Emissions of Gas-Phase Low-Volatility Organic Compounds from Mobile Sources

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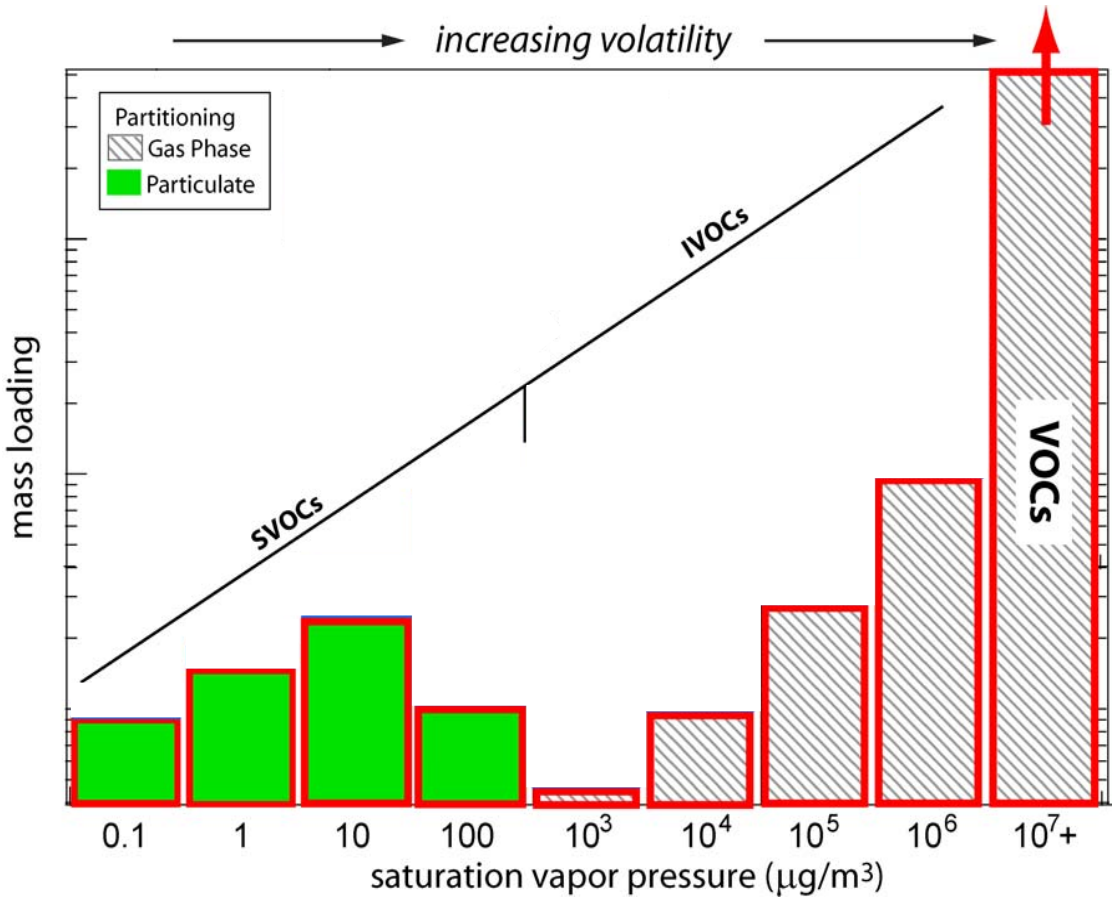
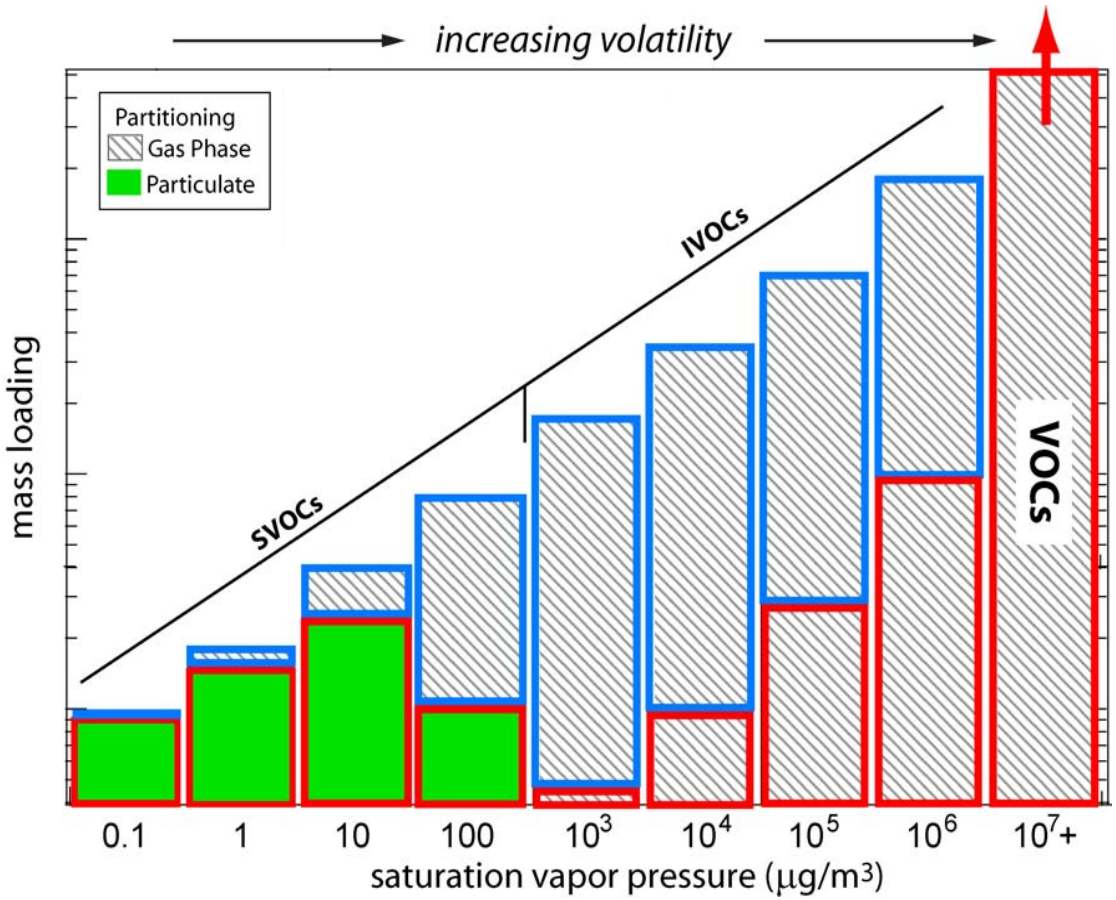
EPA STAR-OTAQ Transportation Emissions Research Forum
4 March 2014

Emissions of organic species



VOC: volatile organic compounds (gas phase)
IVOC: “intermediate volatility” organic compounds (gas phase)
SVOC: semivolatile organic compounds (gas, particle phase)

