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Petroleomic Characterization using an Ion Mobility-Orbitrap Platform

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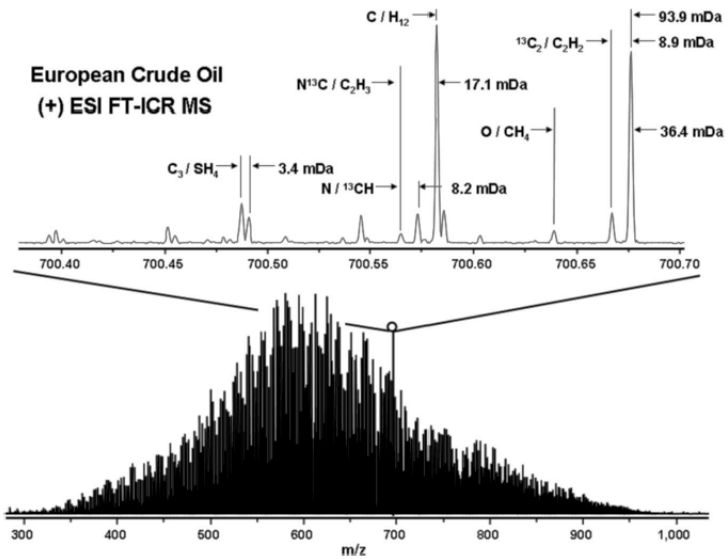
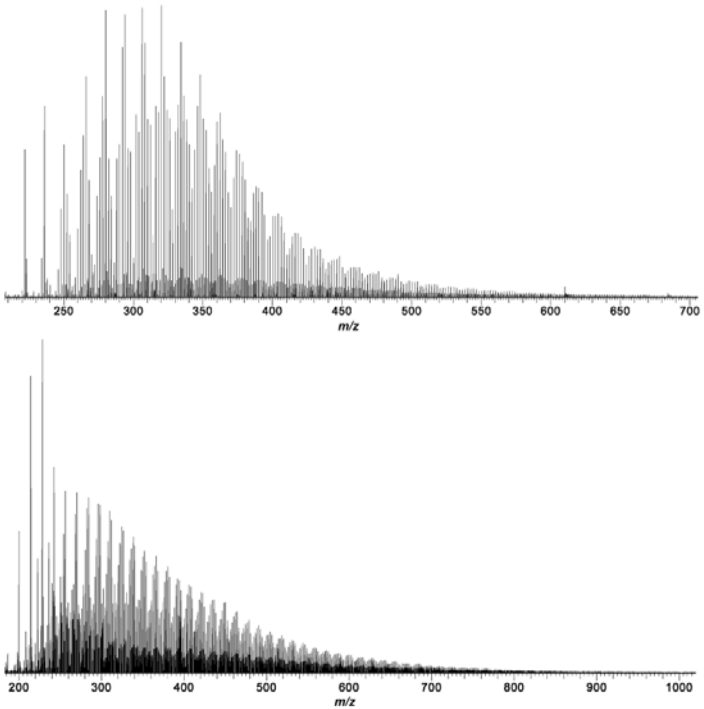
High Resolution Mass Analyzers

FT-ICR



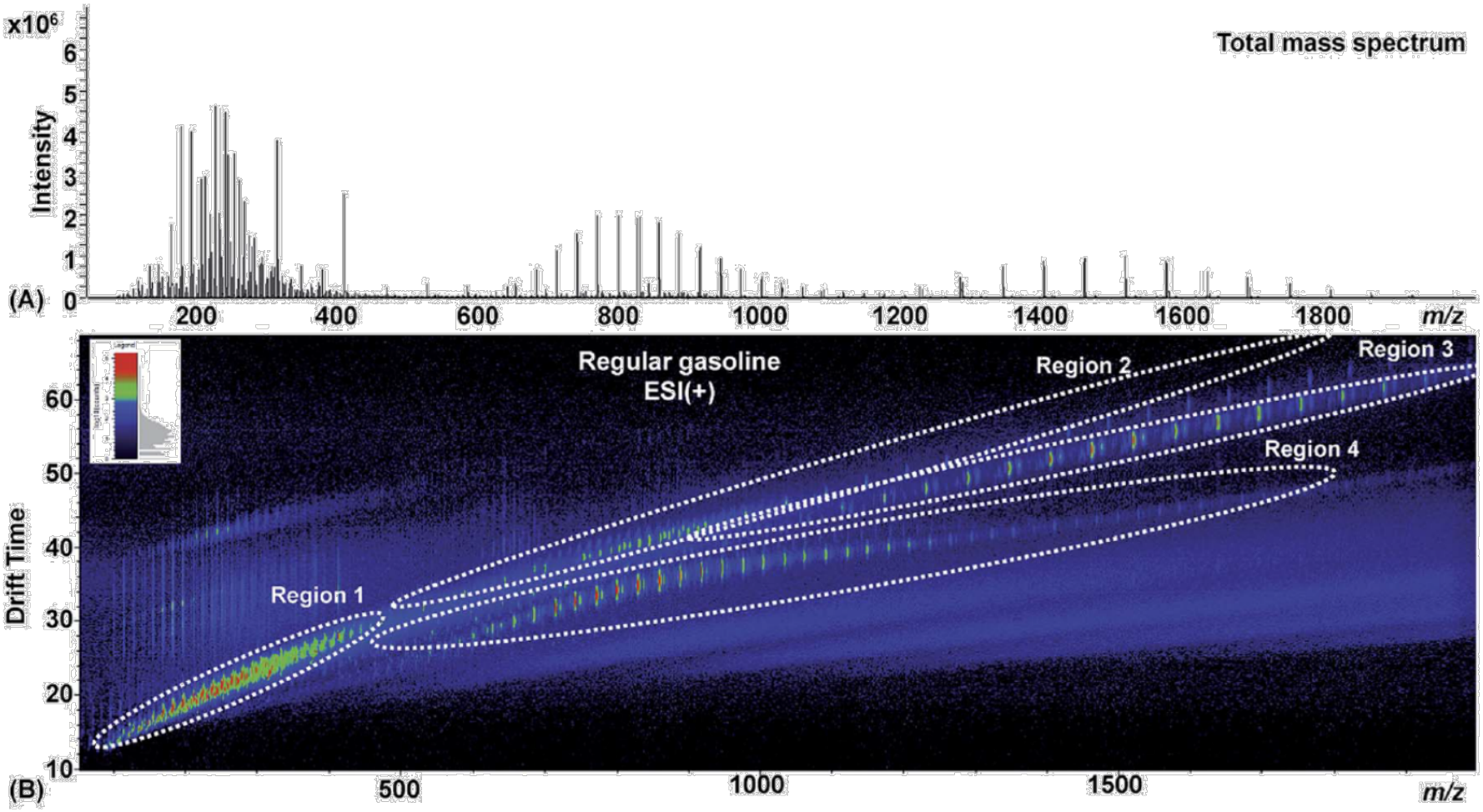
Orbitrap



Marshall A.G. et al. *PNAS* (2008) 105, 1809

Zhurov K.O. et al. *Energy & Fuels* (2008) 105, 1809

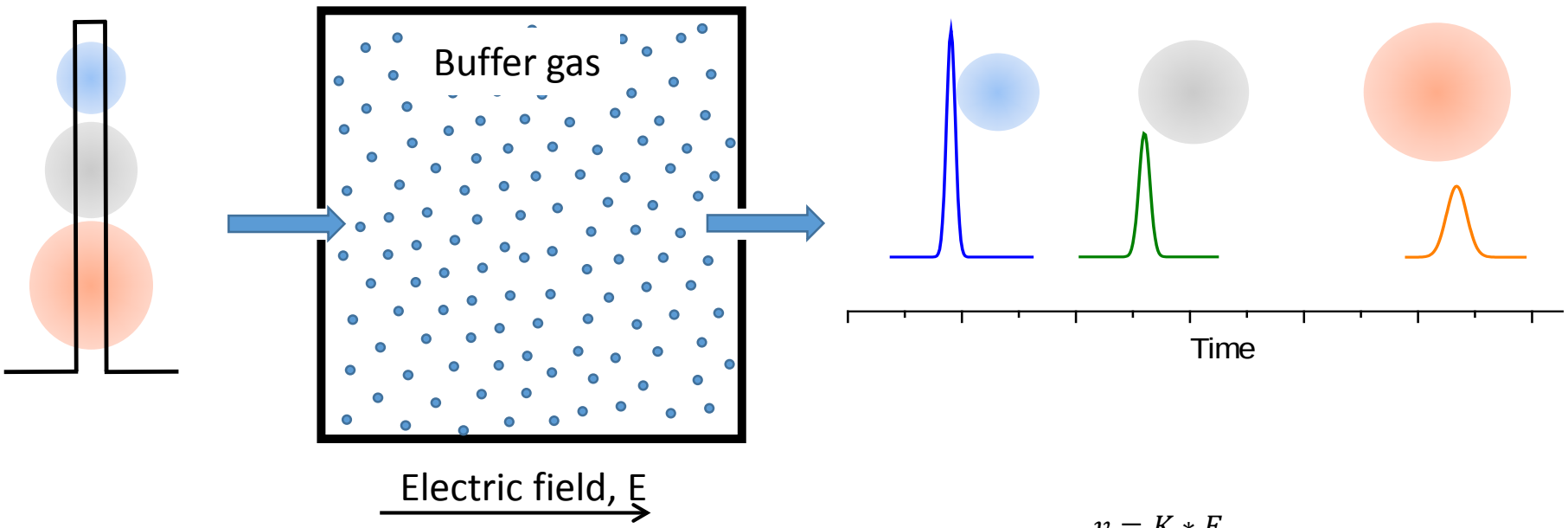
Ion mobility-TOF MS



Santos J.M. et al. *Anal. Methods* (2015) 7, 4450

Fernandez-Lima A. et al. *Anal. Chem.* (2009) 81, 9941

Ion Mobility Spectrometry (IMS)



