PITTCON 2015 Session 60-04

High Resolution, Extreme Field Spectra of Small Molecules with Advanced FAIMS Configuration

Differential Ion Mobility Spectrometry:

New FAIMS Instrumentation and Applications

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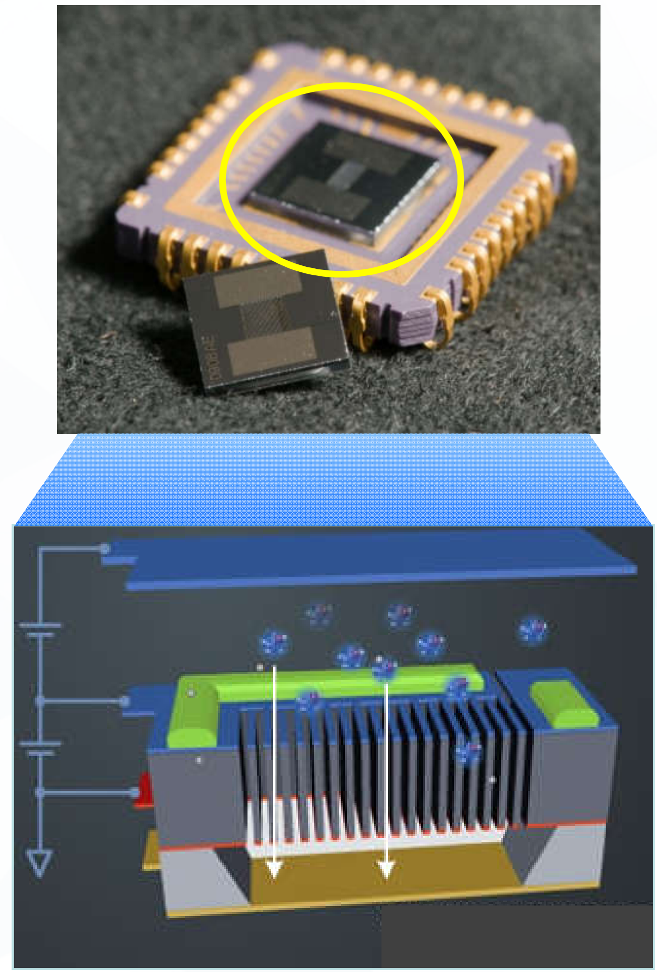
"Differentiating" UH-FAIMS

Ultra High Field Ion Mobility Spectrometry

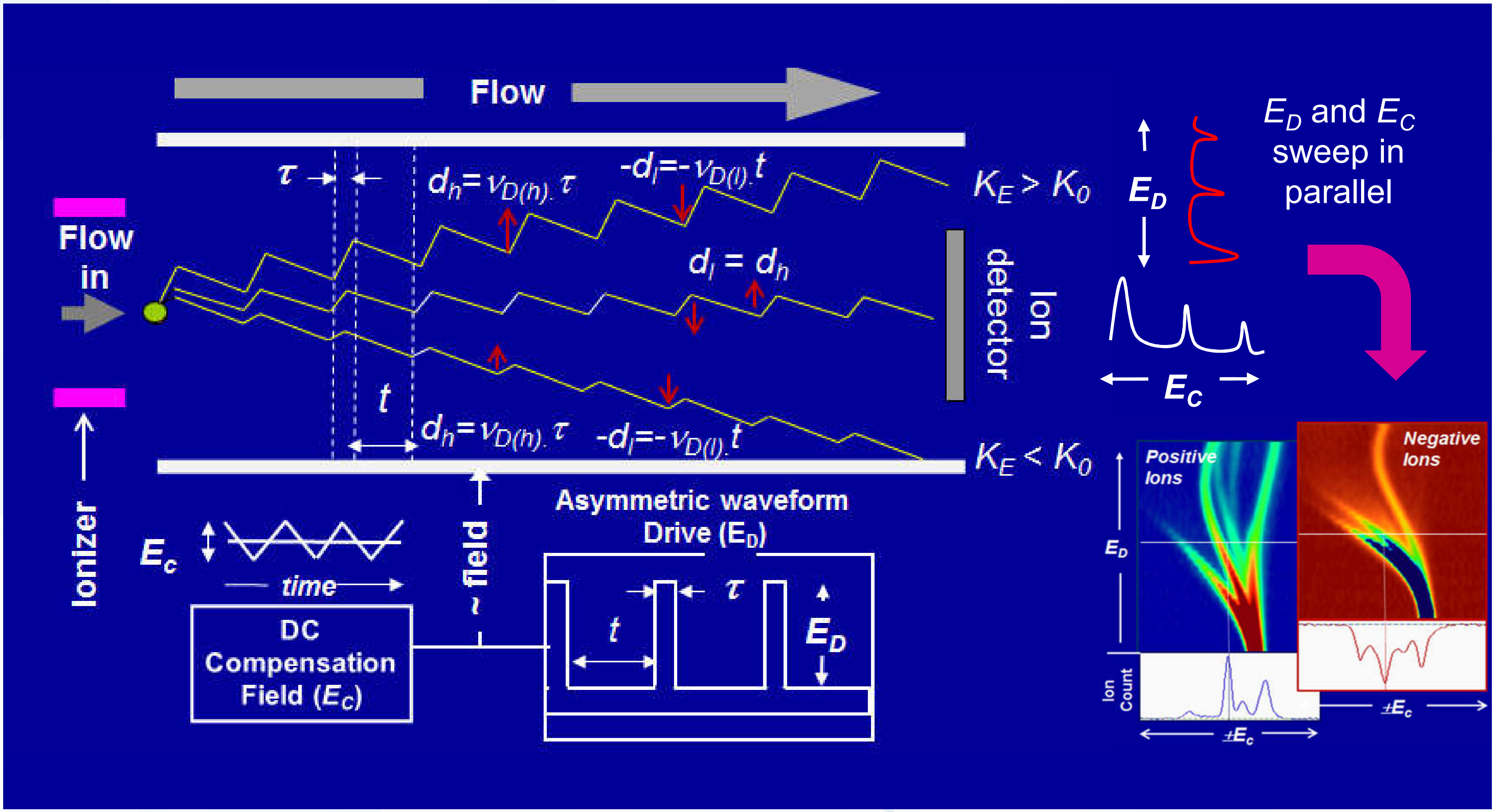
- Foundations in Ion Mobility Spectrometry & variants (Differential Mobility Spectrometry and Field Asymmetric Ion Mobility Spectrometry)
- Filters ions according to behavior in an electric field

Enabling Tech: 0.7cm^2 planar multi-channel ion filter

- Extreme field operation: to >80kV.cm^{-1}, c.f. to ~30kV.cm^{-1} (DMS) & ~ 2kV.cm^{-1} (IMS)
- Very high speed ion separation: ~ 70µs, c.f. to ~20ms (DMS & IMS)
- Multi-channel **micron-gap** ion separators (physically enabling the use of extreme fields)
- Very High Frequency separation waveforms (25MHz)



Phemenology



Significance of High Fields

for lower MW ions…

$$T_{eff} = T + \zeta \cdot M \cdot K_0^{2} \cdot N_0^{2} \cdot (E_D/N)^2/(3k_b)$$