Emissions of organic species



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IVOC: “intermediate volatility” organic compounds (gas phase)
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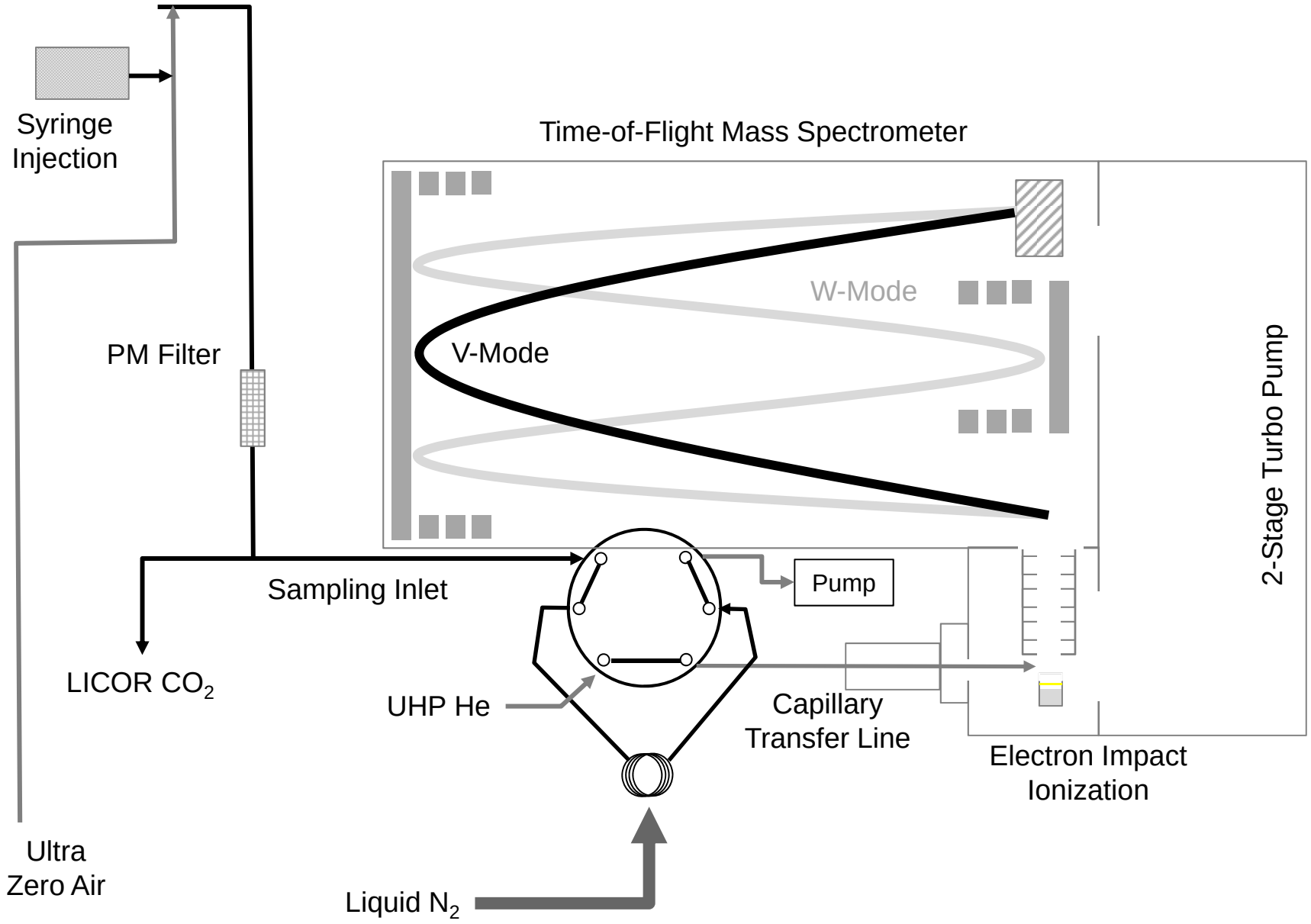
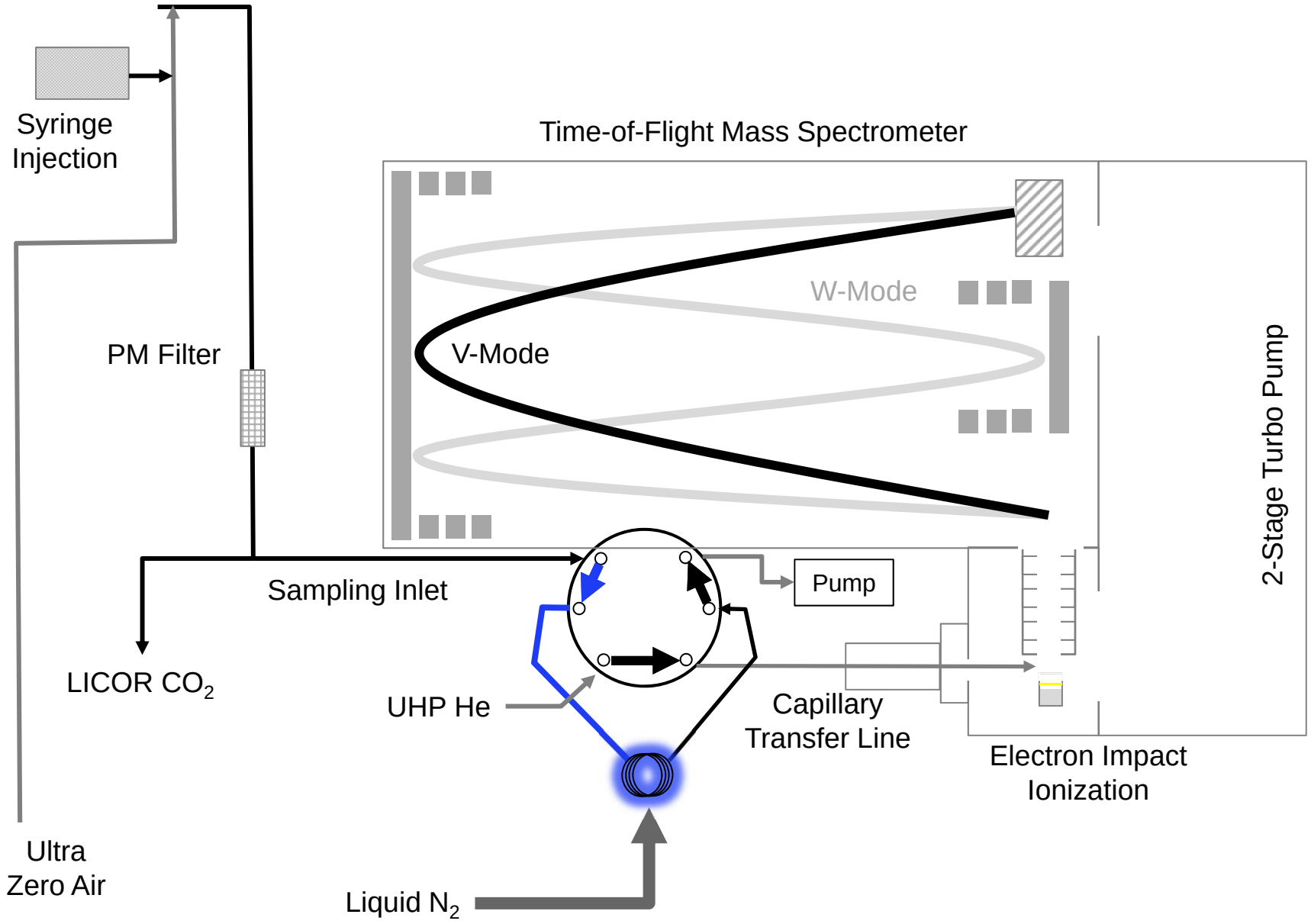
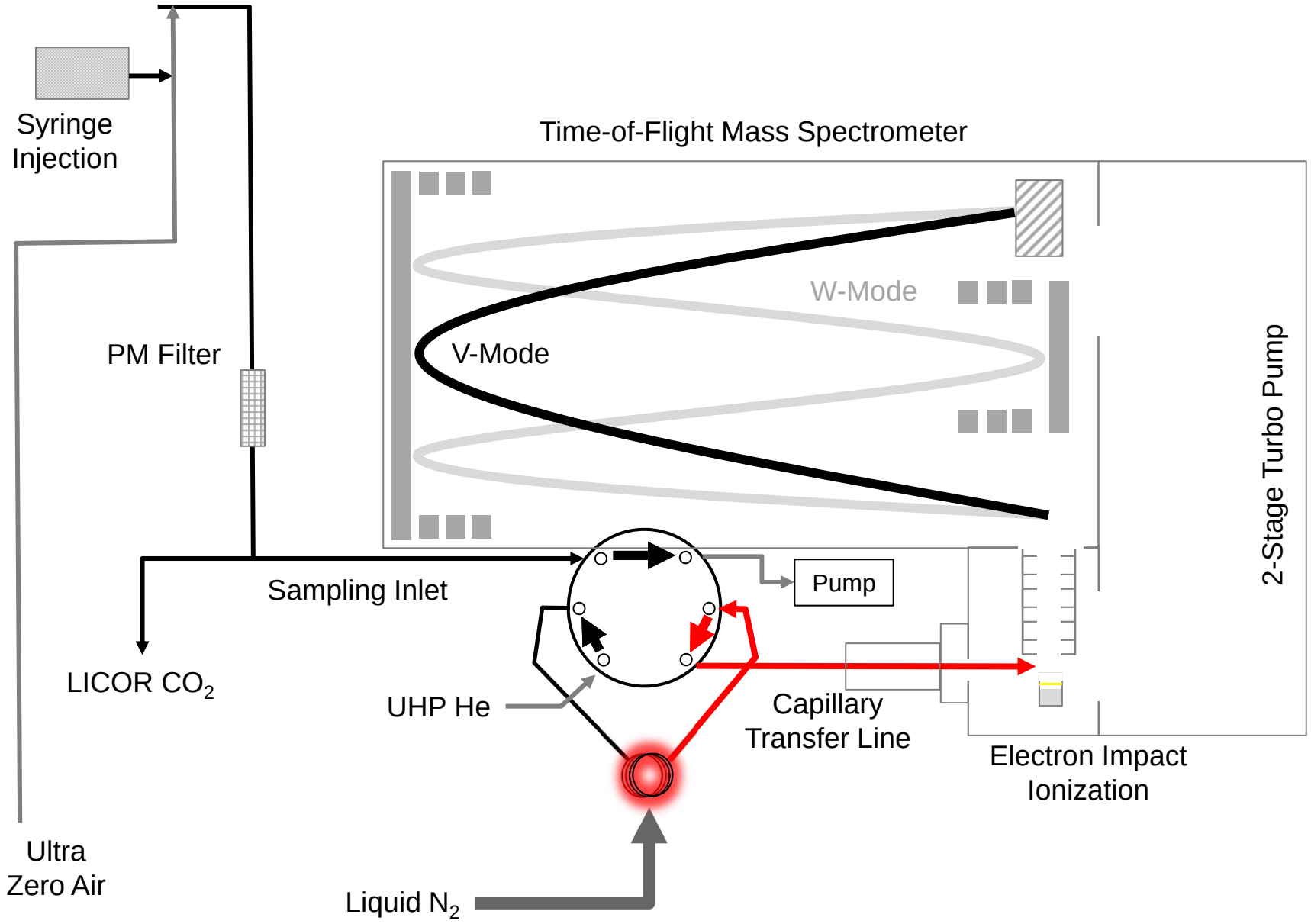
High-resolution electron impact mass spectrometer



