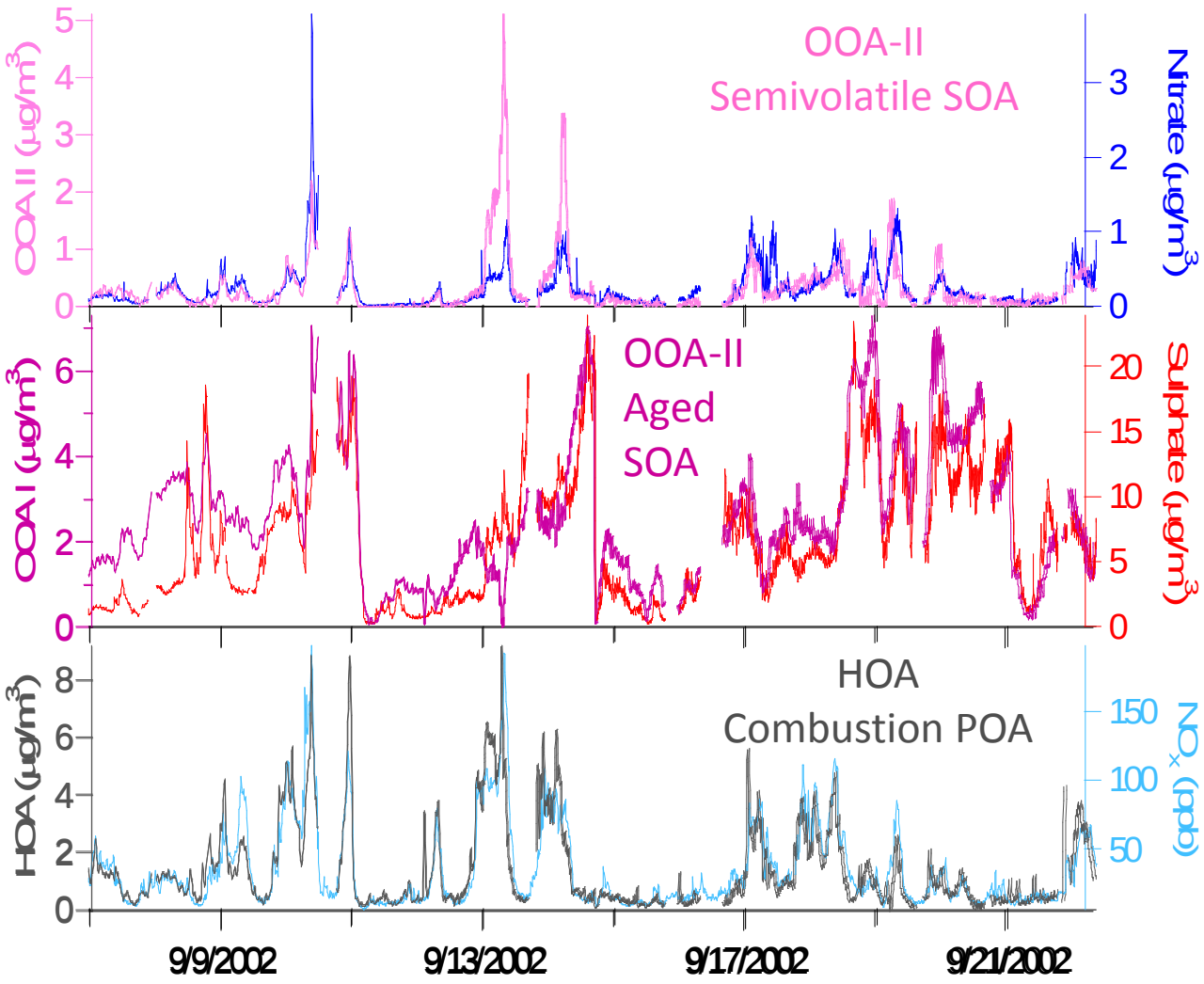
m/z 44 (mostly CO_2^+): Oxygenated Organic Aerosol (OOA; likely SOA)