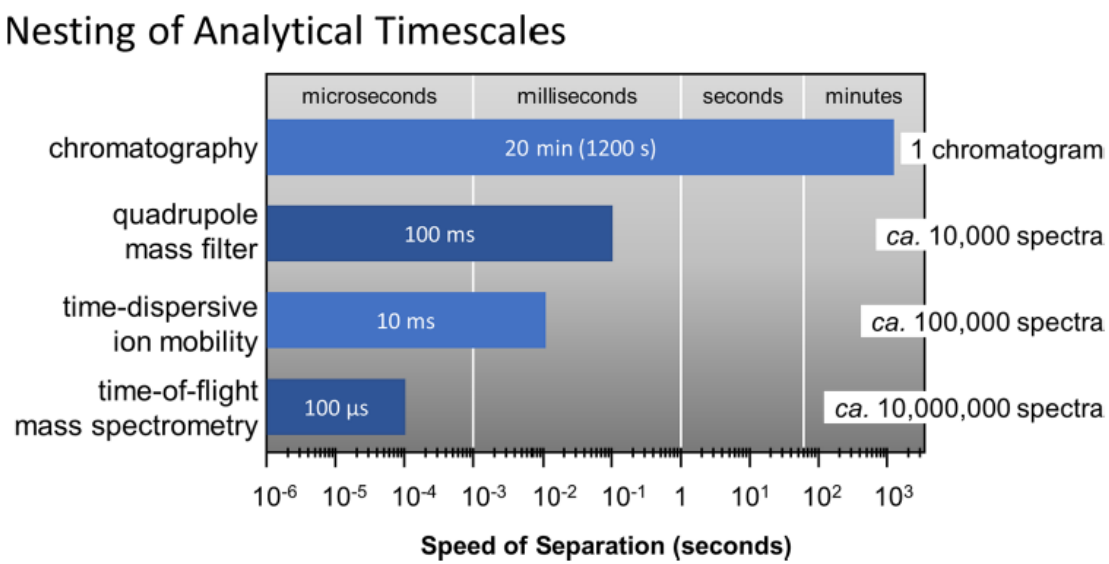
$$v = K * E$$

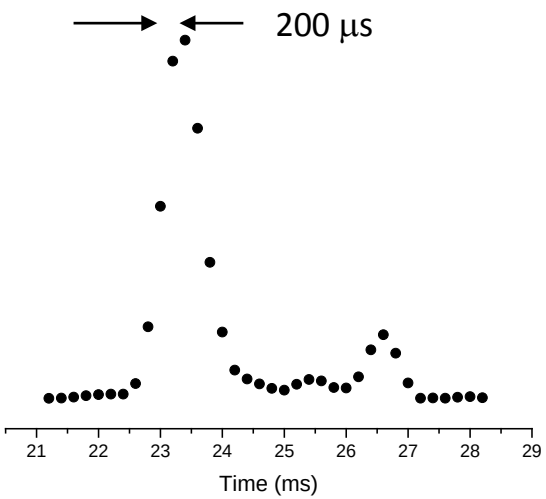
$$K = \frac{L^2}{(V * t)}$$

$$K = C\left(\frac{q}{N}\right)\left(\frac{2\pi}{\mu k T}\right)^{1/2}\left(\frac{1}{\Omega}\right)$$