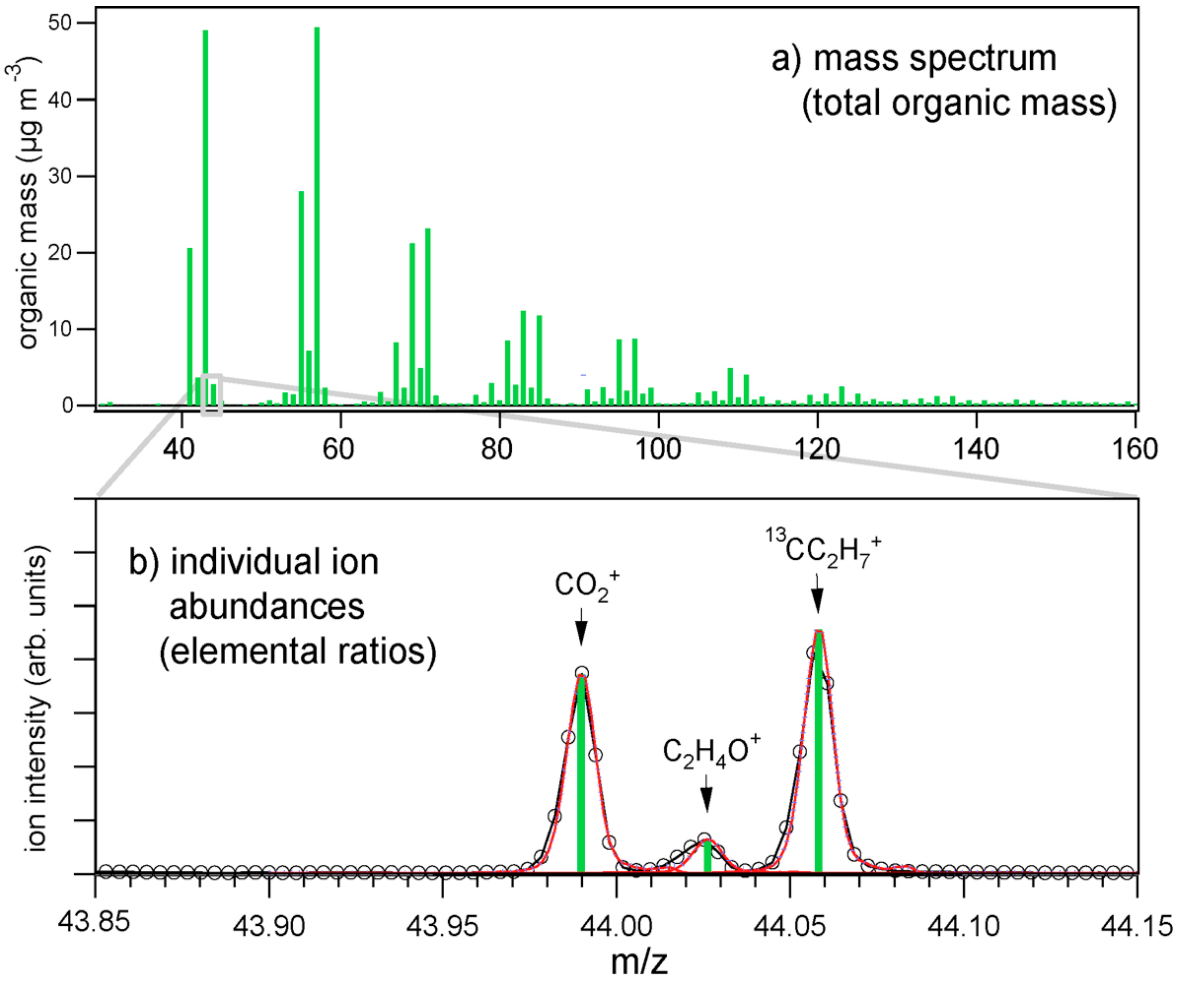
High-resolution electron impact mass spectrometer



High-resolution electron impact mass spectrometer

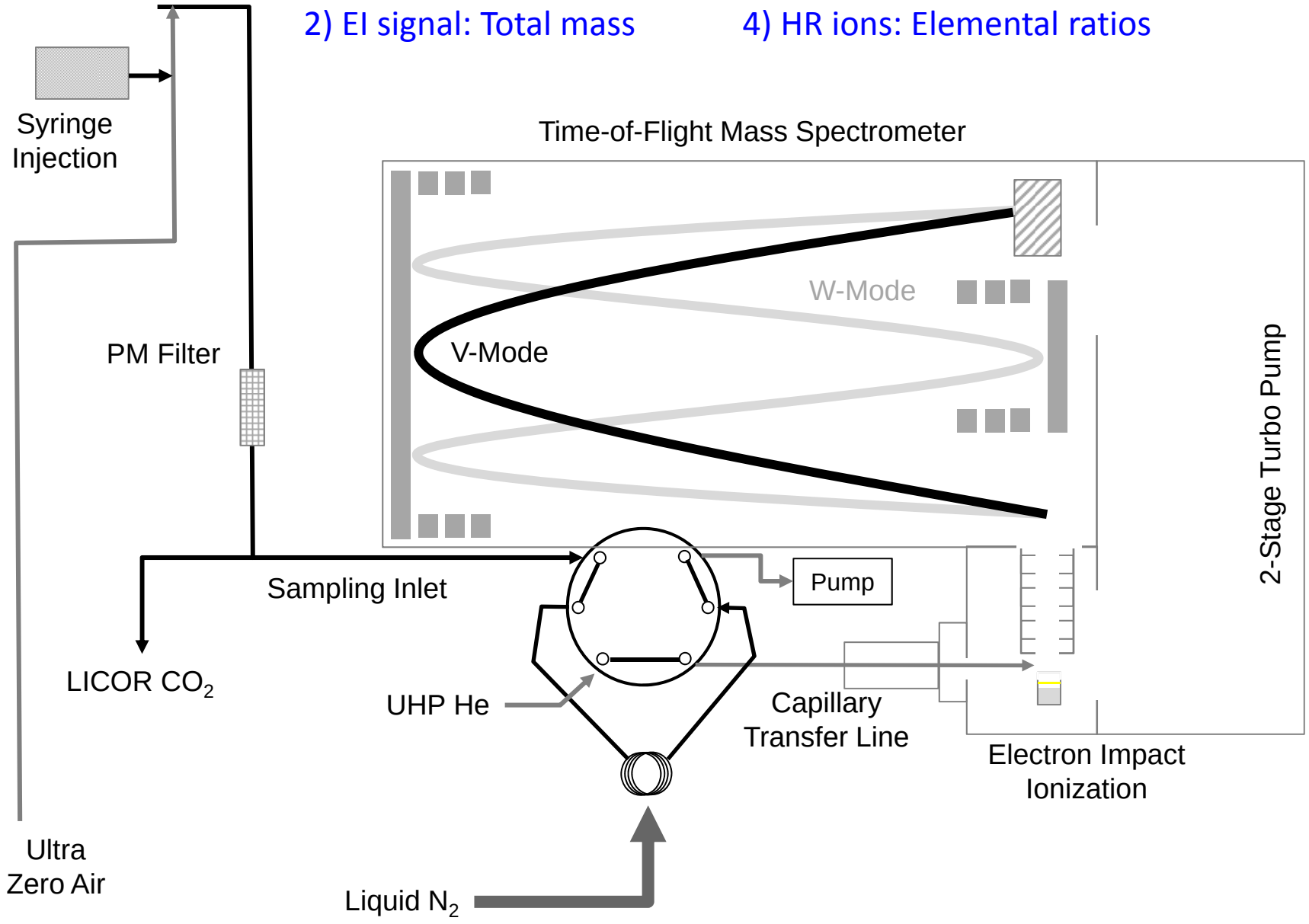


HR-EI-MS data

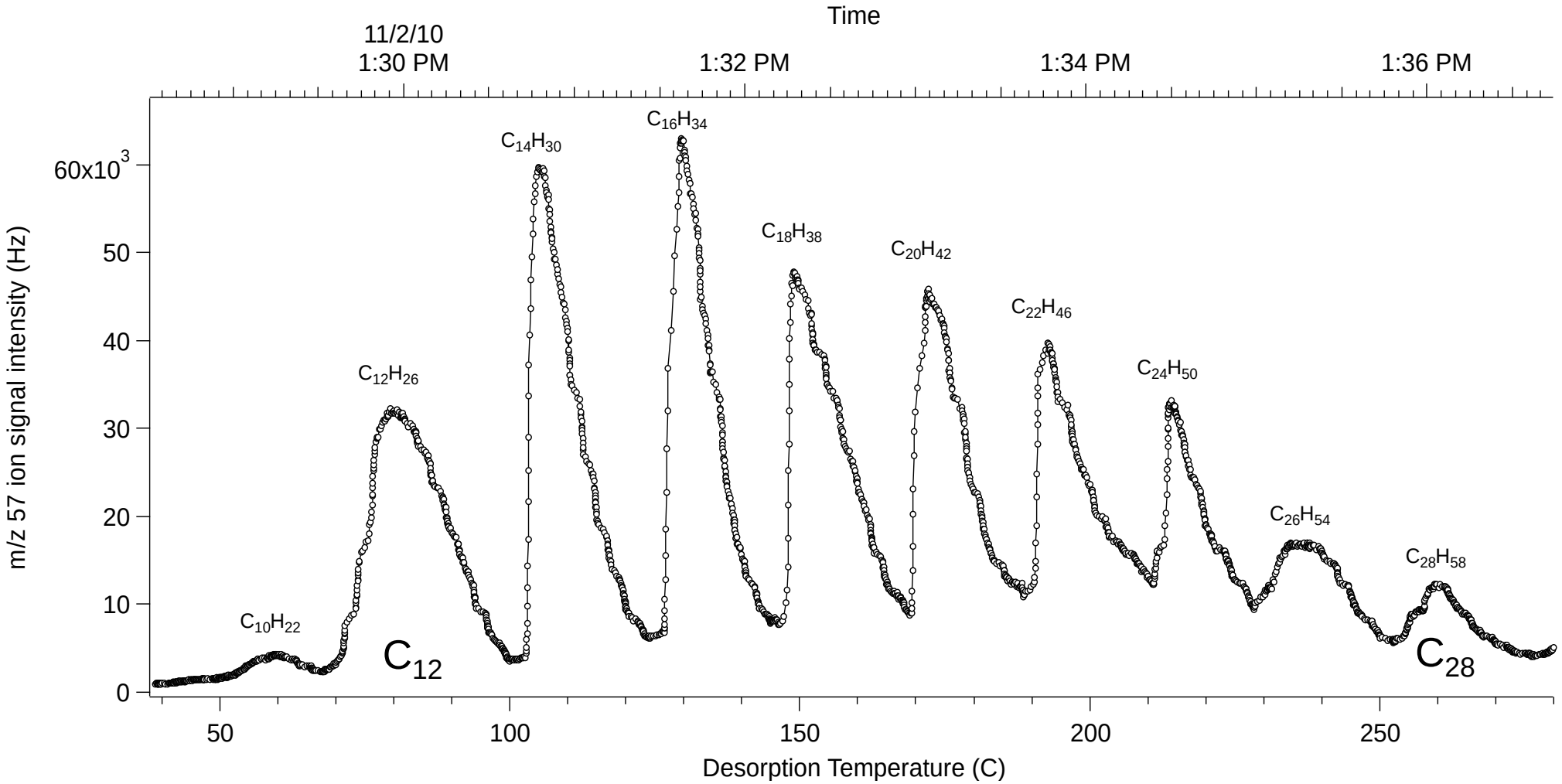

a) mass spectrum
(total organic mass)
organic mass (µg m-3)
50
40
30
20
10
0
40
60
80
100
120
140
160
b) individual ion
abundances
(elemental ratios)
CO2+
C2H4O+
13CC2H7+
ion intensity (arb. units)
43.85
43.90
43.95
44.00
44.05
44.10
44.15
m/z