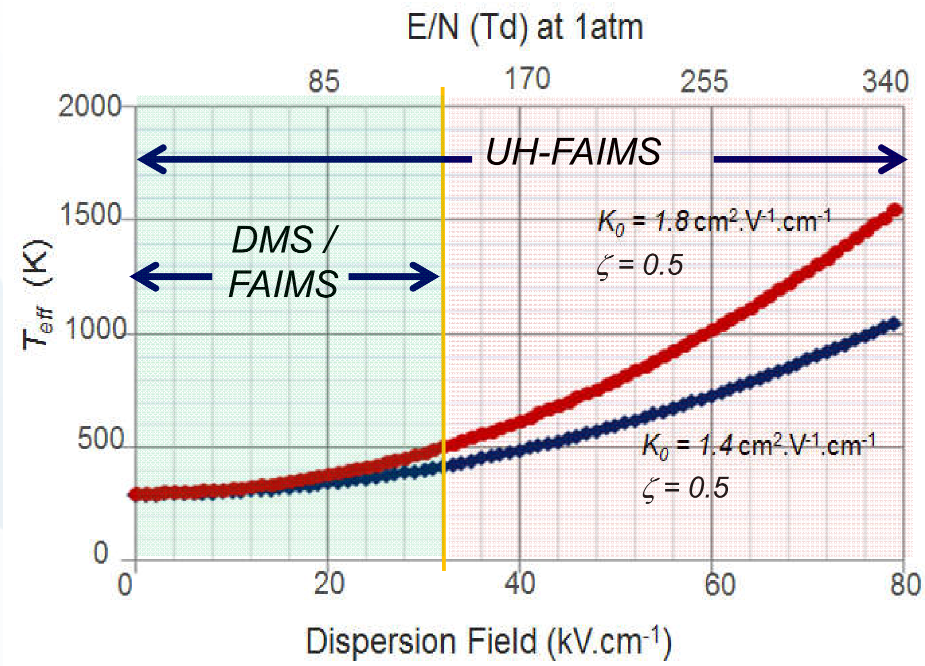
T = Drift gas temperature (K)

M = Av. MW of carrier gas

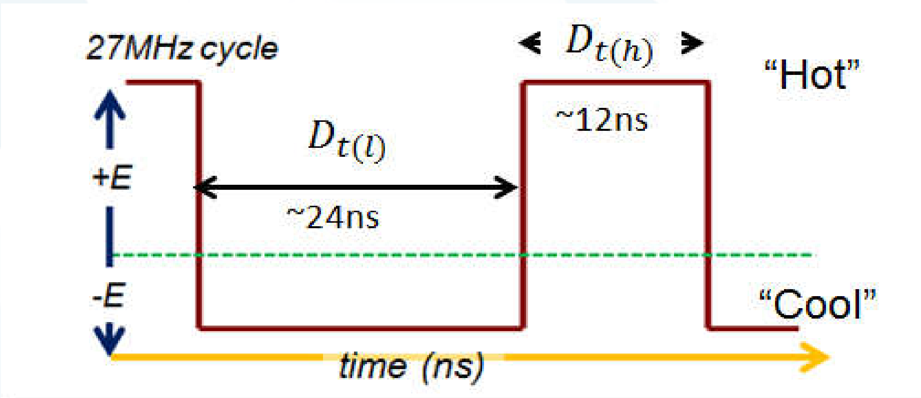
E_D/N = Field / number density ($V.m^2$)

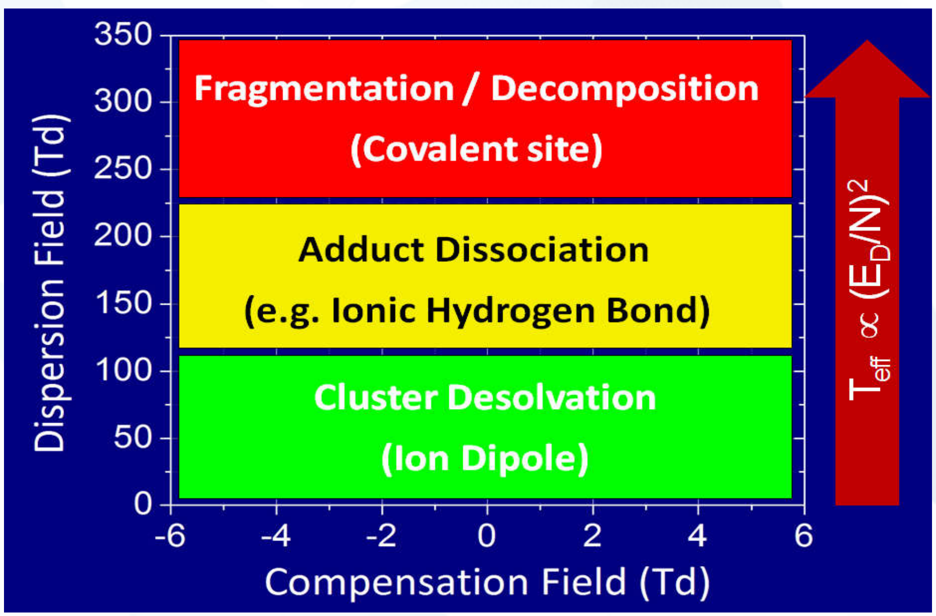
$K_{(0)}$ = Ion Mobility ($m^2.V.s^{-1}$)

ζ = Energy transfer (collisional) efficiency factor



"In filter" ion chemistry





For hypothetical ion dissociation process -

$$MA^+ \xrightarrow{k} M^+ + A$$

$$E_A = \Delta H - RT$$

E_A = Association energy

ΔH = enthalpy of Association

$$k(T_{eff}) = A.\ exp - (E_A / R.T_{eff})$$

"In filter" Dissociation when -

$$1/k(T_{eff}) < \sum D_{t(h)}$$

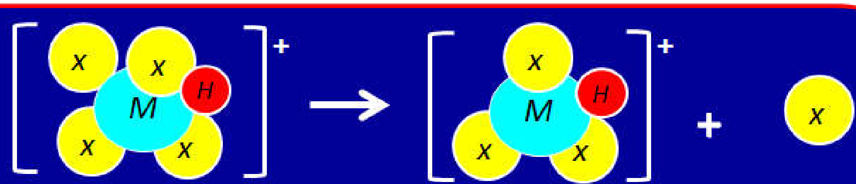
“In filter” ion chemistry

“*In filter*” ion transformations/ reactions…

- ***Desolvation***

  ion-dipole /ion-induced-dipole

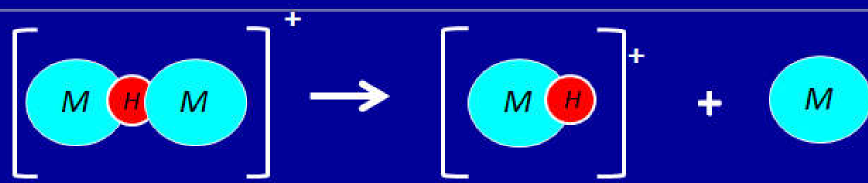
  $M(X_n)^{+/-} \rightarrow M(X_{n-1})^{+/-} + X$



- ***Adduct dissociation***

  (*e.g.*, ionic H bond cleavage)

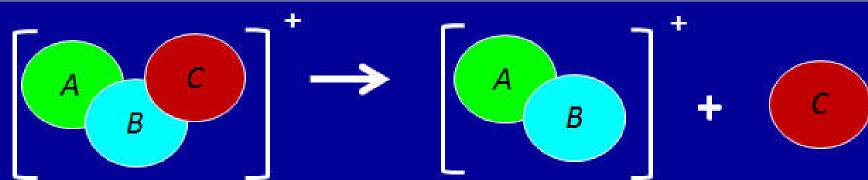
  $(M_2H)^+ \rightarrow (MH)^+ + M$



- ***Fragmentation***

  (covalent site)