Ω depend on:
size/charge,
ion-neutral interaction,
rotationally-averaged shape

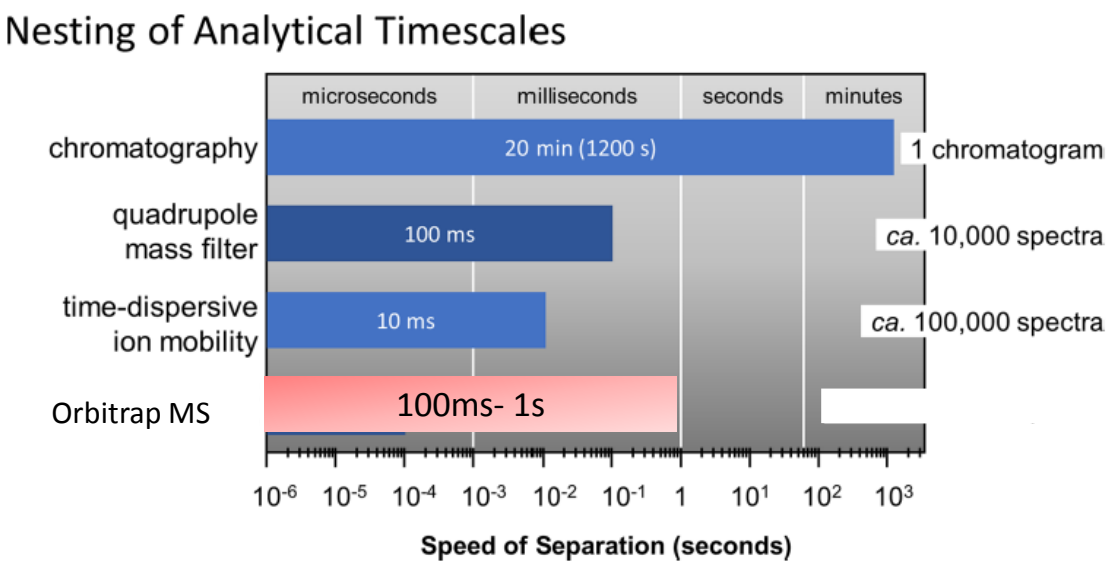
IMS & Multidimensional Separation



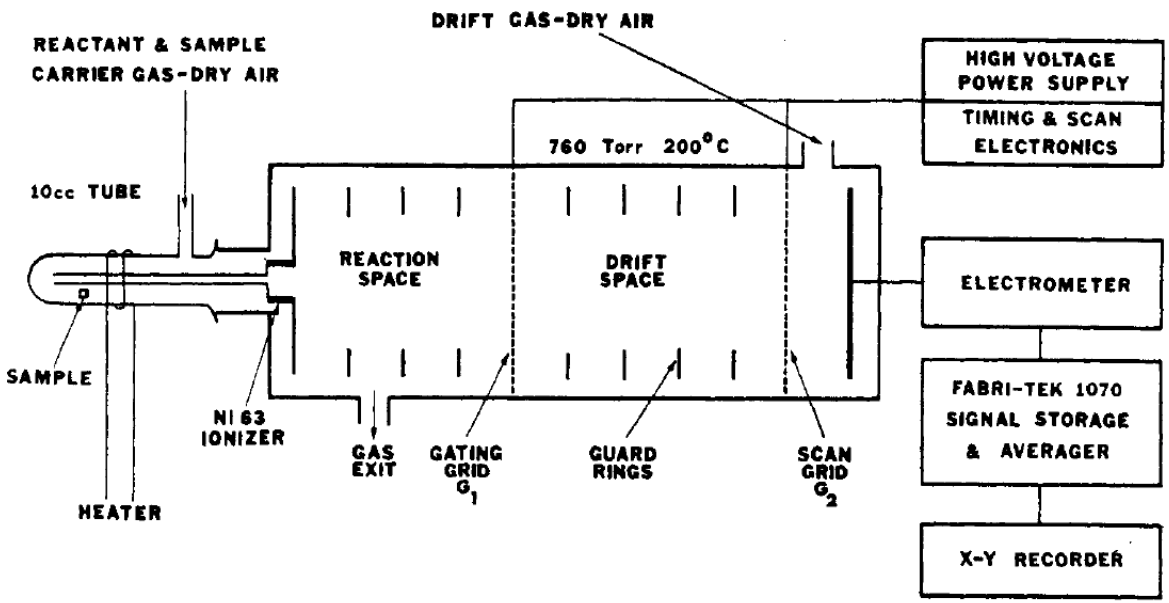


May J.C. and McLean J.A. *Anal. Chem.* (2015) 87, 1422

Timing challenges with Orbitrap



Previous Efforts

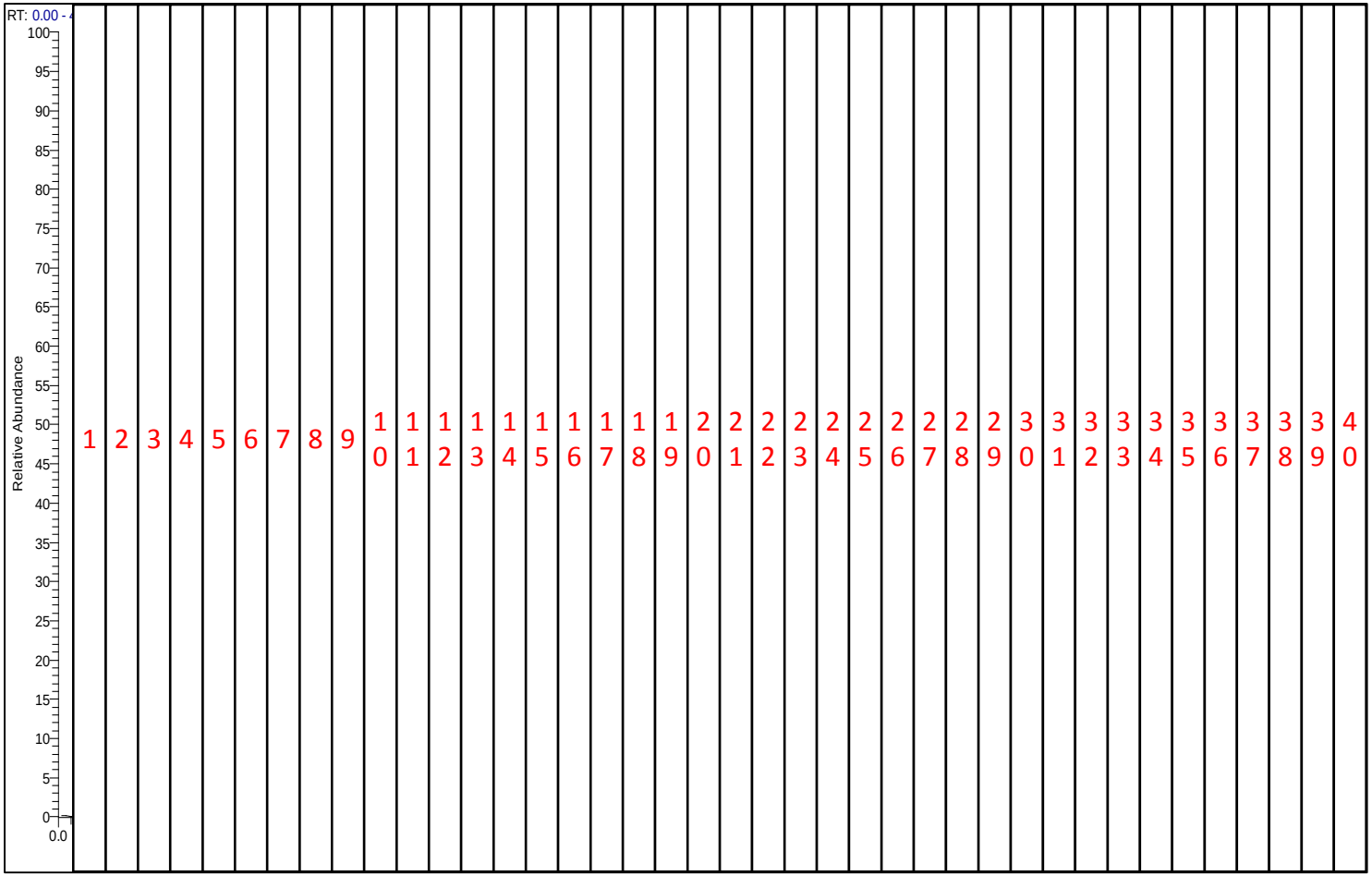


Karasak F.W. et al. *Anal. Chem.* (1971) 43, 1441

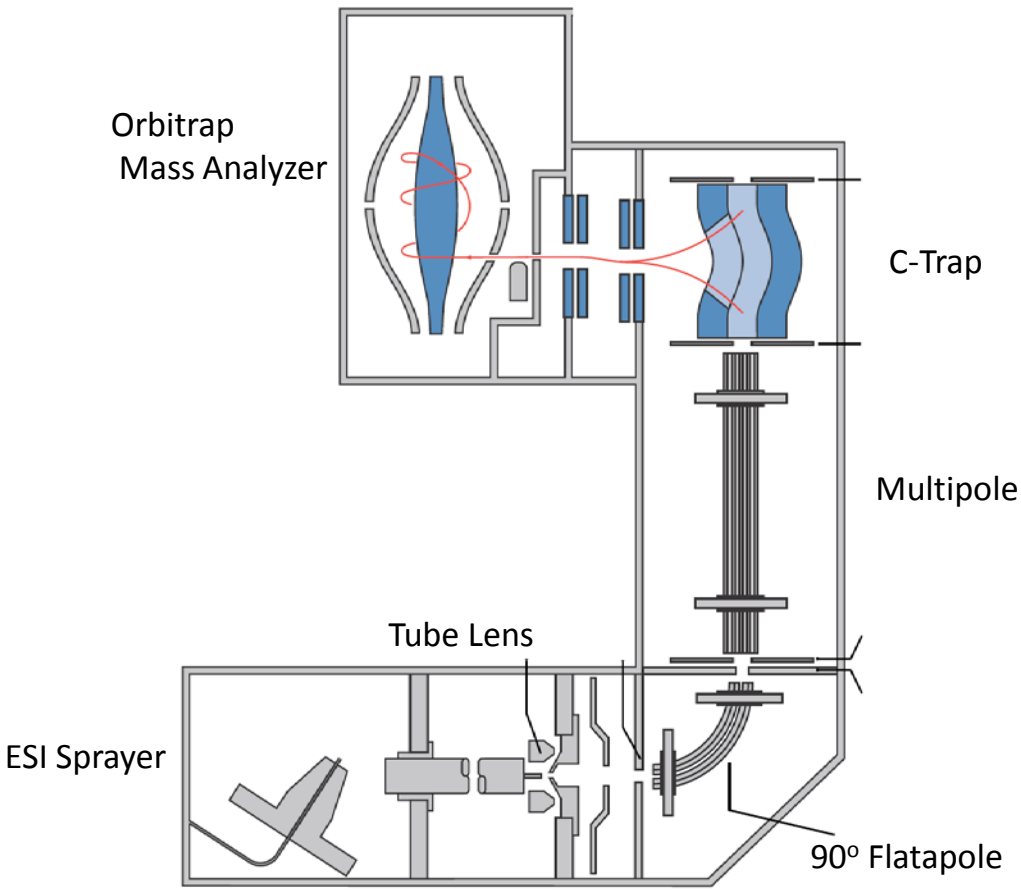
Clowers B.H. et al. *Anal. Chem.* (2005) 77, 5877
Donohoe G.C. et al. *Anal. Chem.* (2014) 86, 8121

The Dual Gate Approach

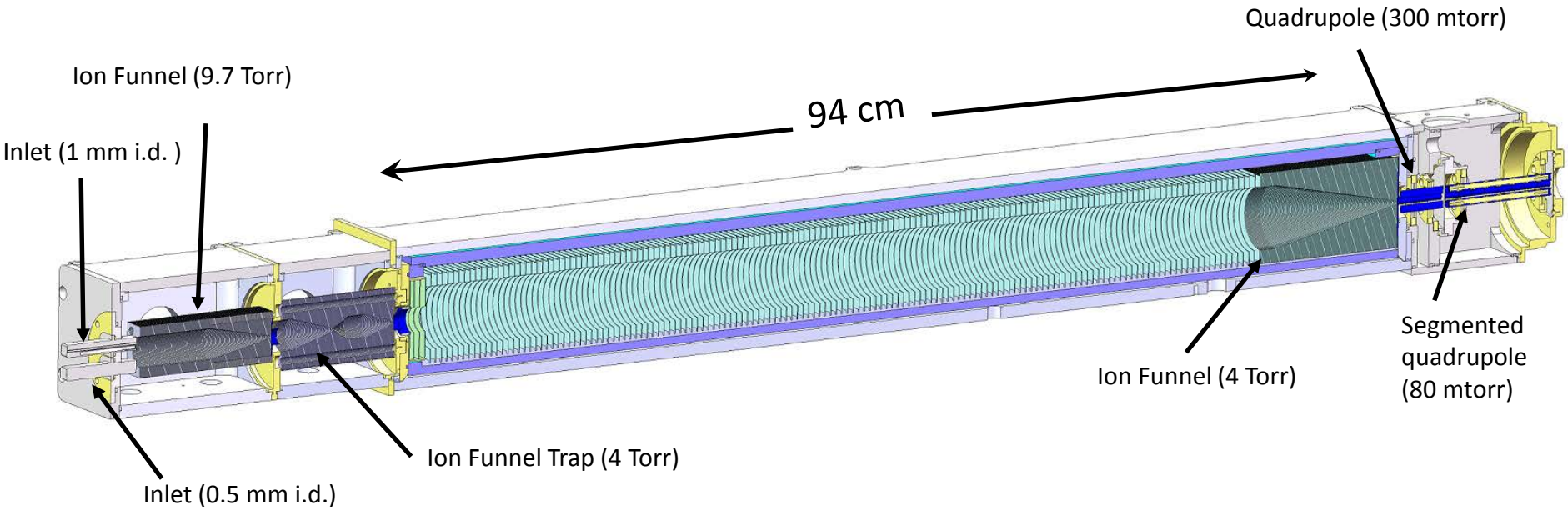
Gating grid



Exactive Orbitrap



PNNL-Drift tube IMS

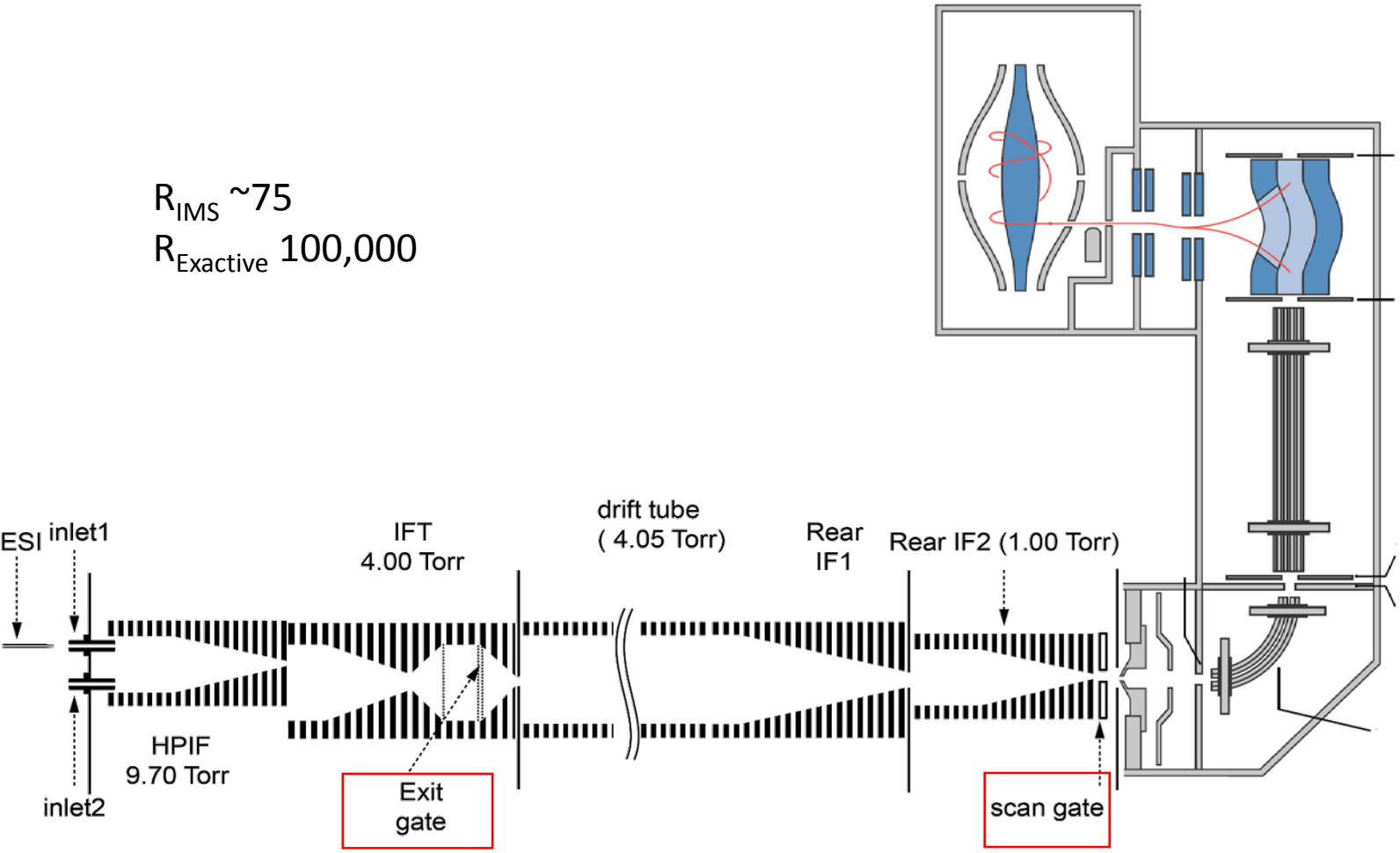


Buffer gas: N_2
Field: E = 18 V/cm

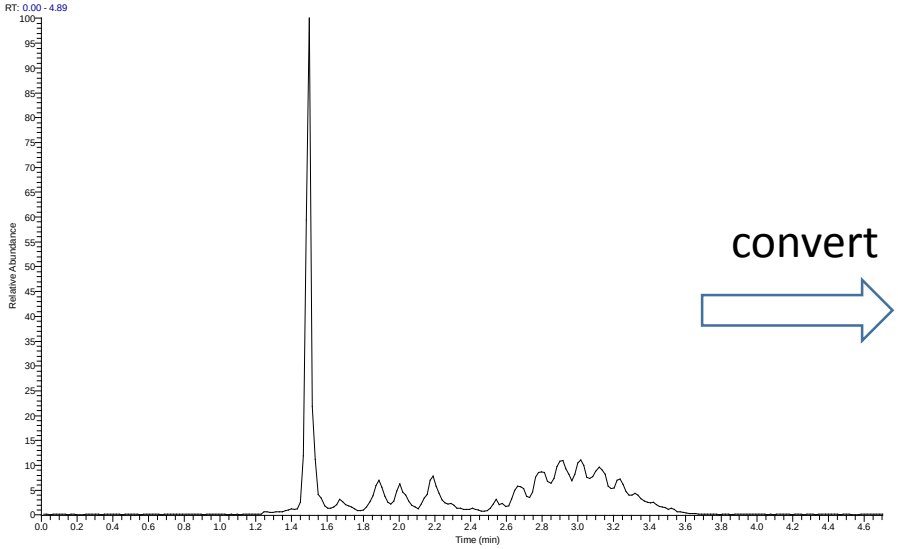
Tang K. et al. *Anal. Chem.* (2005) 77, 3330
Ibrahim Y.M. et al. *Int. J. Mass Spectrom.* (2015) 377, 655