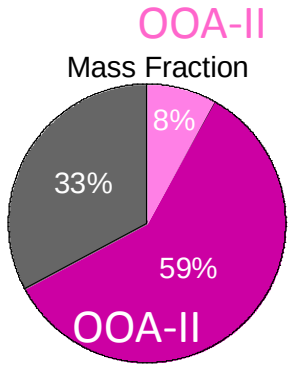


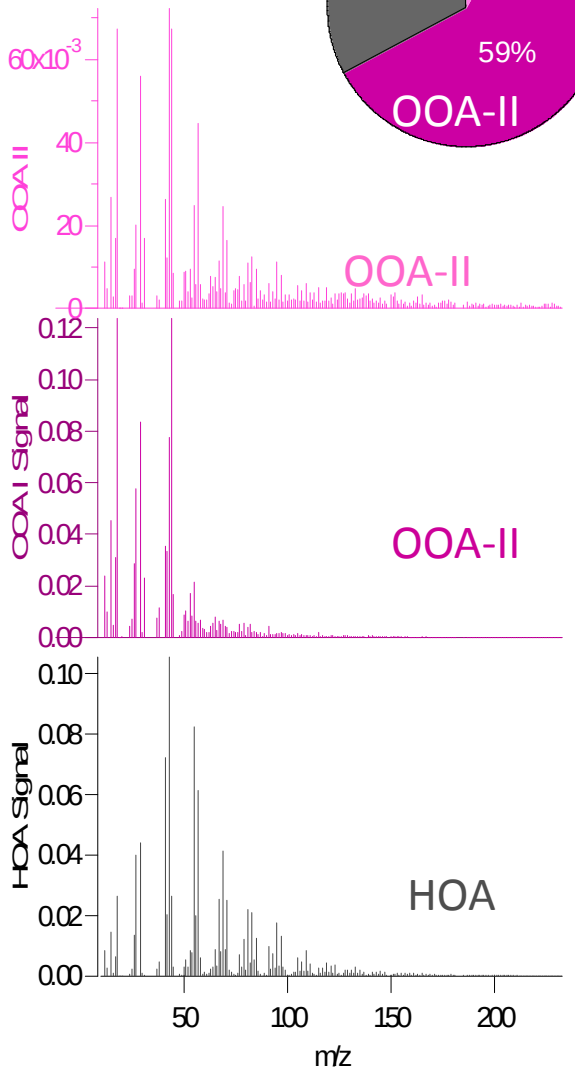


Zhang et al,
ACP, 5, 3289 (2005)