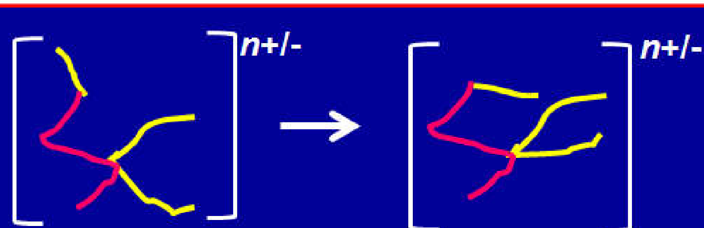
  $(ABC)^{+/-} \rightarrow (AB)^{+/-} + C$



- ***Conformational*** (*geometric*), *e.g.*

  Barrier to internal rotation

  Folding (high MW *multi-charged* molecular ions (peptides, proteins)



Data rich "snapshot" spectra

Large amount of information generated and processed extremely rapidly Gaussian parameters -

→ **Peak Width**

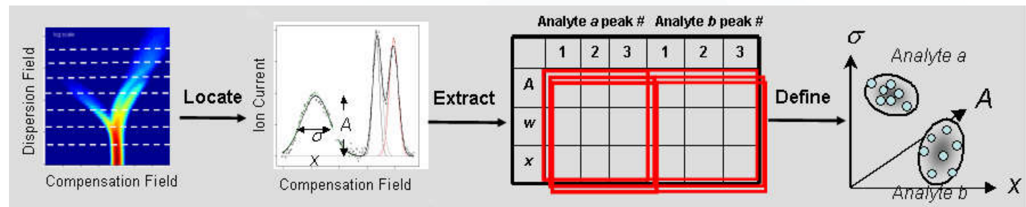
→ **Peak Area**

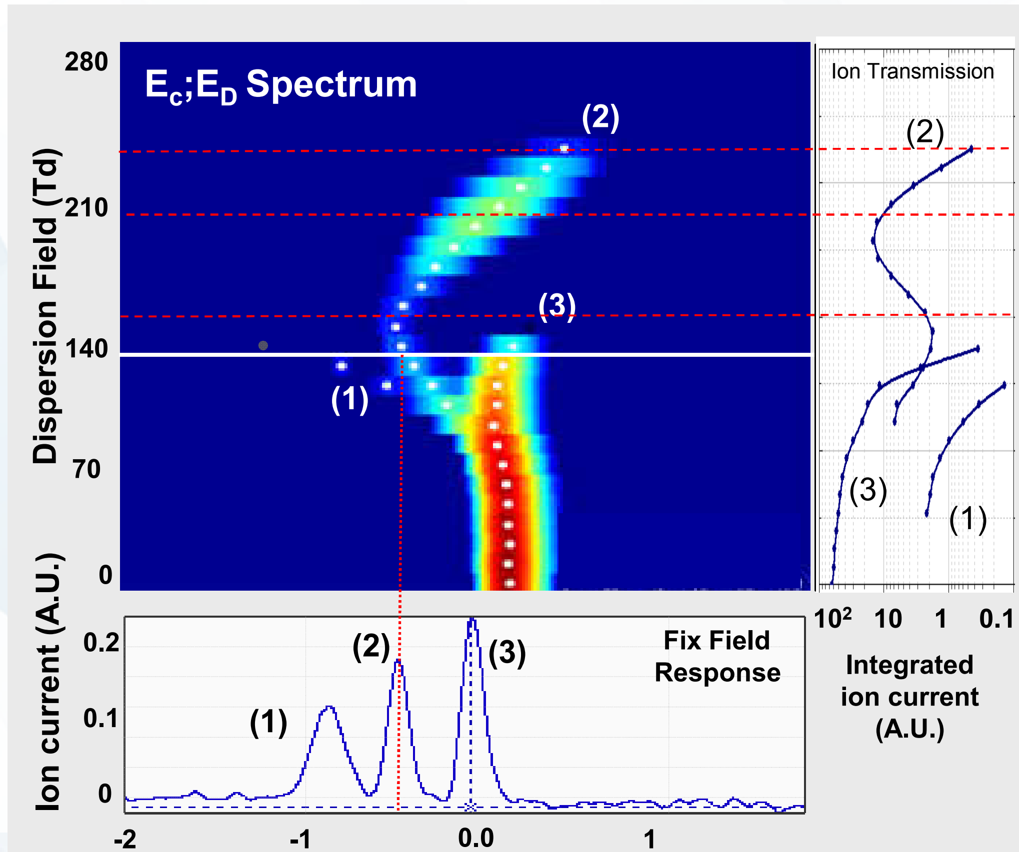
→ **Peak Location**

…….as a function of Dispersion Field

Key Information

Parameter	Information
Peak Width $W_{1/2}(E_D/N)$	Low field mobility Field specific Ion behavior
Ion Transmission $I_A(E_D/N)$	Quantitative Level Field specific Ion behavior (*e.g.* Ion cluster breakdown)
Peak location $E_C(E_D/N)$	Ion (chemical) identity





Design Improvements

Wider Gaps

- Higher flow
- Greater ion transmission without resolution penalty

Longer channel

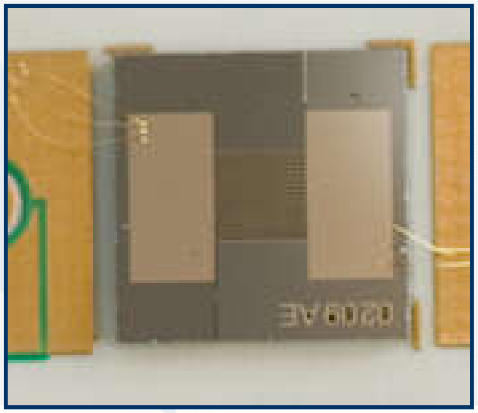
- Increased residence time
- Narrower peak without transmission penalty

But…

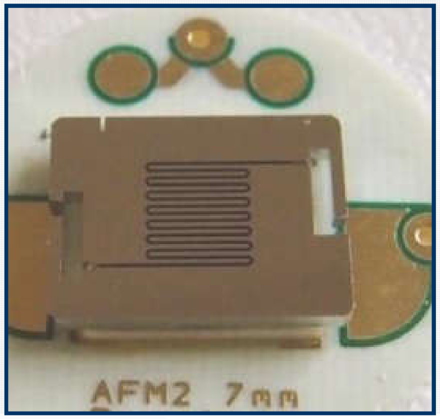
- Need **higher voltage** field drivers to compensate for larger ion filter gap

Material	Silicon *vs* .Metalized
Gap width (g)	35 *vs.*50µm
Length (l)	300 *vs.* 450µm
Area (A)	15 *vs.* 20mm^2
DF range (E_D/N)	350Td *vs.* 320Td
Res. time (t_{res})	~40µs *vs.* 75~µs