High-resolution electron impact mass spectrometer

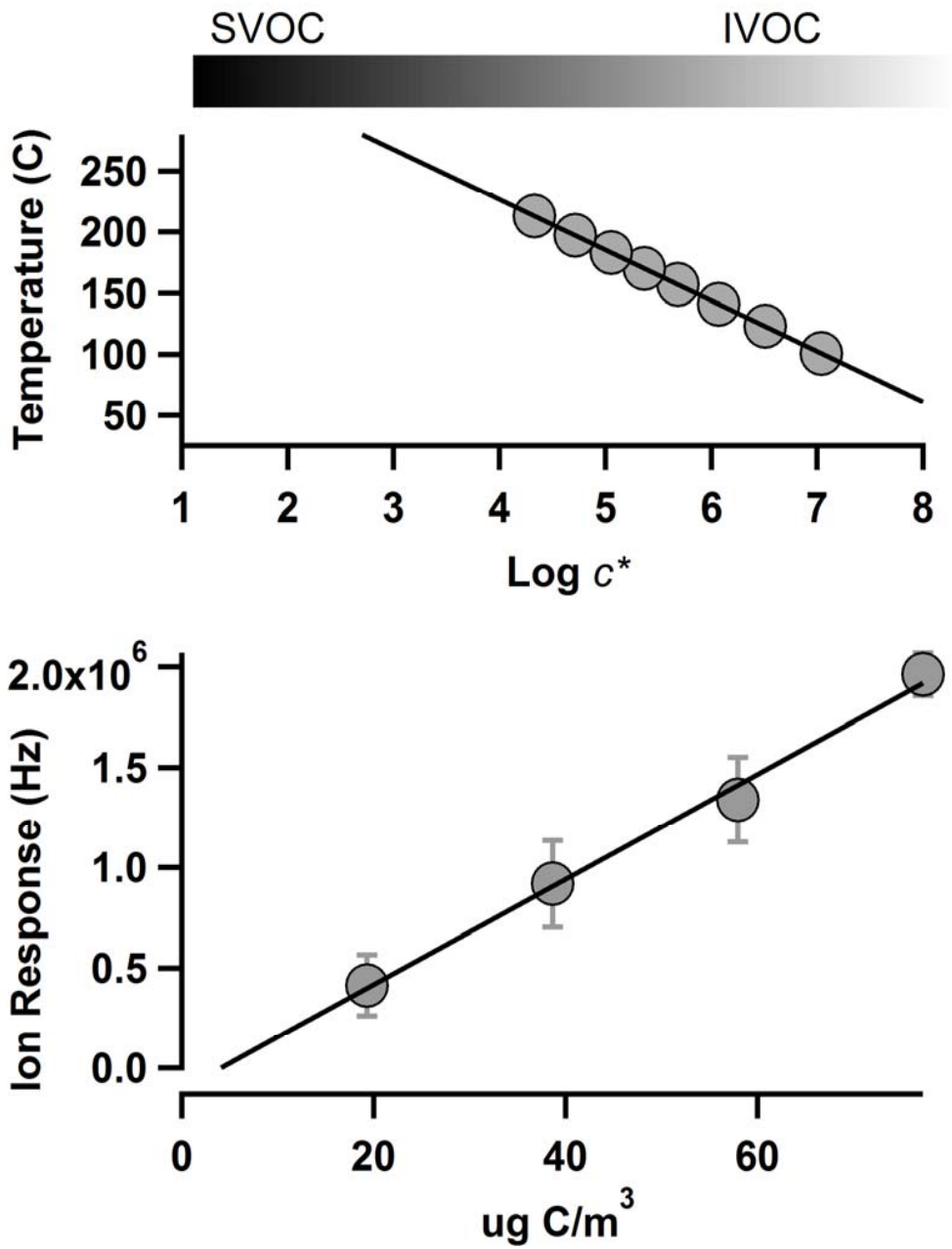
1) Temperature: Volatility
2) EI signal: Total mass
3) Mass spectrum: Composition
4) HR ions: Elemental ratios



Instrument response (*n*-alkanes)



Calibration (volatility, mass concentration)

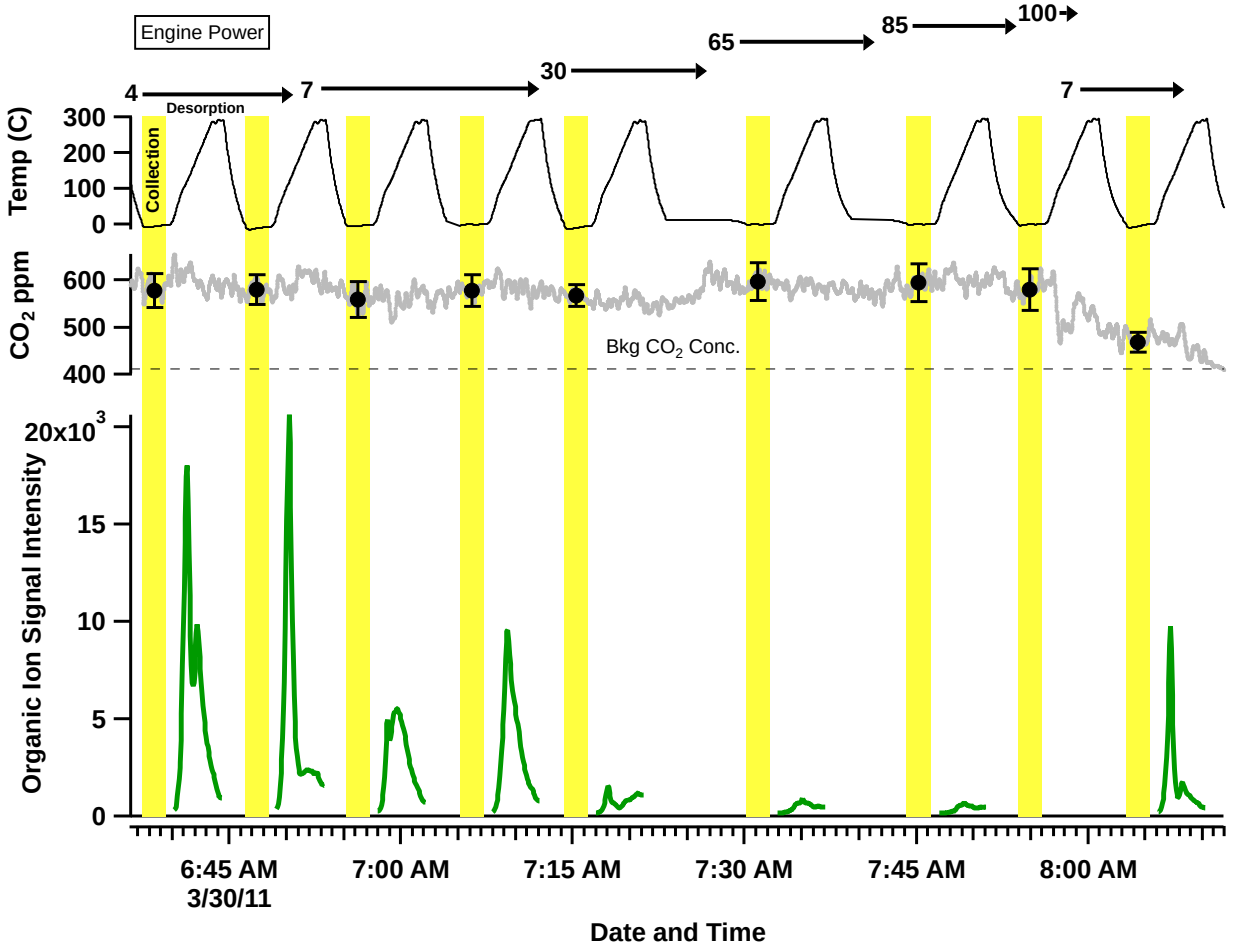


Emissions characterization: aircraft

AAFEX II: Alternative Aviation Fuels Experiment II
Dryden Aircraft Operations Facility, Palmdale CA, March-April 2011

DC-8, two turbofan CFM56-2C1 engines (JP-8 and FT fuels)
Measurements: 150 m downwind