DT-IMS-Orbitrap

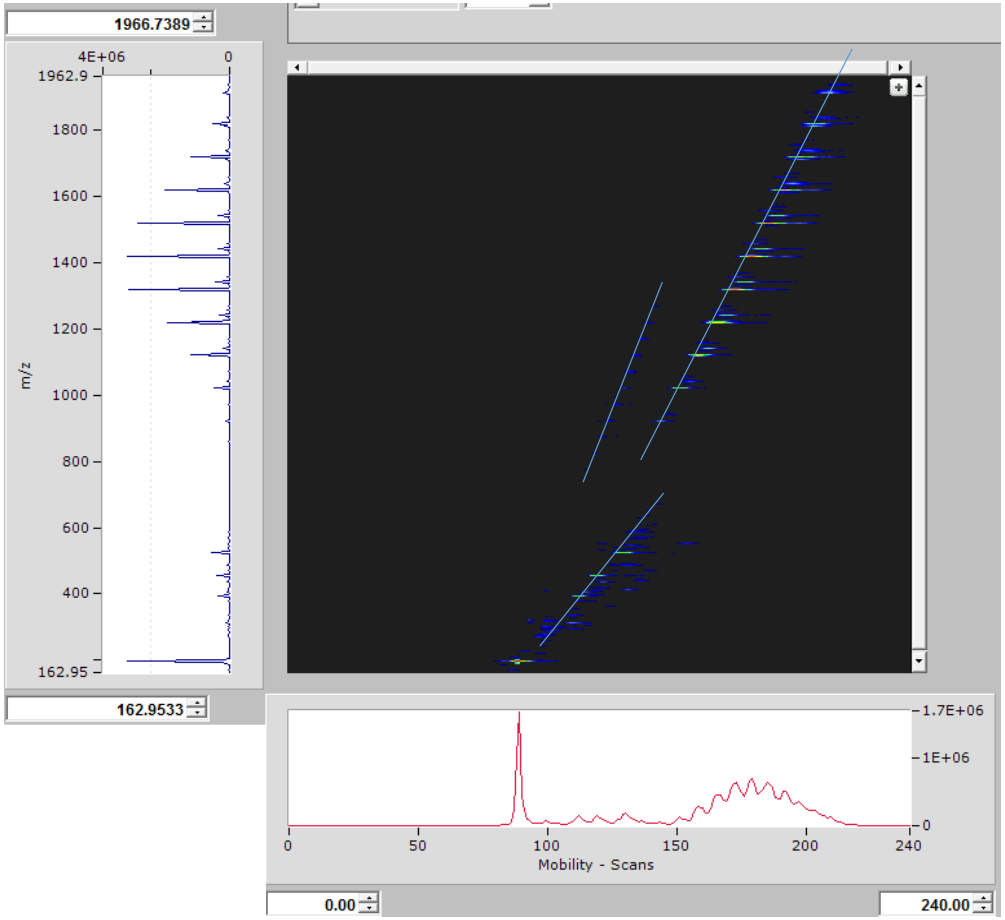
R_{IMS} ~75
$R_{Exactive}$ 100,000



Data processing



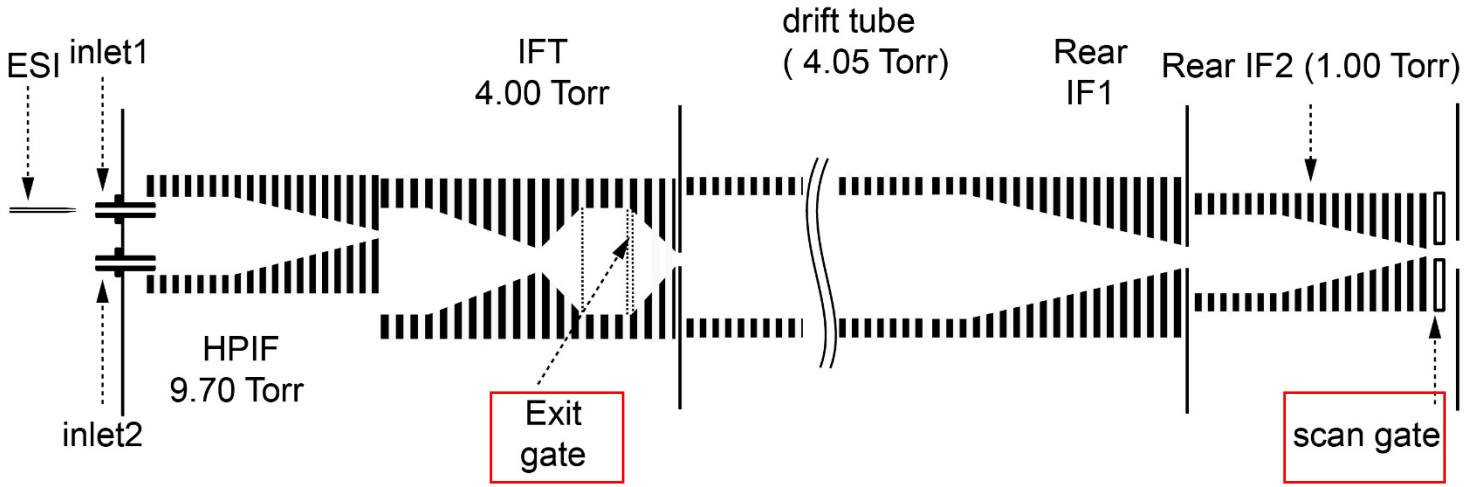
convert



Mobility chromatogram (Thermo .raw)

Time-m/z heat map

Modes of IMS Operation

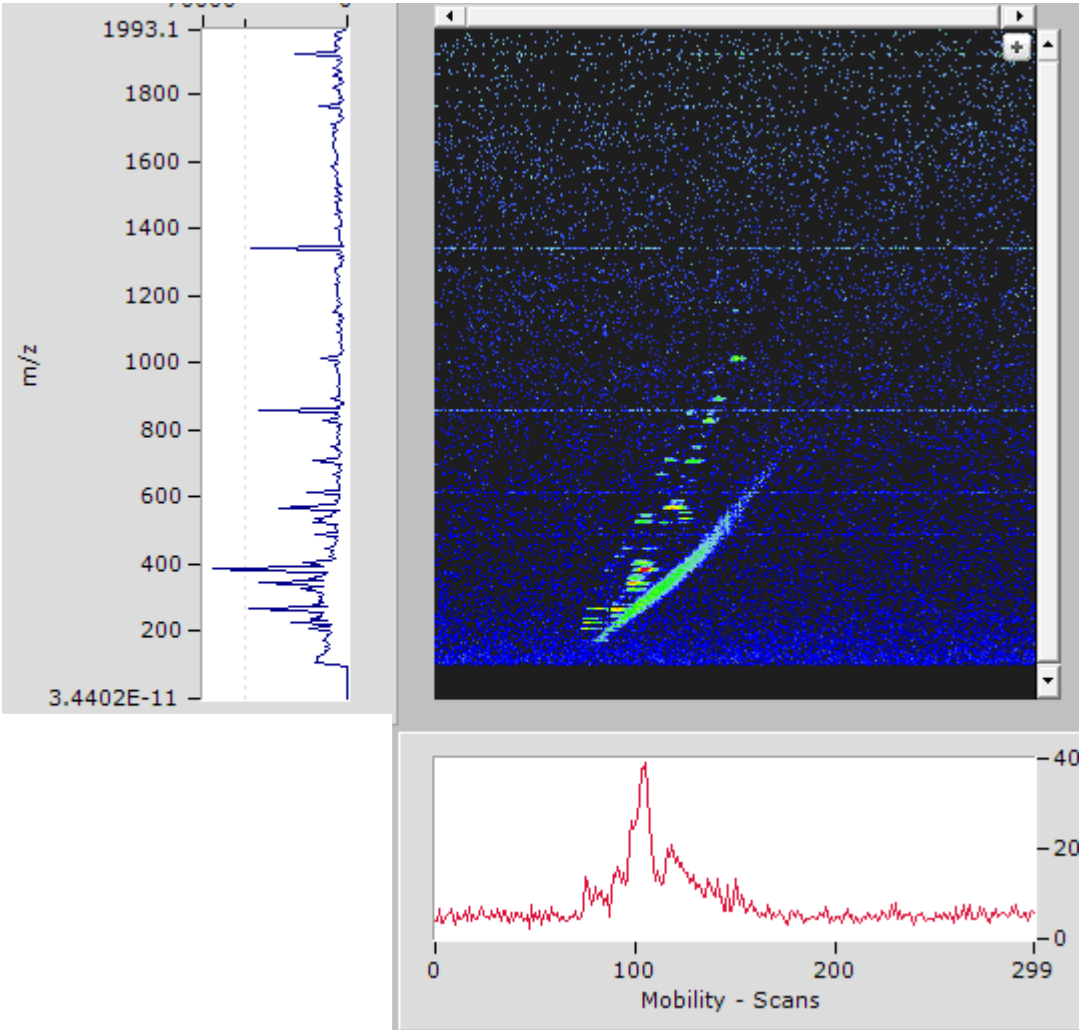


1. Signal averaging	single packet	single pulse
2. Single multiplexing encoding	multiple packets	single pulse
3. Double multiplexing encoding*	multiple packets	multiple pulses