Narrow gap

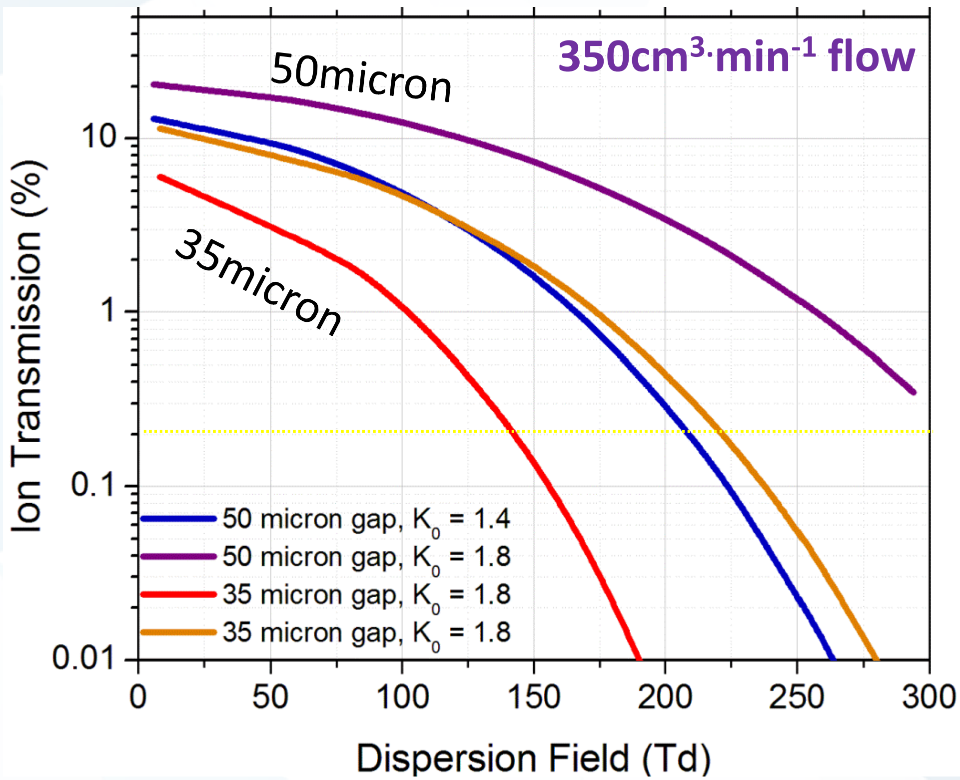


Wide gap

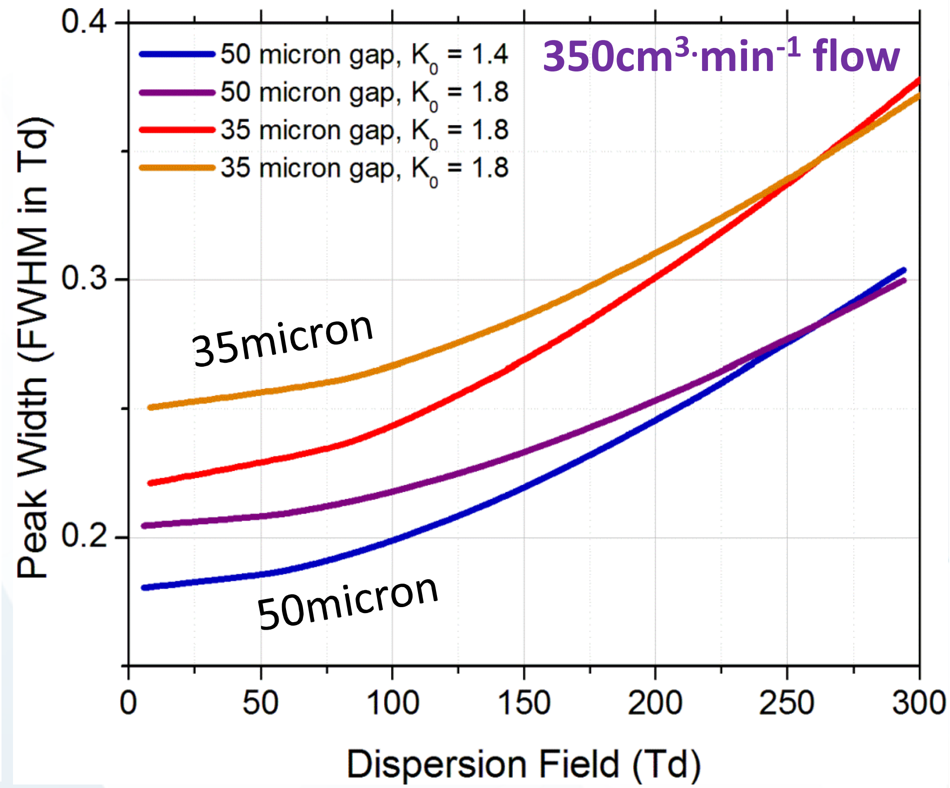


Design Improvements

Ion Transmission



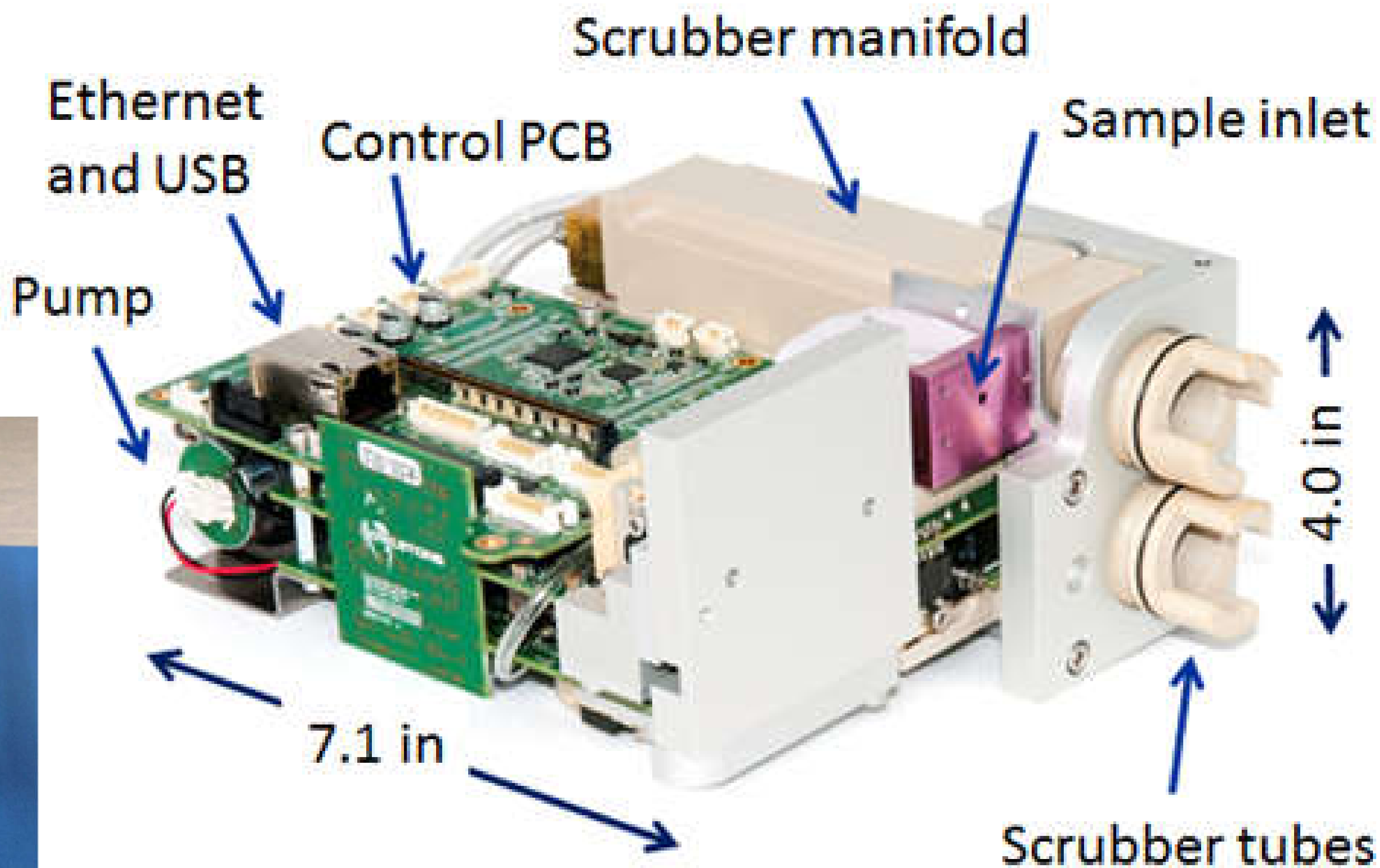
Peak Width (FWHM)