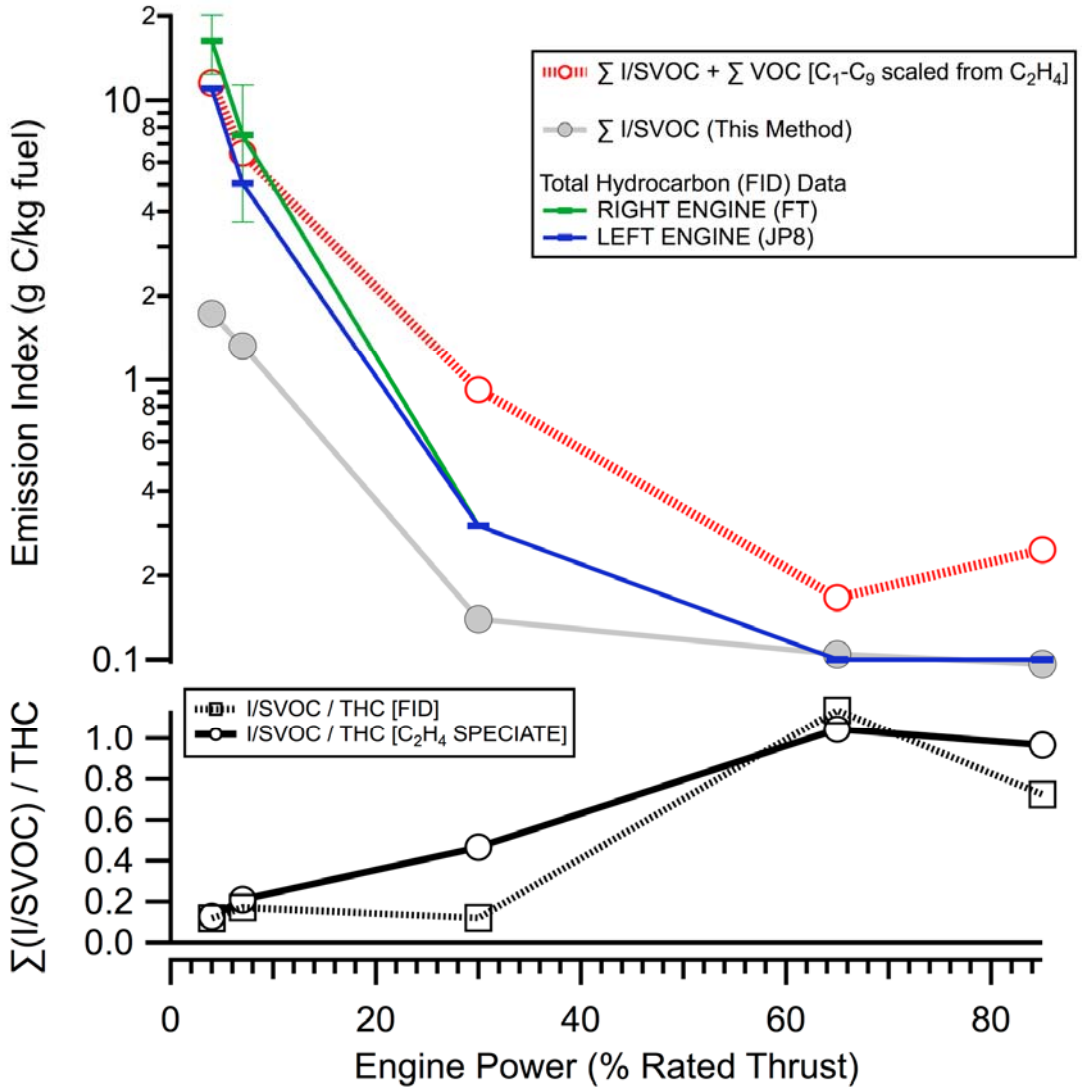
Engine power sweep



- Semicontinuous measurements (2 min collection, 10 min desorption/cooling cycle)
- Can detect rapid changes, transients

[Cross et al., *Atmos. Chem. Phys.*, 2013]

Emission factors, I/SVOC contributions

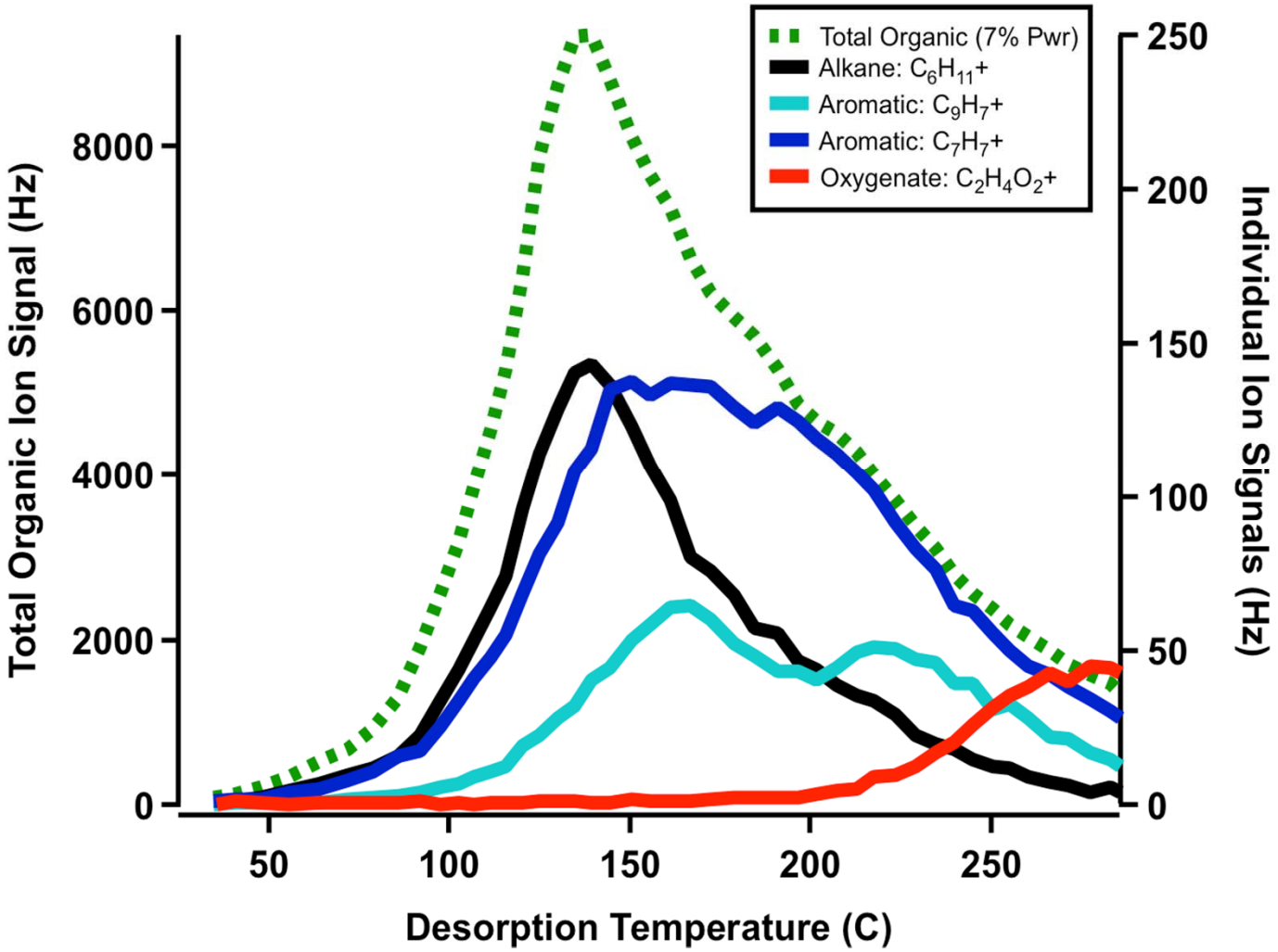


Low powers: I/SVOCs account for 10-20% of organic emissions

High powers: I/SVOCs account for >50% of organic emissions

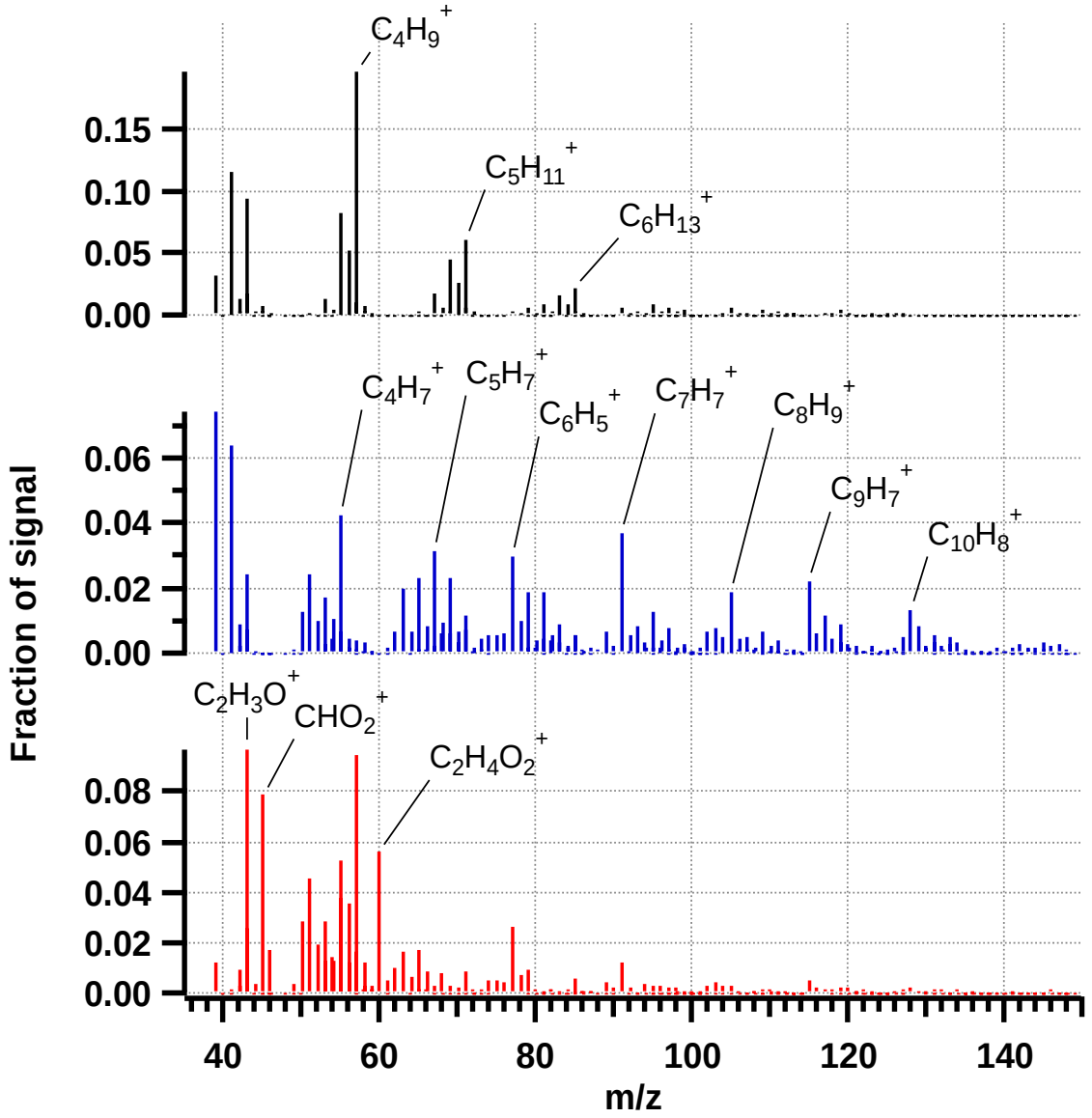
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Volatility distribution (7% power)