*Belov M.E. et al. ASMS 2011

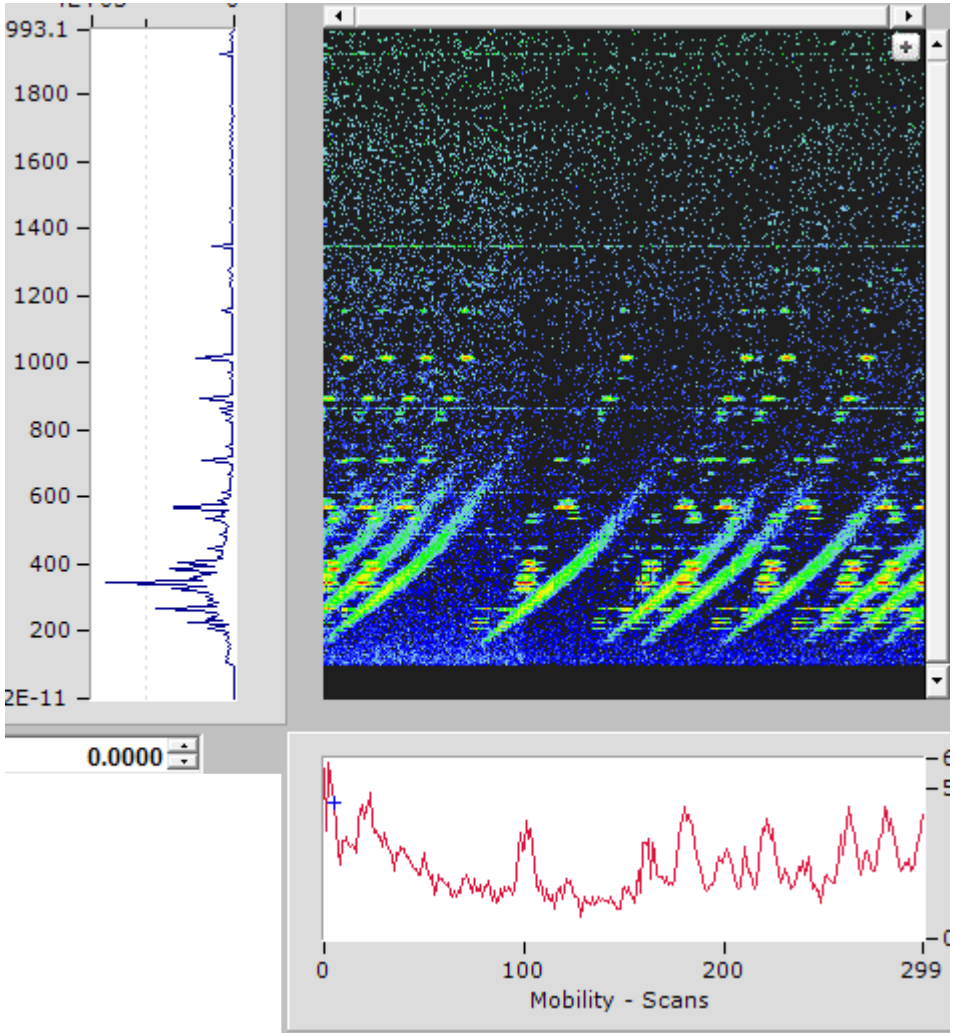
1. Signal Averaging

Heavy gas oil



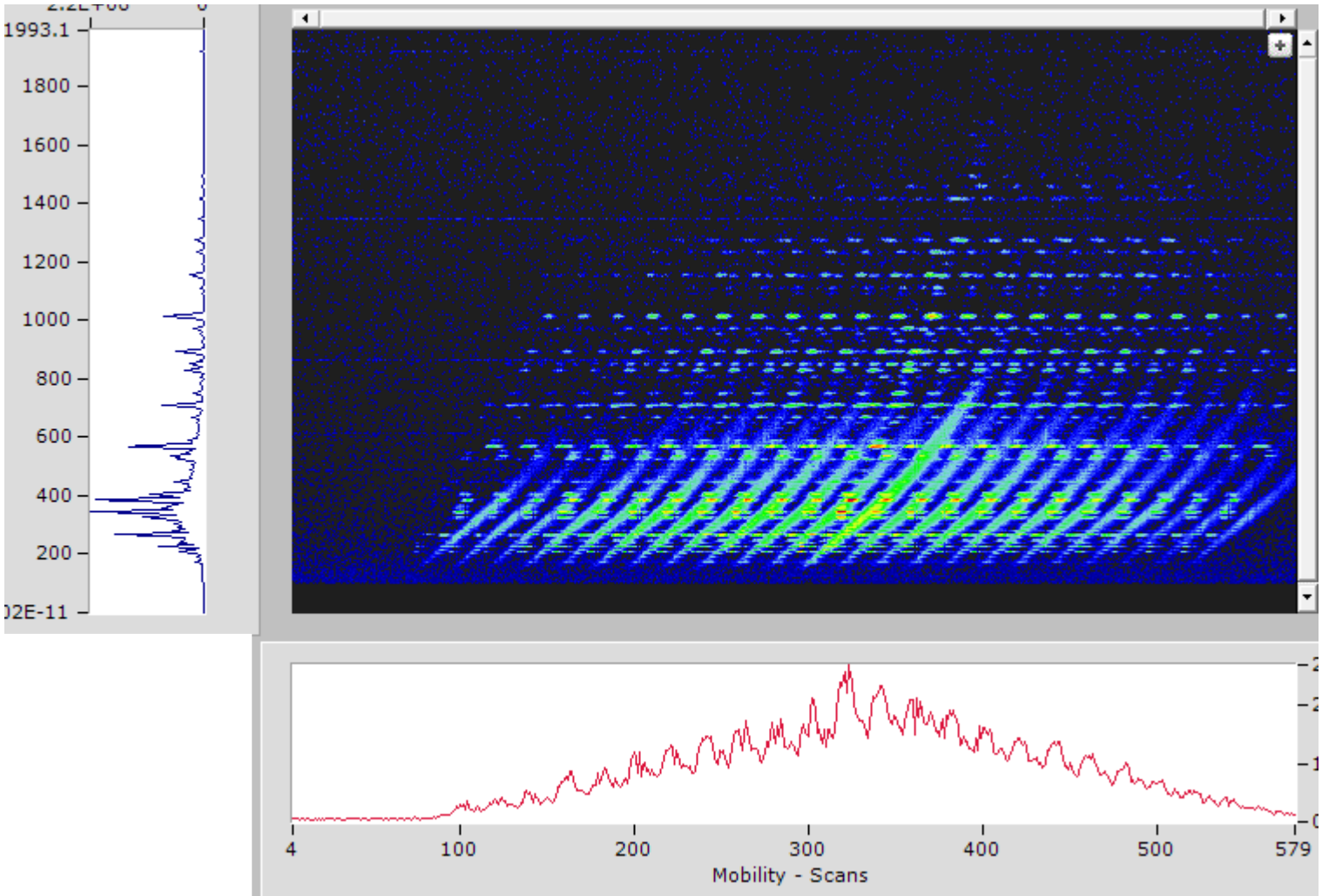
2. Single Multiplexing

Heavy gas oil



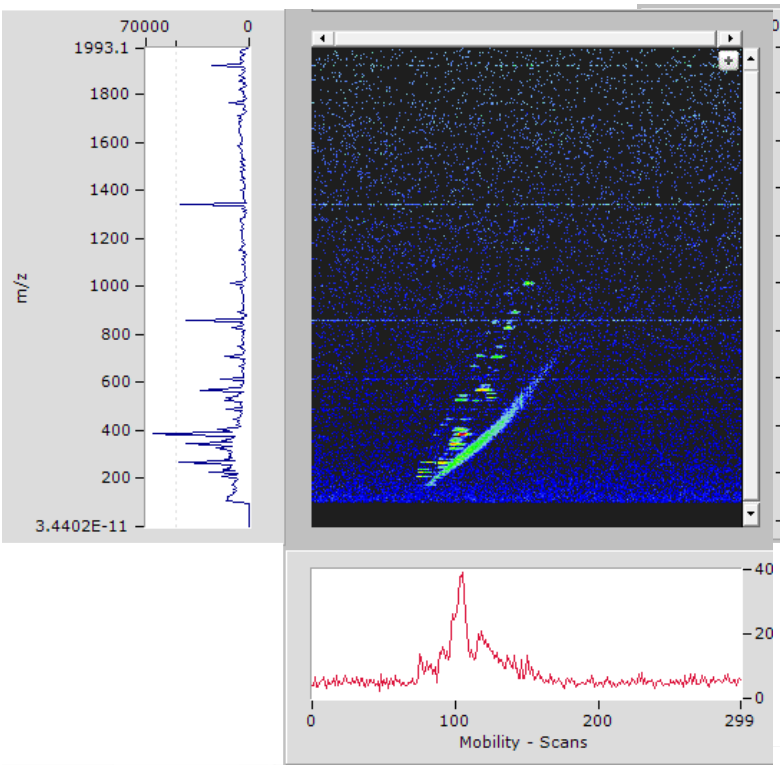
3. Double Multiplexing

Heavy gas oil

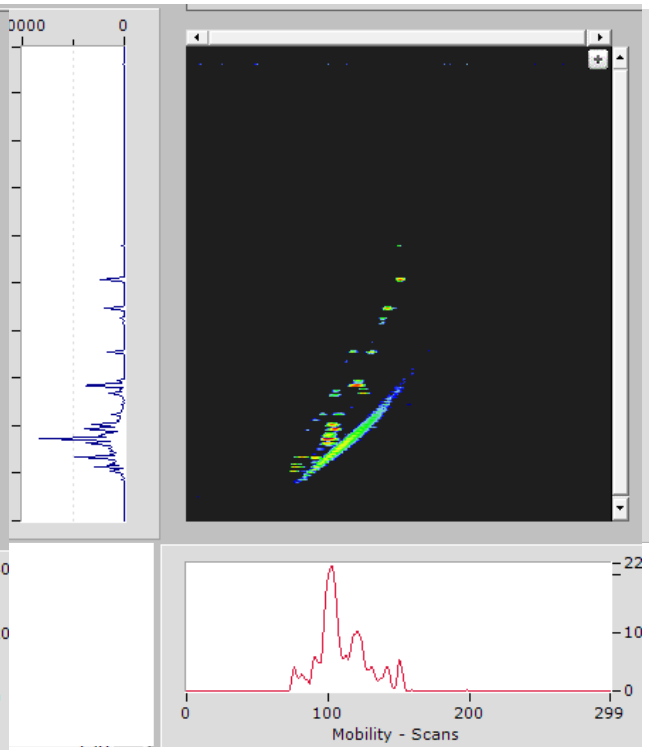


Comparison of the Three Modes (after decoding)