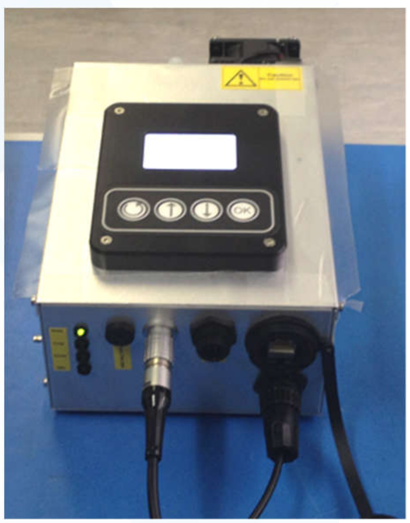


High Field Transmission vastly (~ x50) improved – critical for monomeric ions

40% reduction in Peak FWHM width (Ion peak separation)

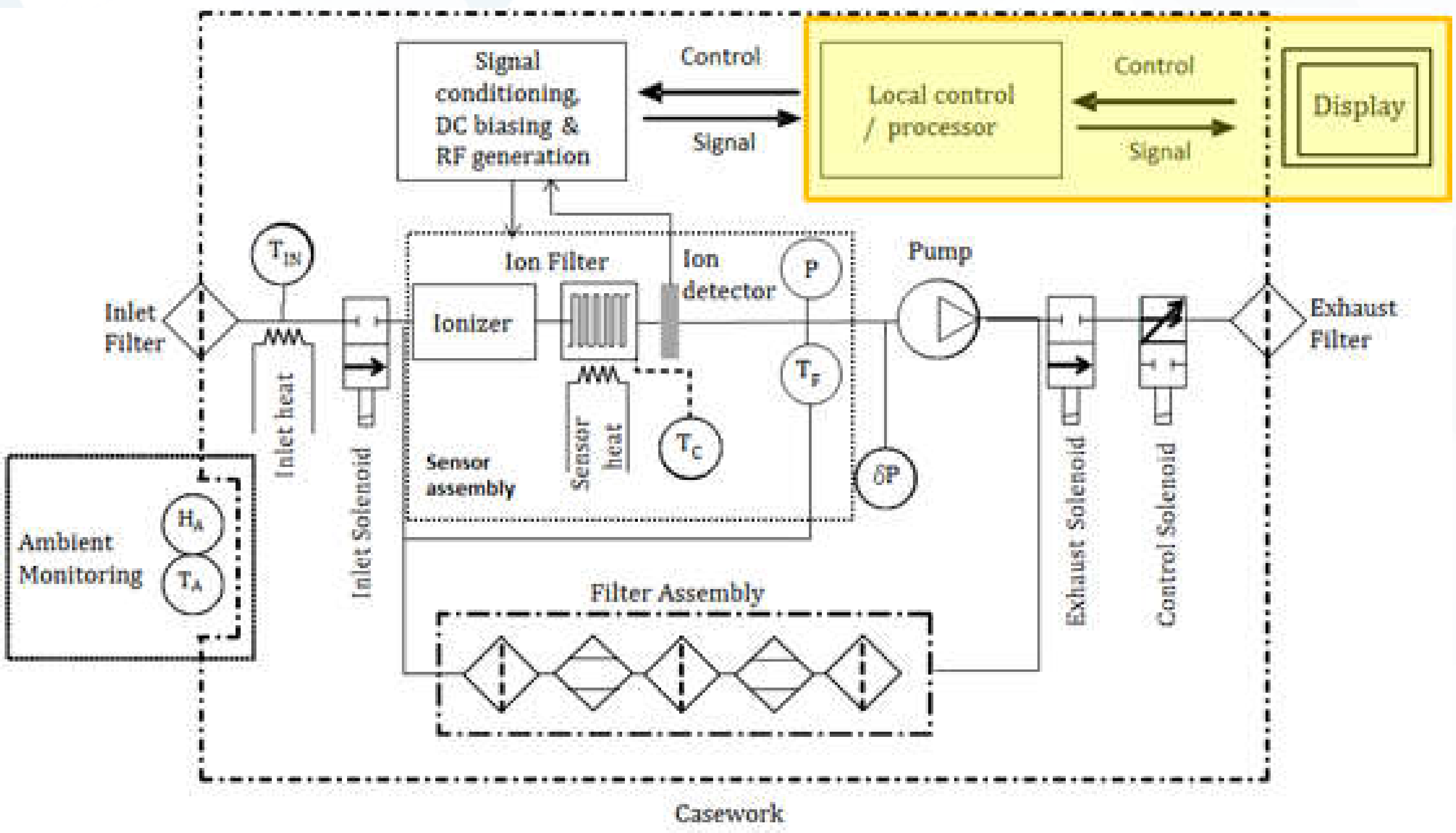
Wholly integrated -





VOC / SVOC Detector

System Configuration

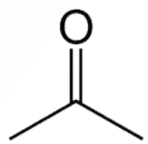


c.f. Wilks et al, Int. J. Ion Mob. Spectrom. ***15*** (2012) *199 - 222*

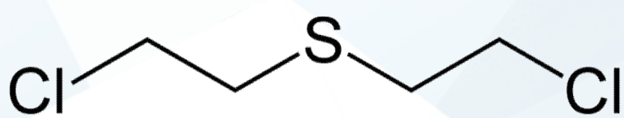
Case Studies 1 – Organophos.

Reference Controls

Acetone
MW = 48 AMU
Positive Ion Mode

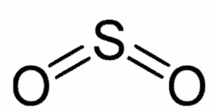


Bis (2-chloroethyl) sulfide
MW = 159 AMU Negative Ion Mode



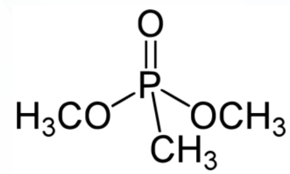
Chlorine **MW = 71 AMU**
Negative Ion Mode