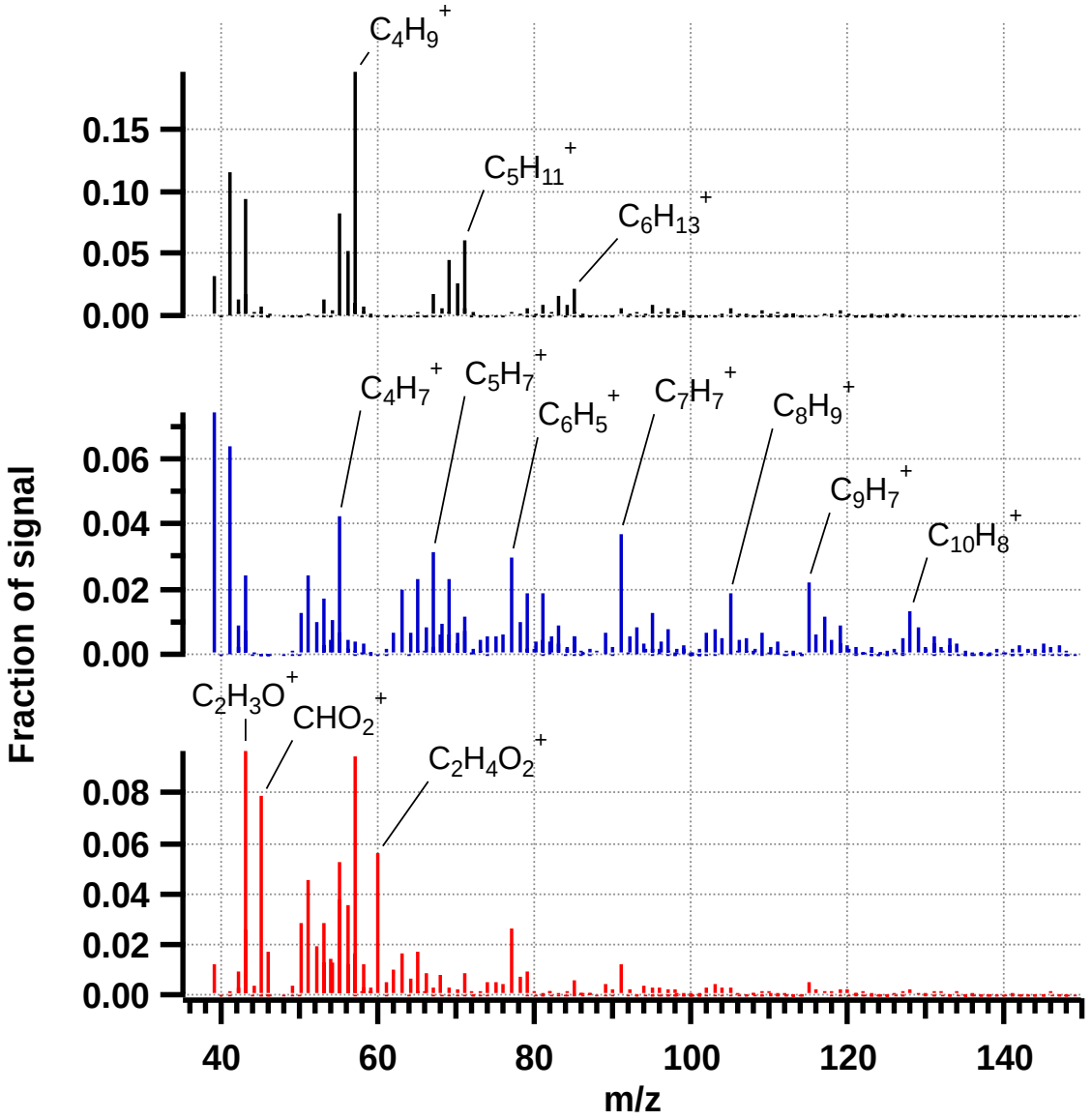
[Cross et al., *Atmos. Chem. Phys.*, 2013]

PMF factors



[Cross et al., *Atmos. Chem. Phys.*, 2013]

PMF factors



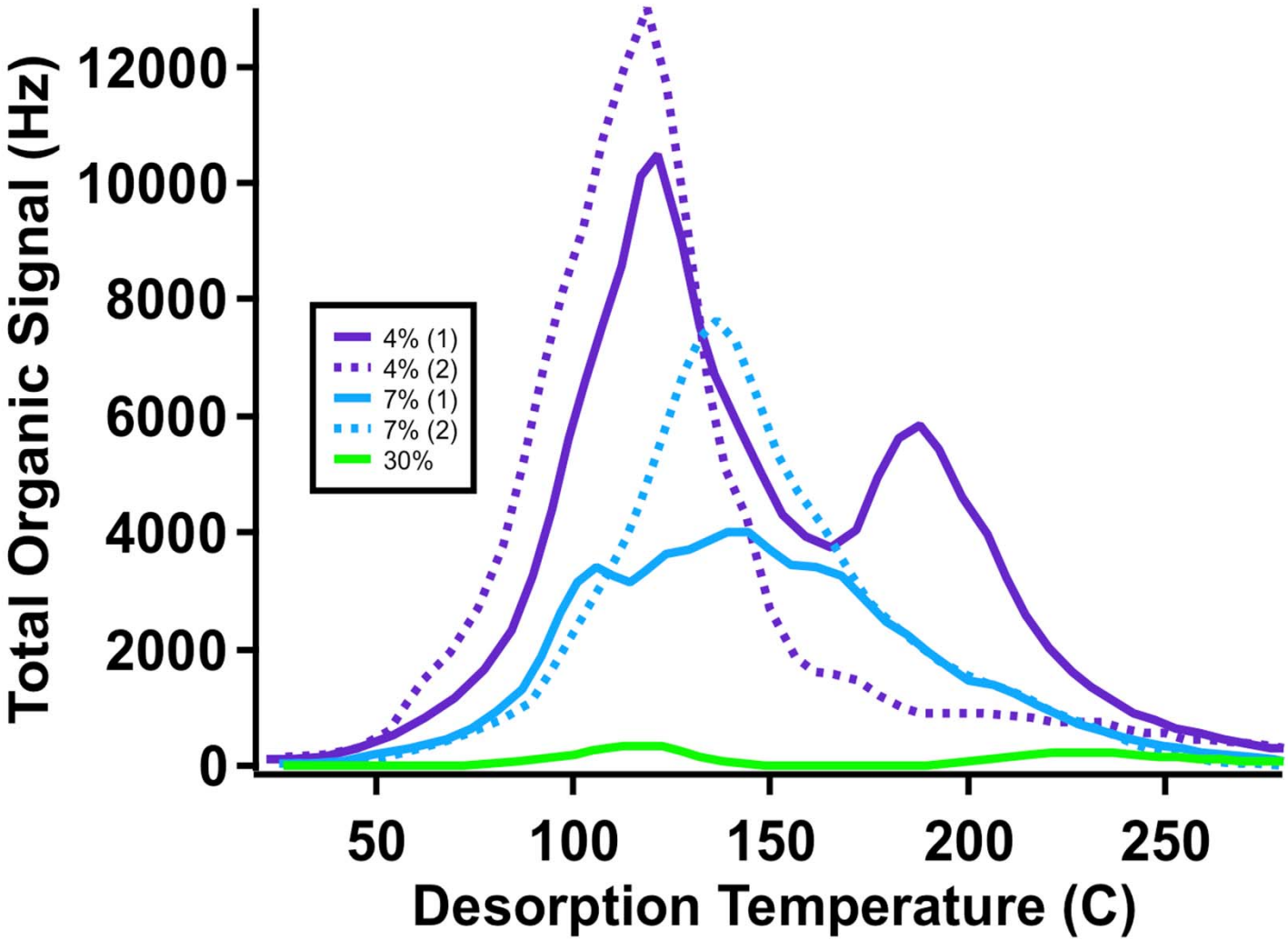
Saturated HC Factor
H:C = 2.07
O:C = 0.03

Aromatic HC Factor
H:C = 1.36
O:C = 0.04

Oxygenated HC Factor
H:C = 1.46
O:C = 0.26

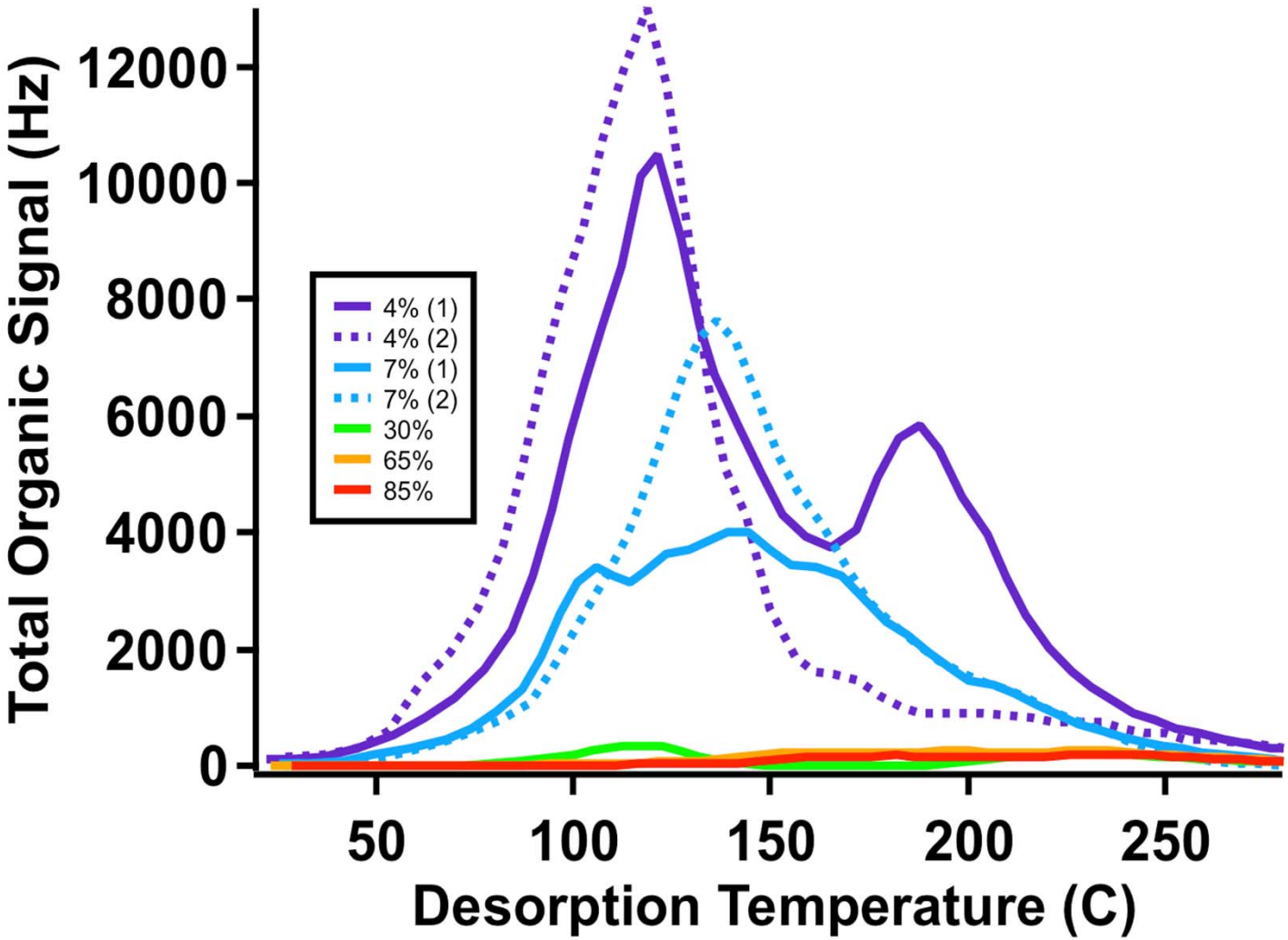
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Unsaturated HC factor