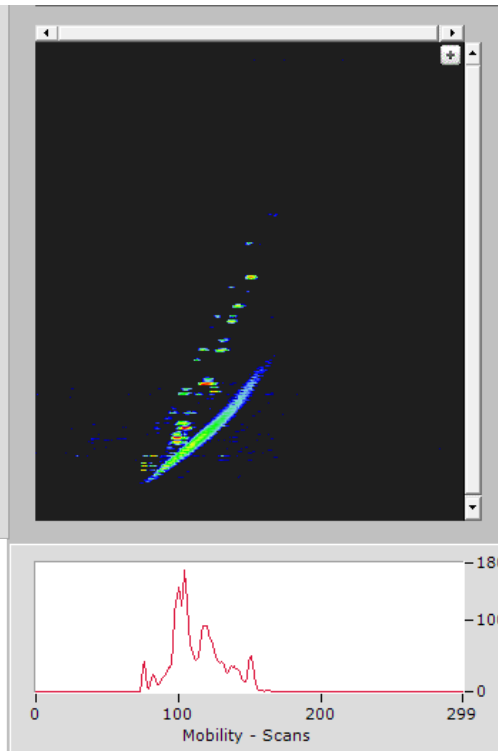
Signal averaging



Single decoding

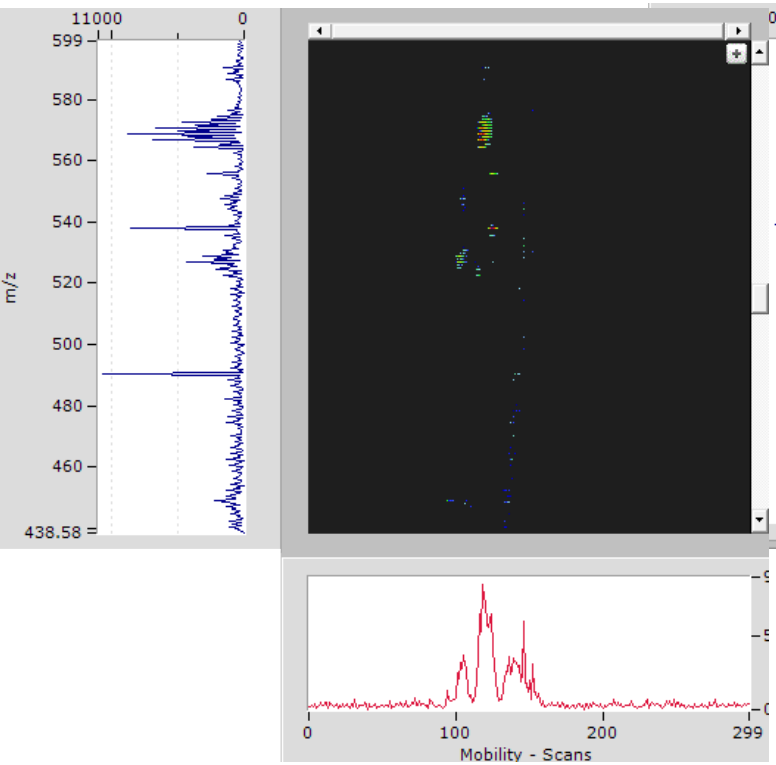


double decoding

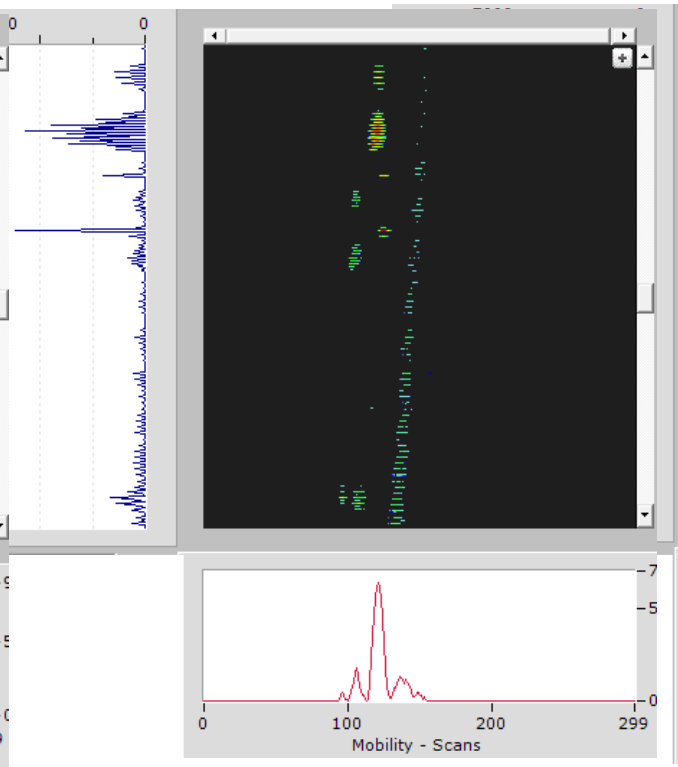


Increased Sampling and S/N

Signal averaging



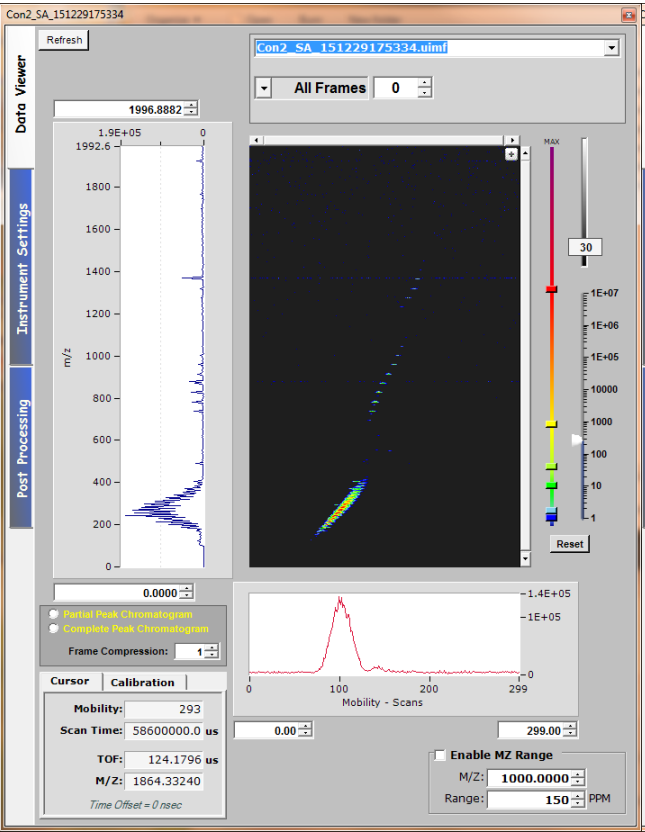
Single decoding



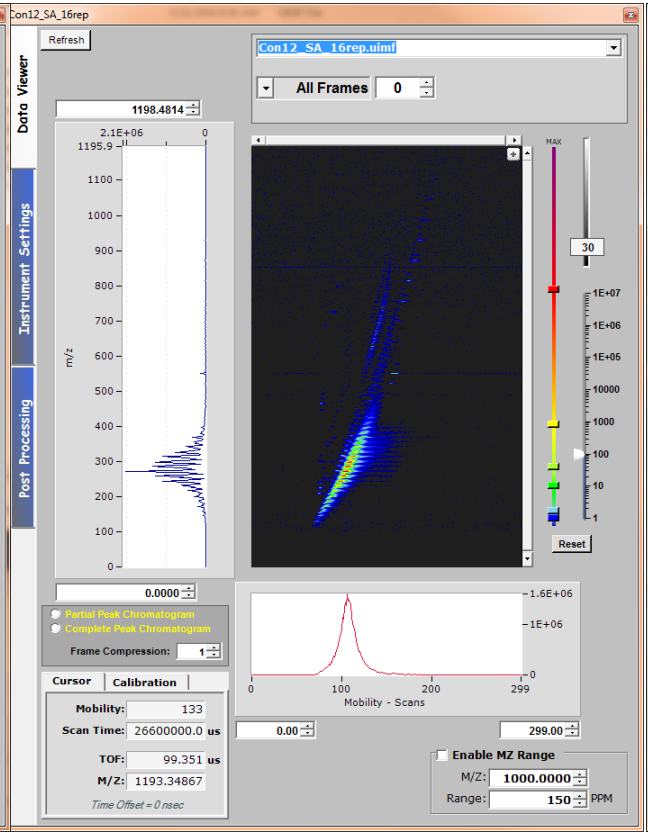
double decoding

IMS of Petroleum Samples

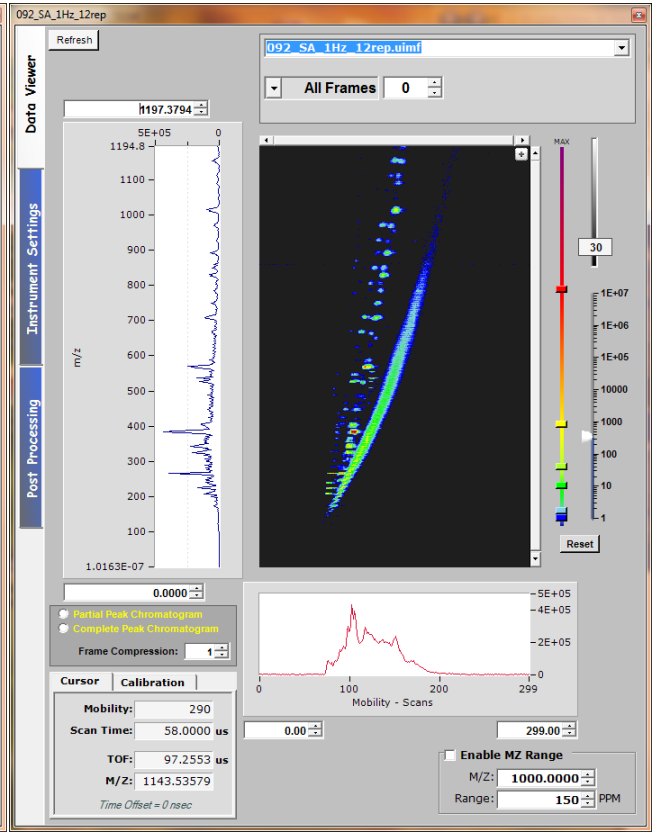
Straight Run
Gas Oils



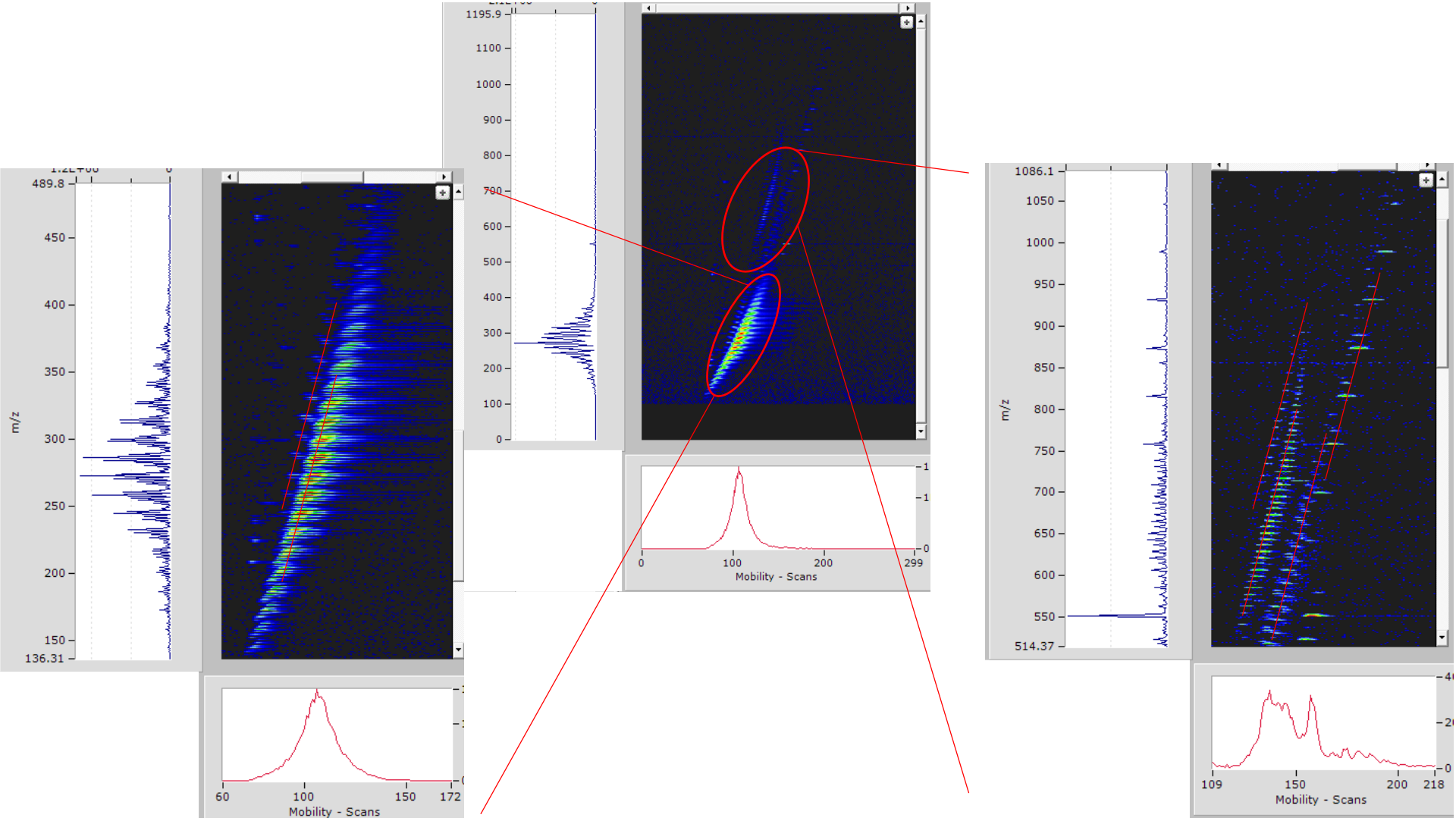
Vacuum &
Hydrotreated Gas oils



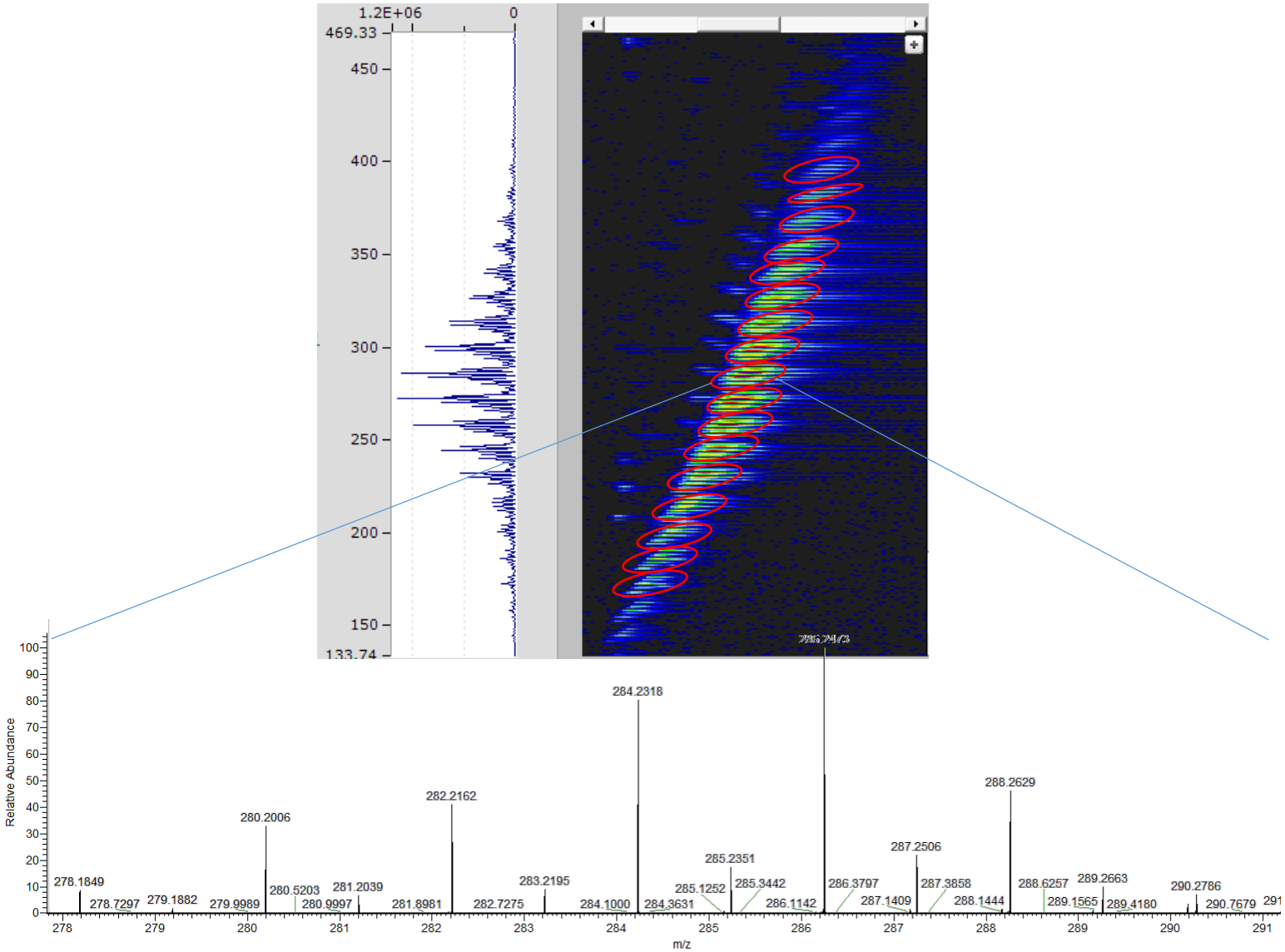
Heavy
Gas Oils



Trendlines in Petroleomic Data

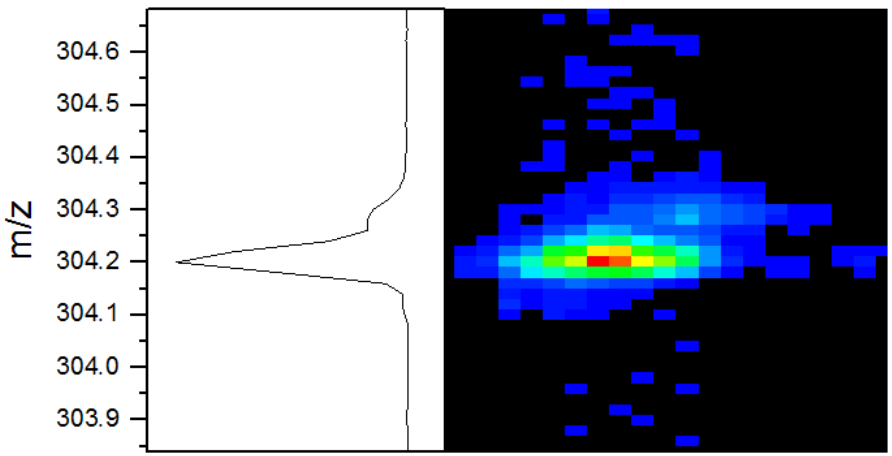


Structural Changes

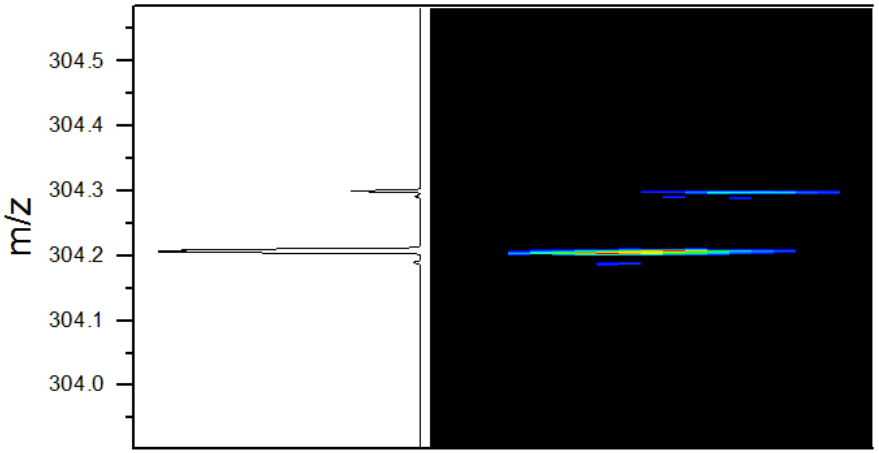


IMS-TOF vs IMS-Orbitrap

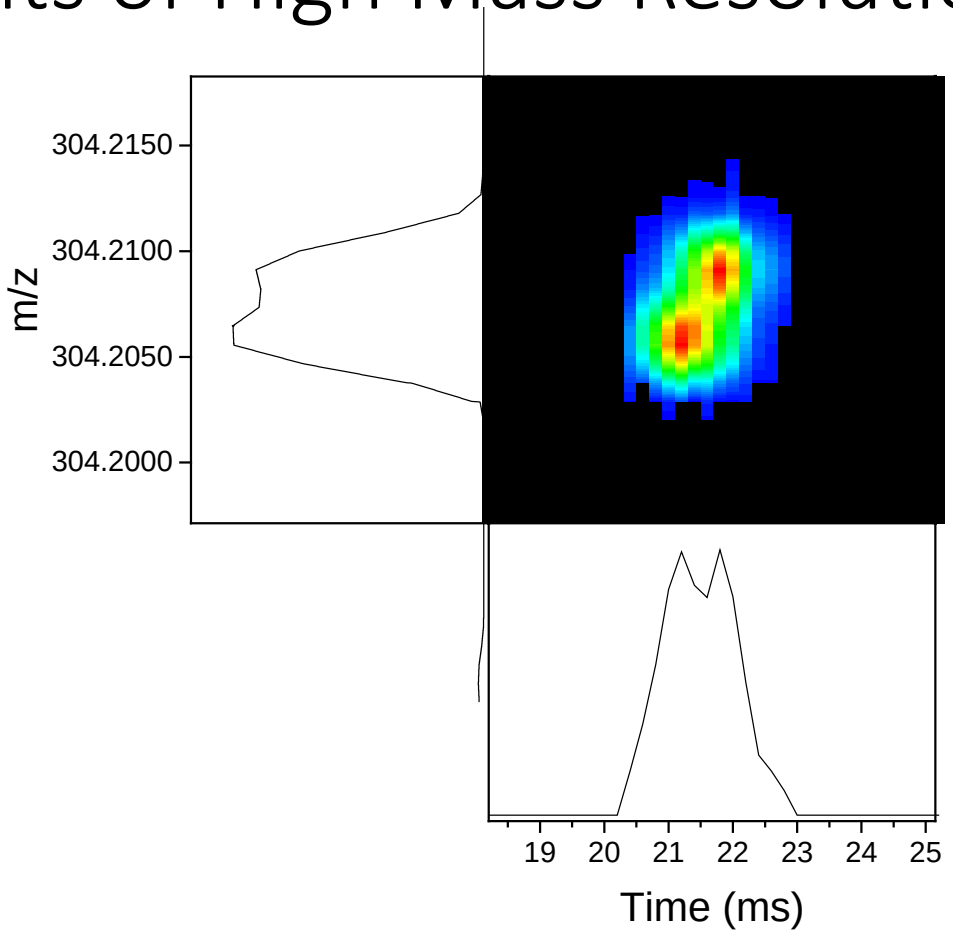
IMS-TOF