Sulfur Dioxide **MW = 64AMU**
Negative Ion Mode

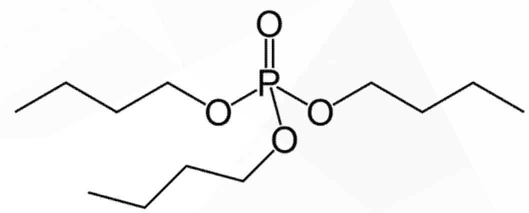


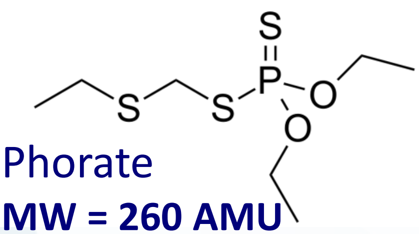
Organophos. compounds

Dimethyl Methyl Phosphonate (DMMP)
MW = 124 AMU

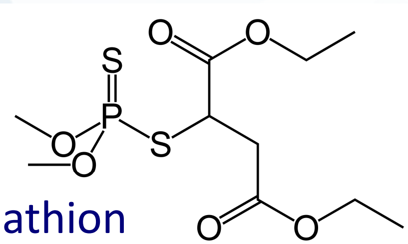


Tributyl Phosphate (TBP)
MW = 266 AMU

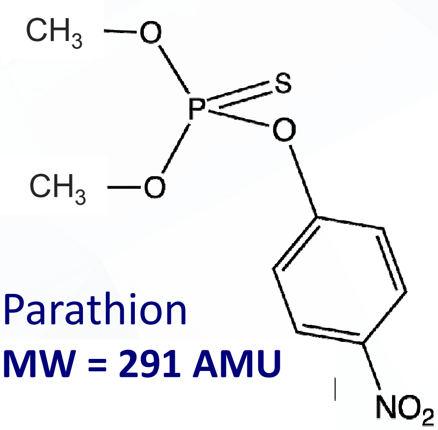




Phorate
MW = 260 AMU

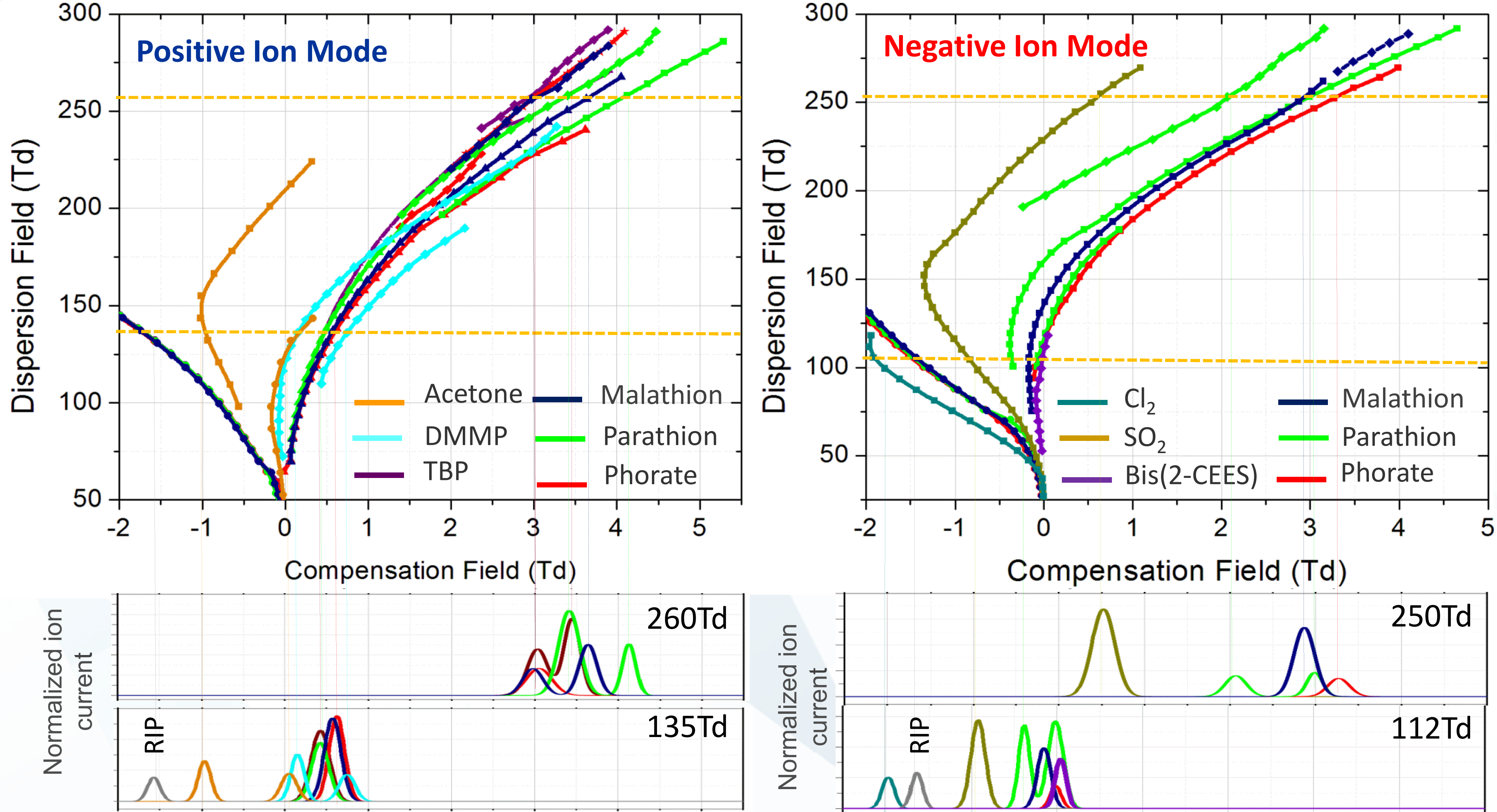


Malathion
MW = 330 AMU



Parathion
MW = 291 AMU

Organophos



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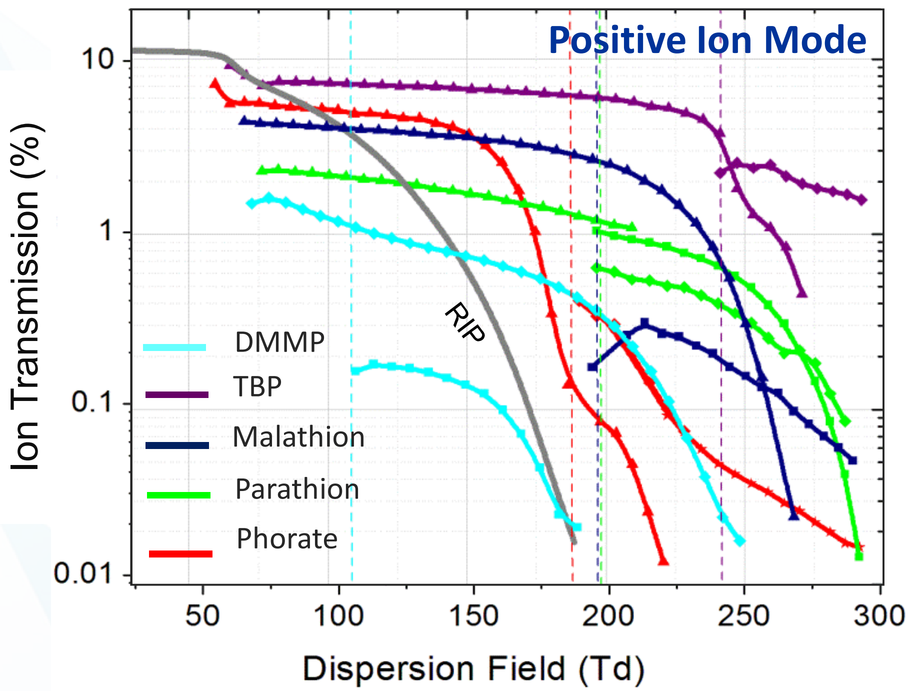
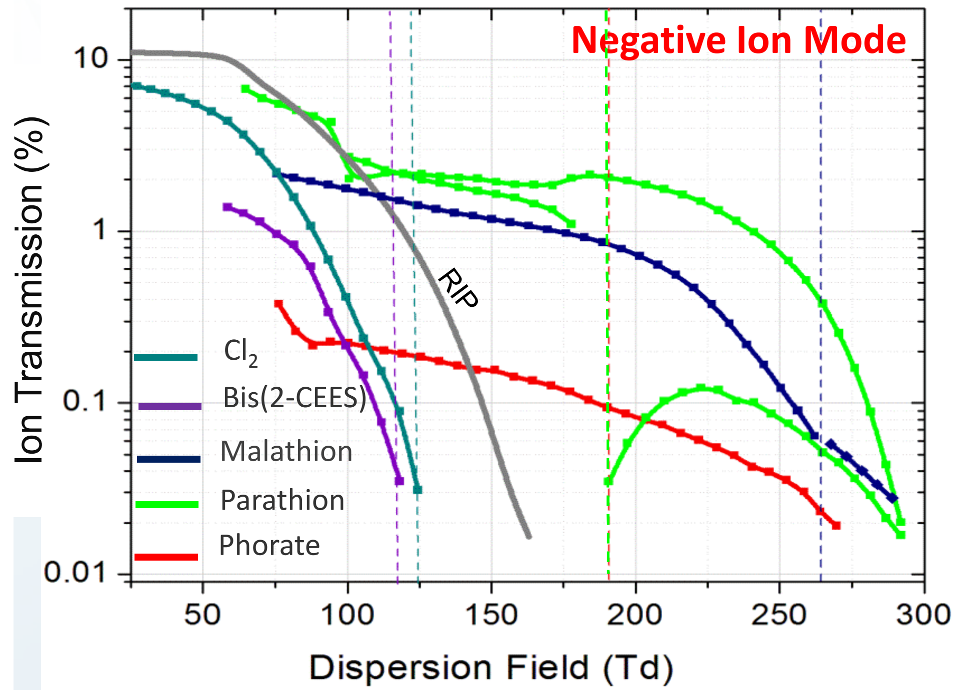
Interpretation