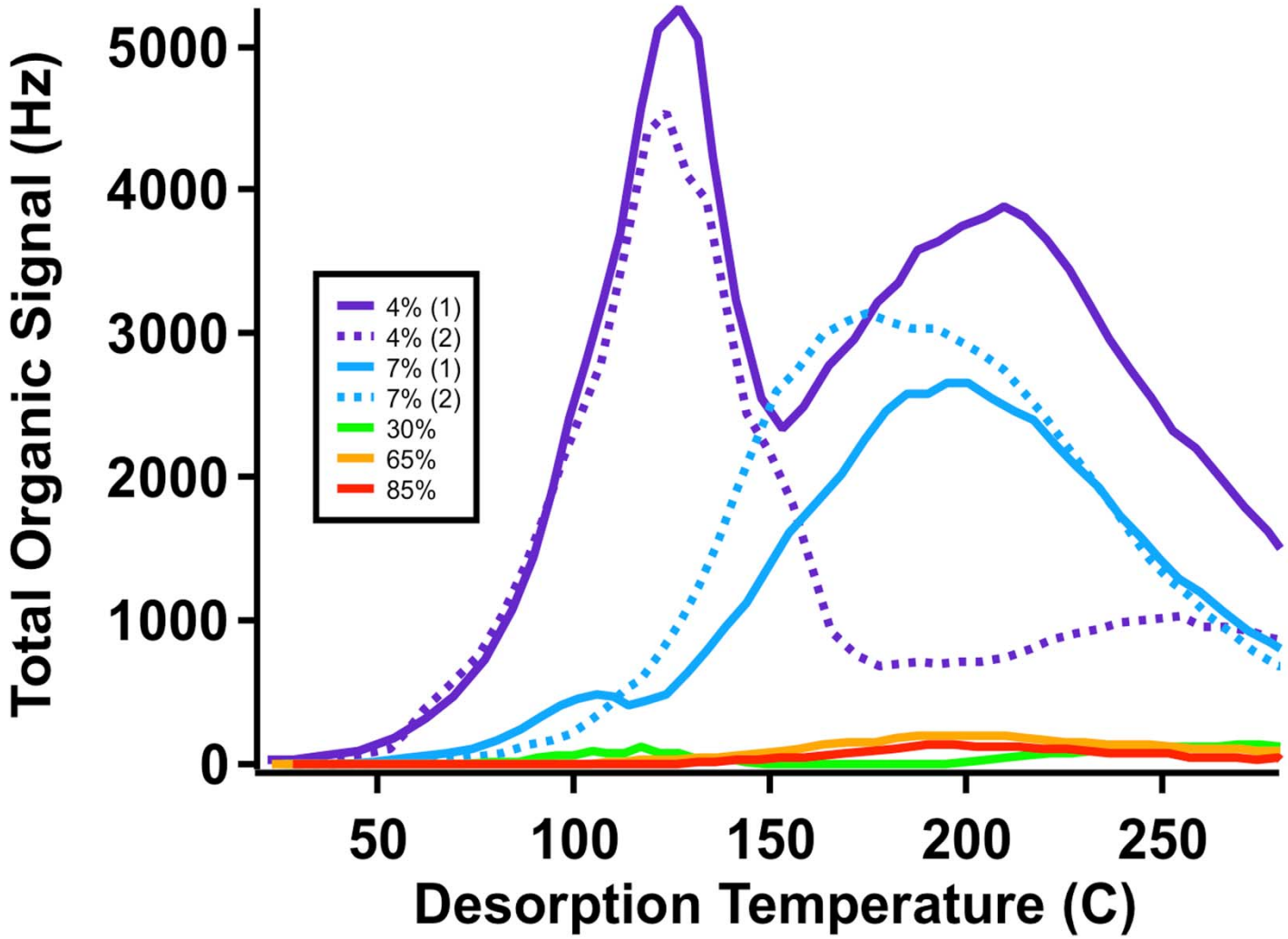
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Unsaturated HC factor



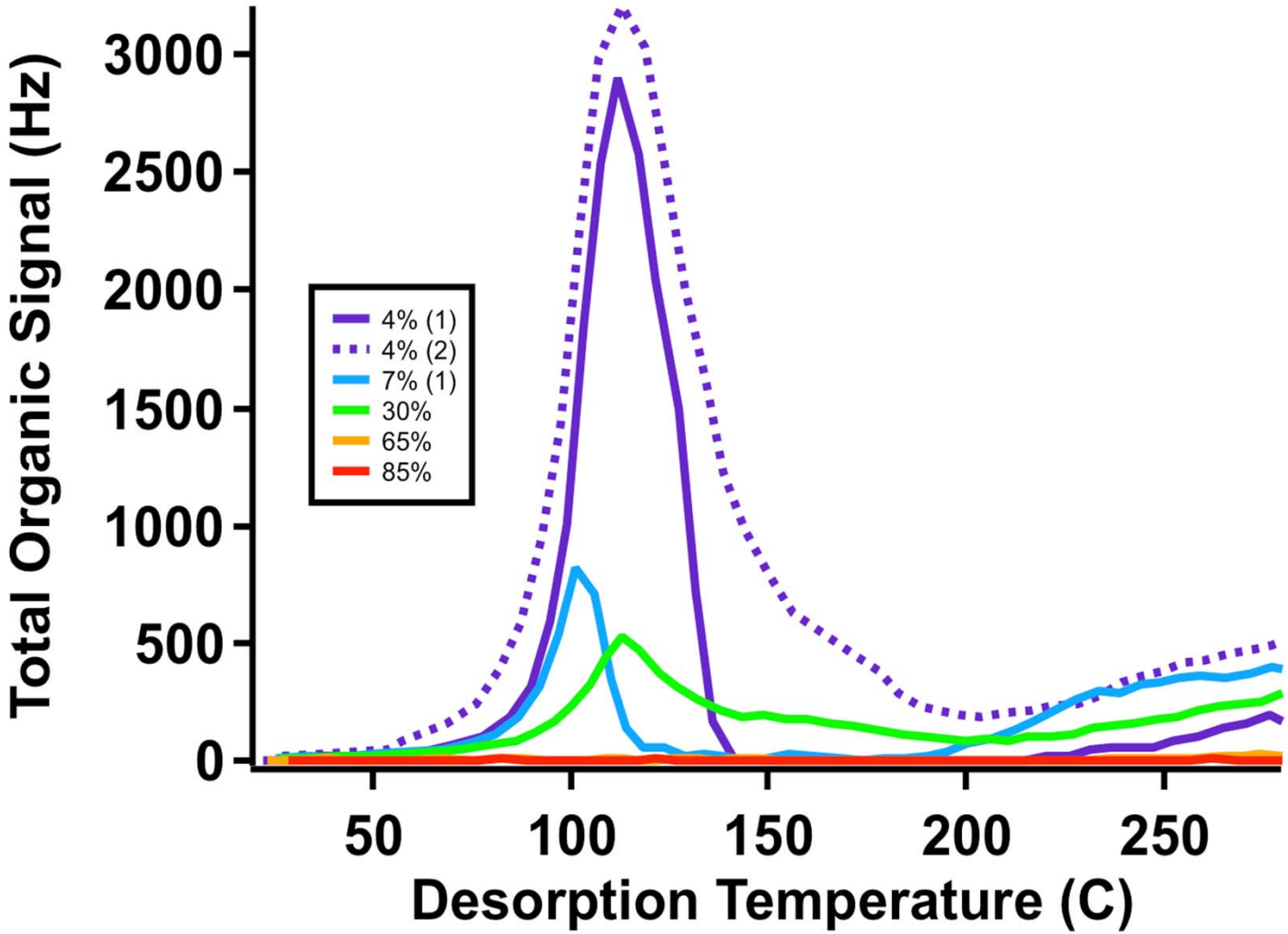
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Aromatic HC factor