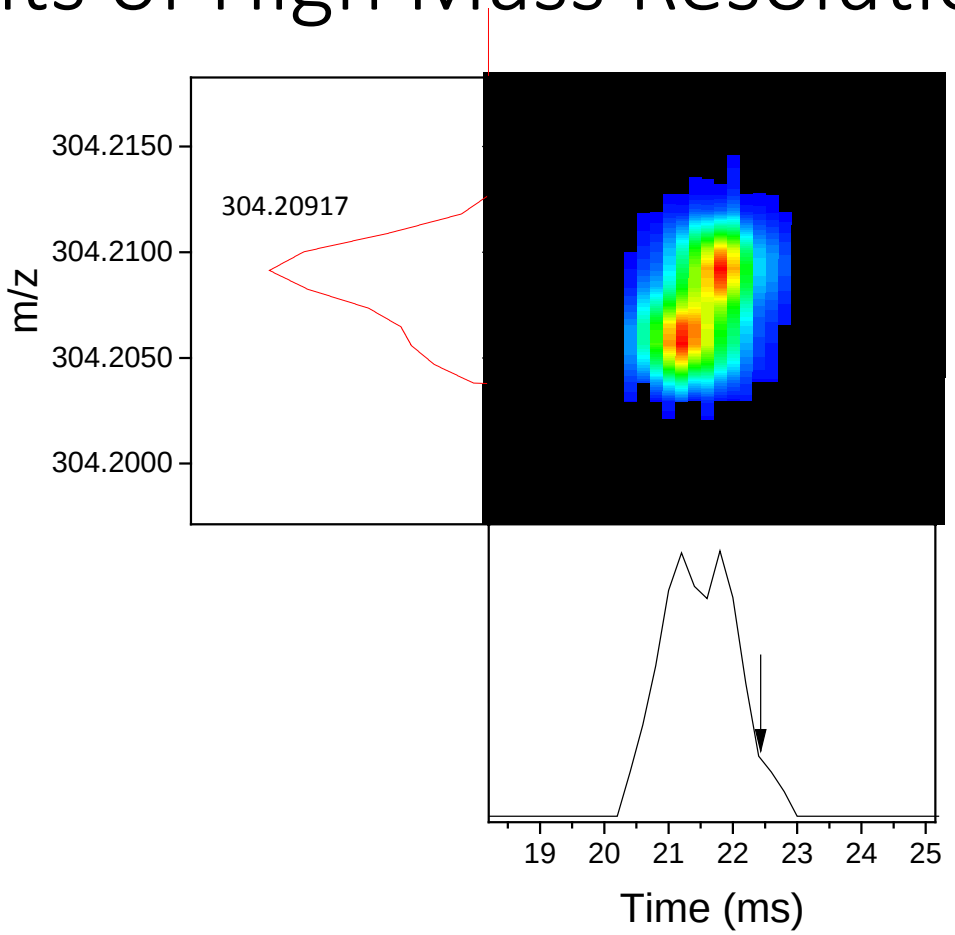
IMS-Orbitrap



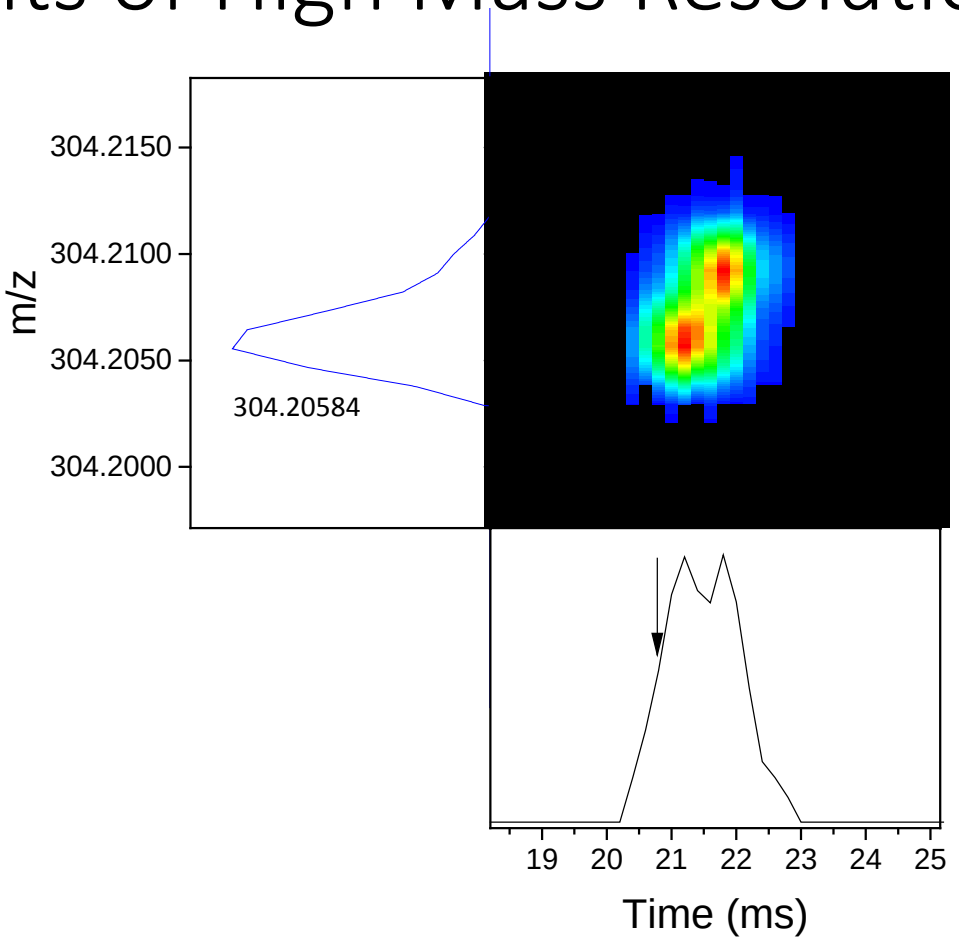
Benefits of High Mass Resolution & IMS



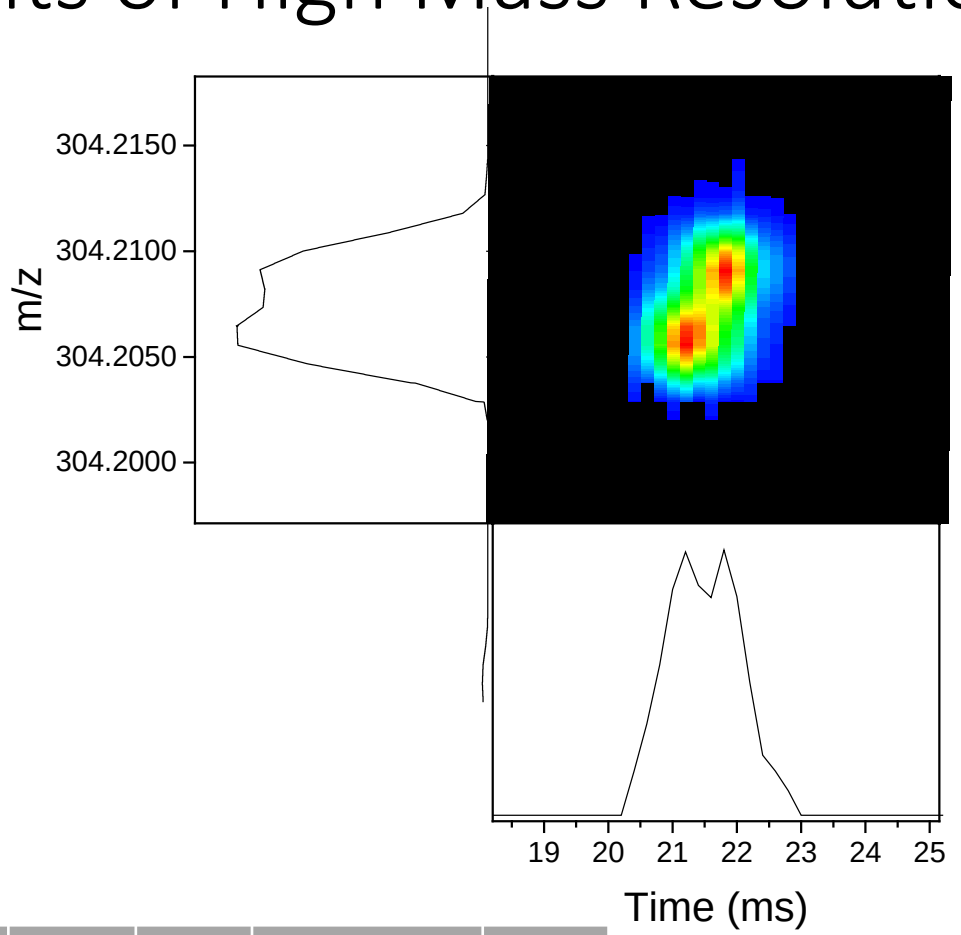
Benefits of High Mass Resolution & IMS



Benefits of High Mass Resolution & IMS



Benefits of High Mass Resolution & IMS

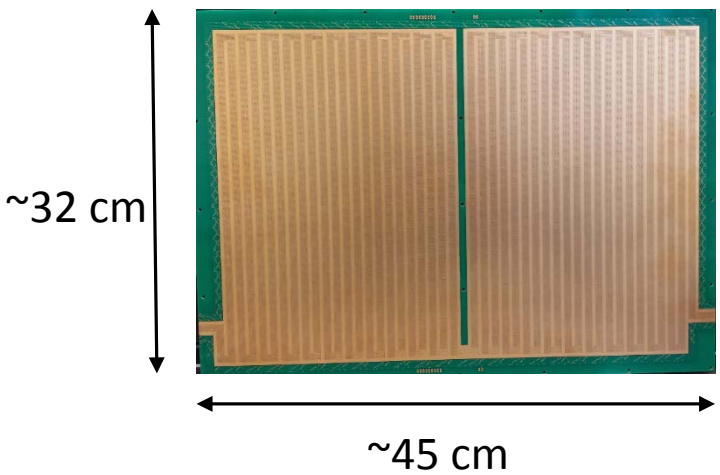


Theo. Mass	Exp. Mass	Error (ppm)	DBE	Mol. Formula	Class
304.20935	304.20917	0.59	5.5	C19H30N1S1	N1S1
304.20598	304.20584	0.46	10.5	C22H26N1	N1

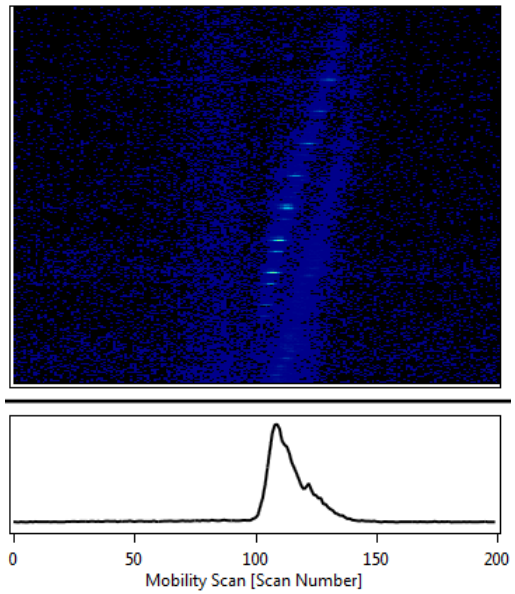
C3 vs. SH4

The Next Leap in Ion Mobility

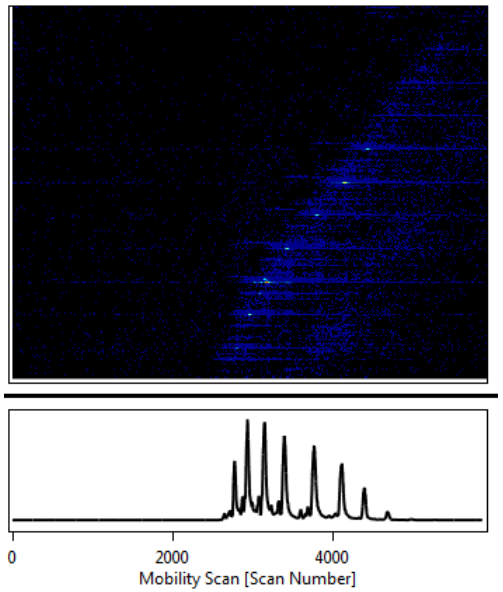
13 m SLIM-IMS



94 cm DTIMS



13 m DTIMS



- Structures for Lossless Ion Manipulations (SLIM)
- Peak capacity ~250 as compared to ~30 for DTIMS
- Drift time of seconds for better matching with Orbitrap

see oral presentation TOD pm

Summary

- Ion mobility is complementary to Orbitrap (and FT-ICR)
- Improved S/N was obtained using double multiplexing
- Ion mobility spread ions into bands of chemical classes (trend lines) for improved diagnostics/identifications
- Faster Orbitrap acquisition and/or slower ion mobility separation improves the matching
- Higher mobility resolution is possible in Structures for Lossless Ion Manipulations (SLIM)

Acknowledgment

PNNL

Daniel Orton
Malak Tfaily
Rosalie Chu

Thermo Scientific

Satendra Prasad
Jean Jacques Dunyach
Alexander Makarov

Composer software
David Stranz-Sierra Analytics, Inc.

Funding
PNNL Laboratory Directed Research & Development

EMSL **William R. Wiley Environmental Molecular Sciences Laboratory**