Ion Transmission profiles help with interpretation of Dispersion Spectra



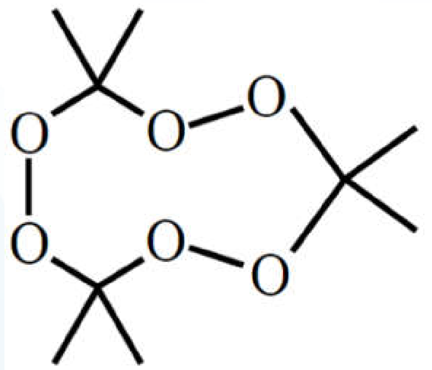


Field induced ion chemistry beyond breakdown of the proton bound dimer?

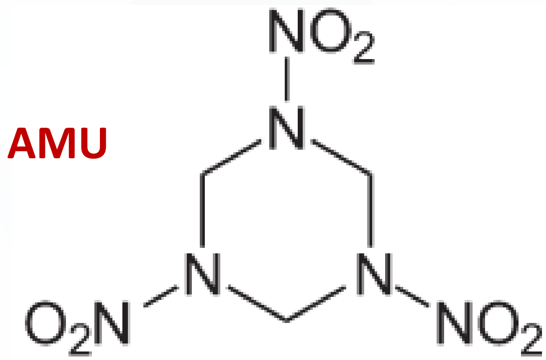
High Field induced ion chemistry seems to be observed in malathion and parathion