Pittsburgh: 3 factors in PMF



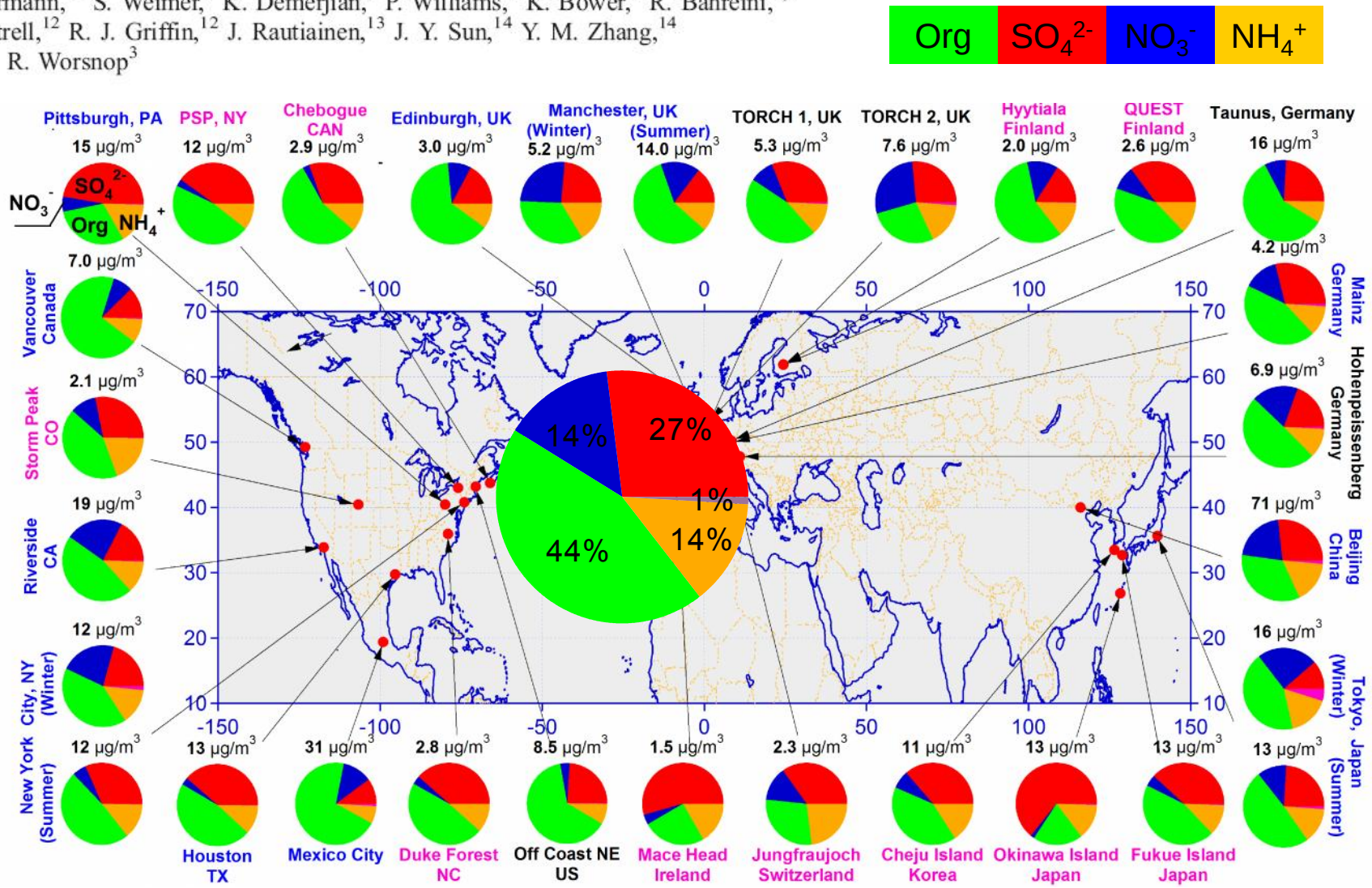




Ulbrich et al., *ACPD*, 2008

Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes

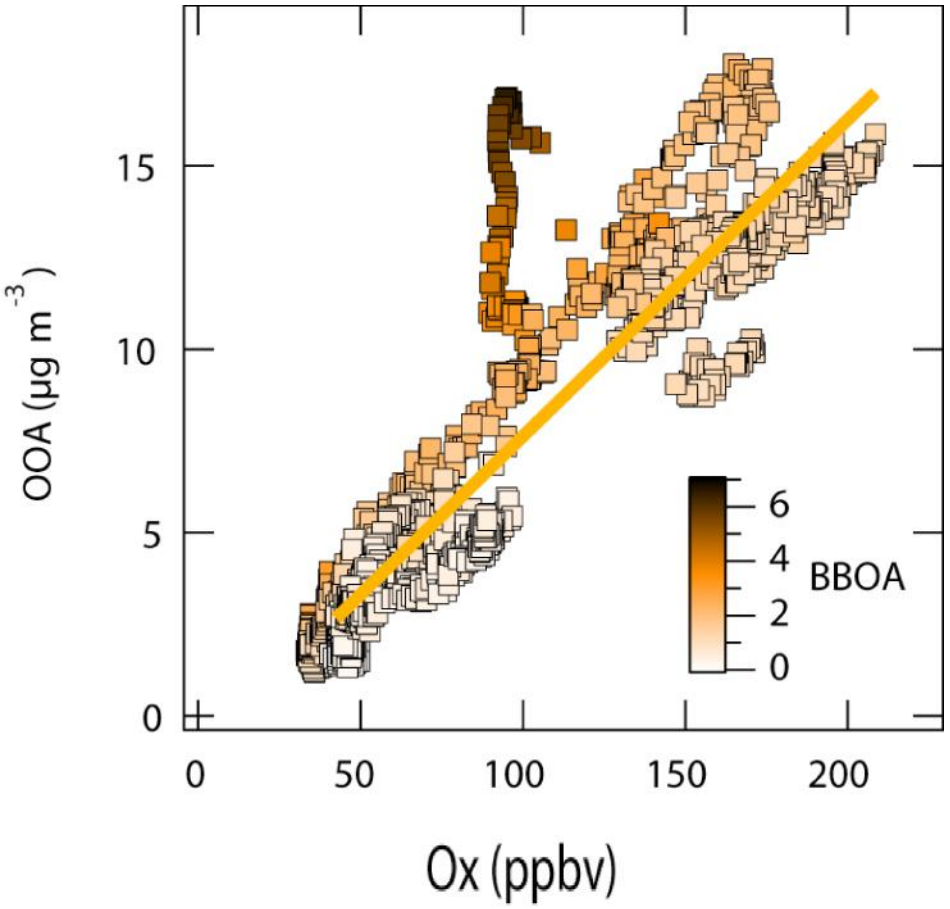
Q. Zhang,[1] J. L. Jimenez,[2] M. R. Canagaratna,[3] J. D. Allan,[4] H. Coe,[4] I. Ulbrich,[2] M. R. Alfarra,[5] A. Takami,[6] A. M. Middlebrook,[7] Y. L. Sun,[1] K. Dzepina,[2] E. Dunlea,[2] K. Docherty,[2] P. F. DeCarlo,[2] D. Salcedo,[8] T. Onasch,[3] J. T. Jayne,[3] T. Miyoshi,[6] A. Shimono,[9] S. Hatakeyama,[6] N. Takegawa,[10] Y. Kondo,[10] J. Schneider,[11] F. Drewnick,[11] S. Borrmann,[11] S. Weimer,[1] K. Demerjian,[1] P. Williams,[4] K. Bower,[4] R. Bahreini,[2,7] L. Cottrell,[12] R. J. Griffin,[12] J. Rautiainen,[13] J. Y. Sun,[14] Y. M. Zhang,[14] and D. R. Worsnop[3]



GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L15804, doi:10.1029/2008GL034058, 2008

Correlation of secondary organic aerosol with odd oxygen in Mexico City

Scott C. Herndon,[1] Timothy B. Onasch,[1] Ezra C. Wood,[1] Jesse H. Kroll,[1] Manjula R. Canagaratna,[1] John T. Jayne,[1] Miguel A. Zavala,[2,3] W. Berk Knighton,[4] Claudio Mazzoleni,[5] Manvendra K. Dubey,[5] Ingrid M. Ulbrich,[6] Jose L. Jimenez,[6] Robert Seila,[7] Joost A. de Gouw,[8] Benjamin de Foy,[9] Jerome Fast,[10] Luisa T. Molina,[2,3] Charles E. Kolb,[1] and Douglas R. Worsnop[1]



$O_x = O_3 + NO_2$