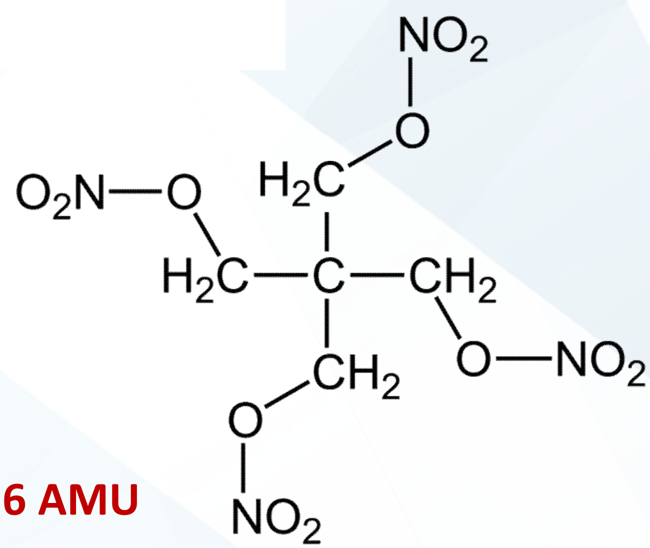
Case Studies 2 – Explosives

Acetone Peroxide Trimer (TATP)
MW = 222 AMU



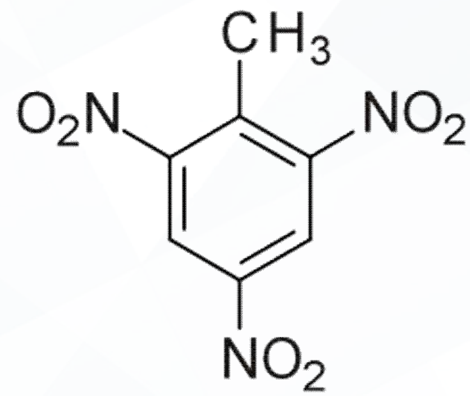
RDX
MW = 222 AMU



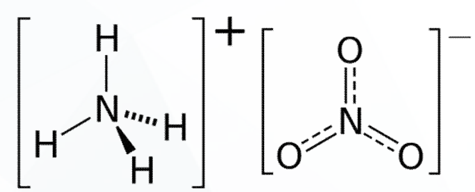


PETN
MW = 316 AMU

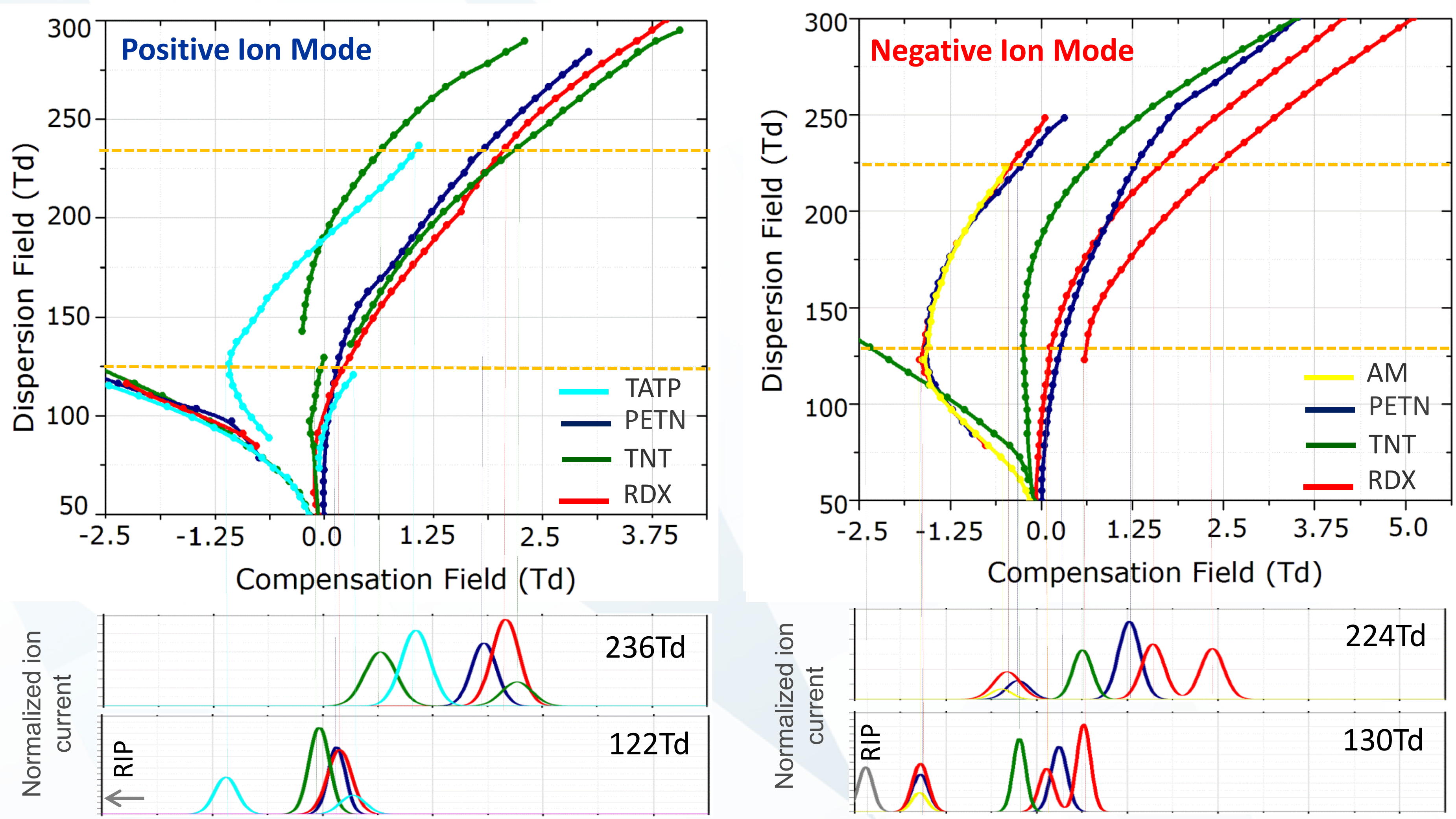
TNT
MW = 227AMU



Ammonium Nitrate (ionic)
MW = 80 AMU

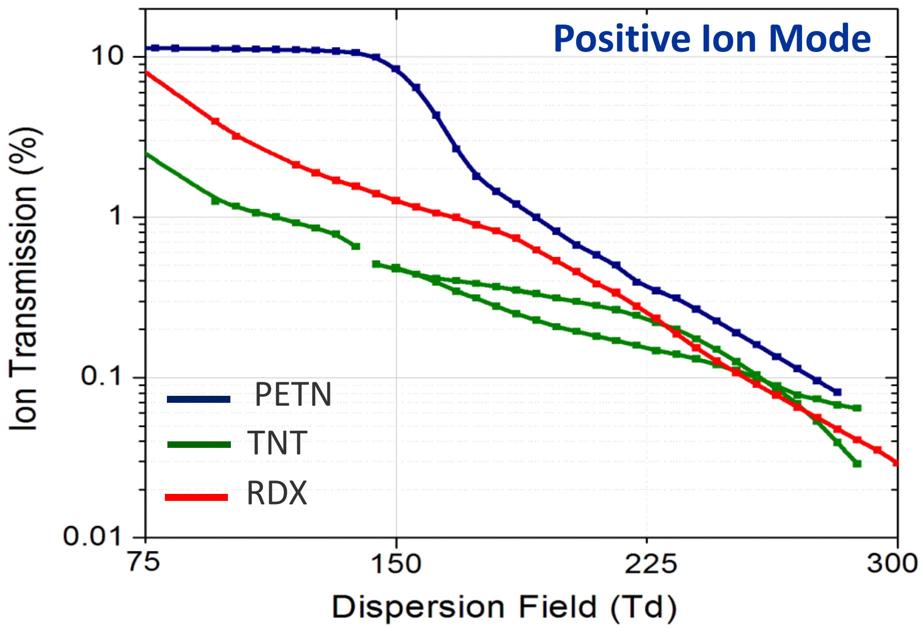


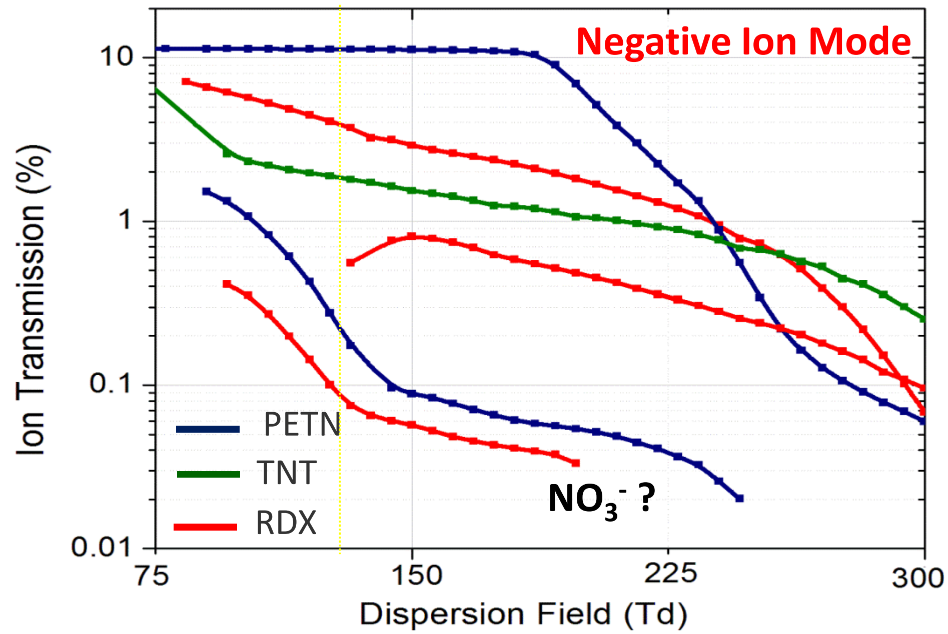
Exps


Positive Ion Mode
Dispersion Field (Td)
300
250
200
150
100
50
-2.5
-1.25
0.0
1.25
2.5
3.75
Compensation Field (Td)
TATP
PETN
TNT
RDX
Negative Ion Mode
5.0
AM
Normalized ion current
236Td
122Td
RIP
224Td
130Td

Interpretation

Again - Ion Transmission profiles help with interpretation of Dispersion Spectra





Positive ions observed but not the prominent case (neg ion current ~10x pos ion current)

Selective cleavage of NO_2 in PETN & RDX with NO_3^- Formation?

Summary

- New system configuration for “detector” type application – specifically **VOCs** and **SVOCs**
- Developed with a view of application as Selective GC detector (comparable sensitivity to NPD and ECD detectors (**sub-ppb** by volume detection of **OPs** and **sub-nanogram** real time detection of **Explosive** compounds
- Critical design aspects -
  - **New generation waveform drivers**
  - **Wider ion channels (enabling much better expoitation of high field ion chemistry by dramically improving high field ion transmission)**
  - **Novel low power design**
  - **Higher Voltage (to compensate for broader filter gap)**
  - **Better “quality” separation waveforms**

Acknowledgements

Owlstone Team

Useful References

A. A. Shvartsburg (2009) Differential Ion Mobility Spectrometry. CRC Press, Boca Raton

E. V. Krylov , E. G. Nazarov, R. A. Miller (2007) Differential mobility spectrometer: Model of operation. Int J Mass Spectrom 266:76–85

E. V. Krylov , E. G. Nazarov, R. A. Miller (2007) Differential mobility spectrometer: Model of operation. Int J Mass Spectrom 266:76–85

An X, Eiceman GA, Rodriguez JE, Stone JA (2011) Gas phase fragmentation of protonated esters in air at ambient pressure through ion heating by electric field in DMS. Int J Mass Spectrom 303:181–190

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