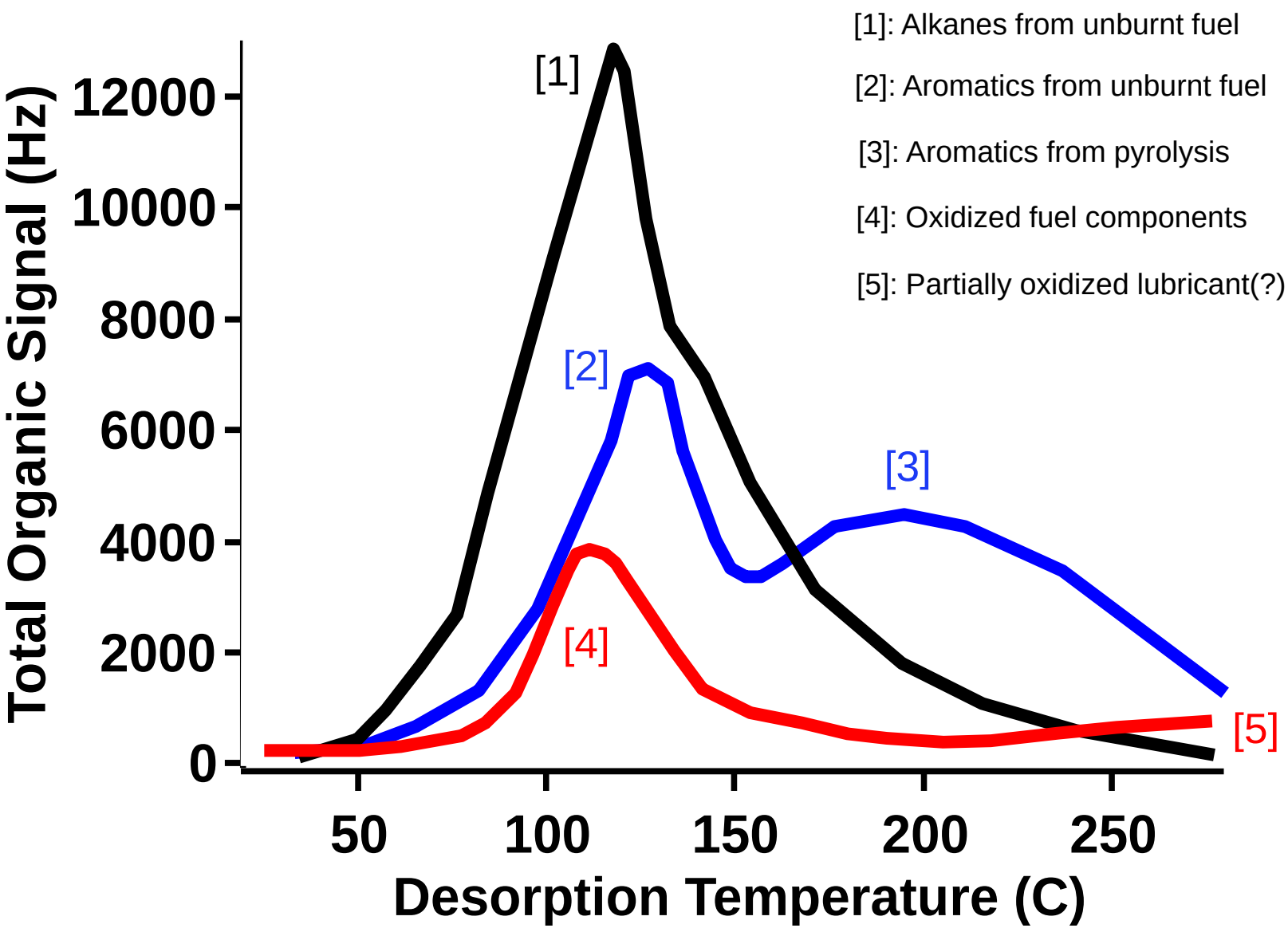
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Oxygenated HC factor



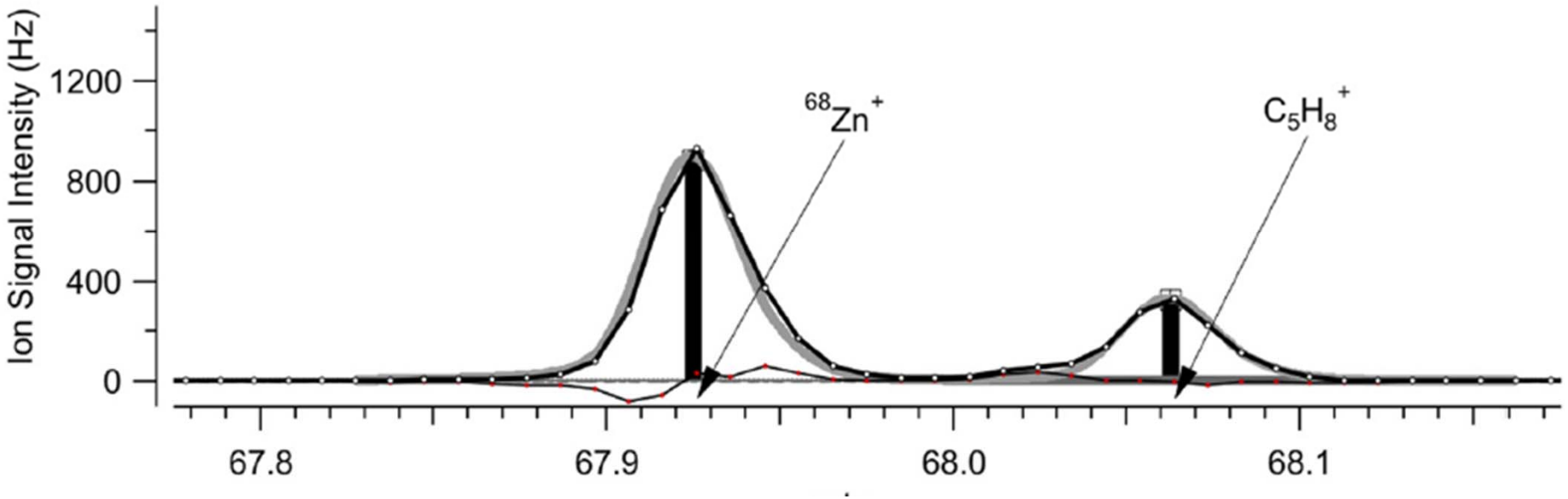
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Summary: I/SVOCs from aircraft



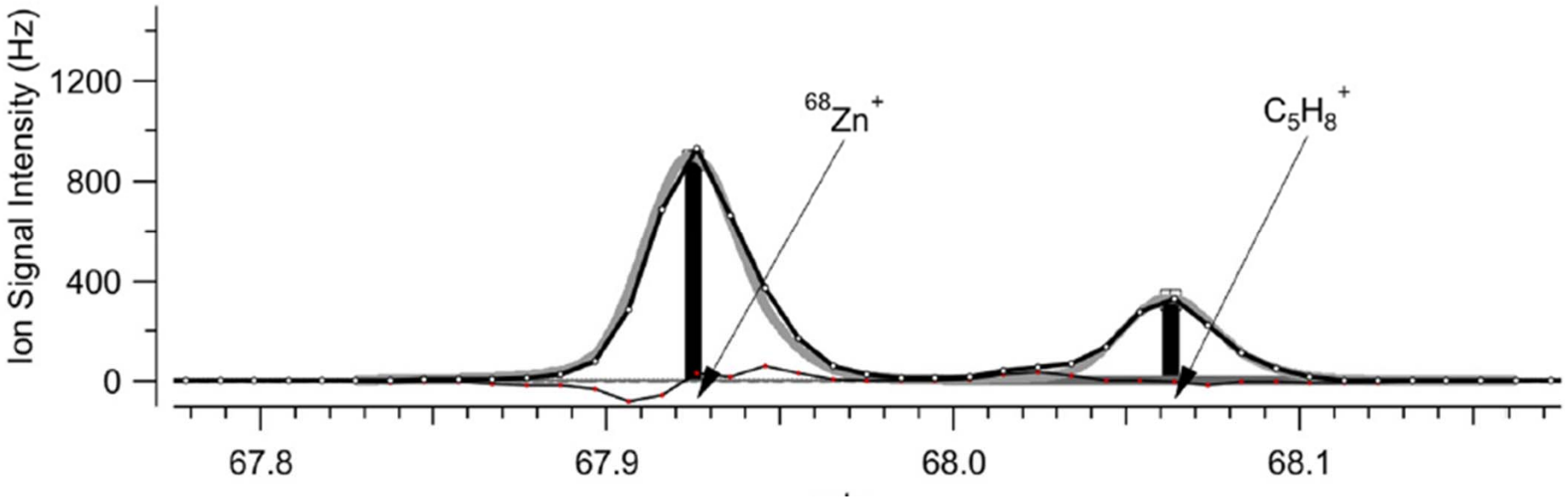
[Cross et al., *Atmos. Chem. Phys.*, 2013]

Trace elements in emitted particles

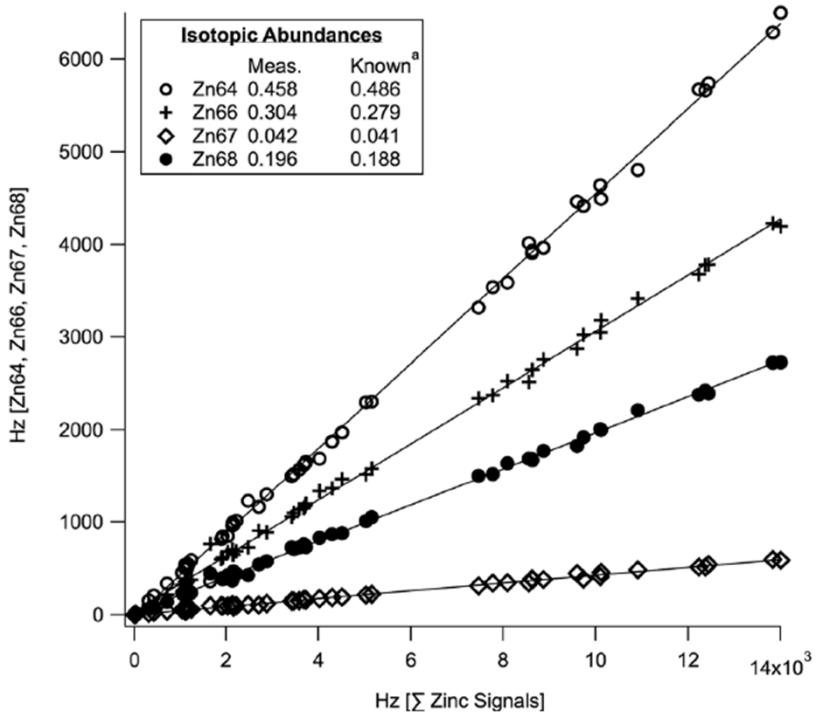


[Cross et al., *J. Eng. Gas Turbines and Power*, 2012]

Trace elements in emitted particles



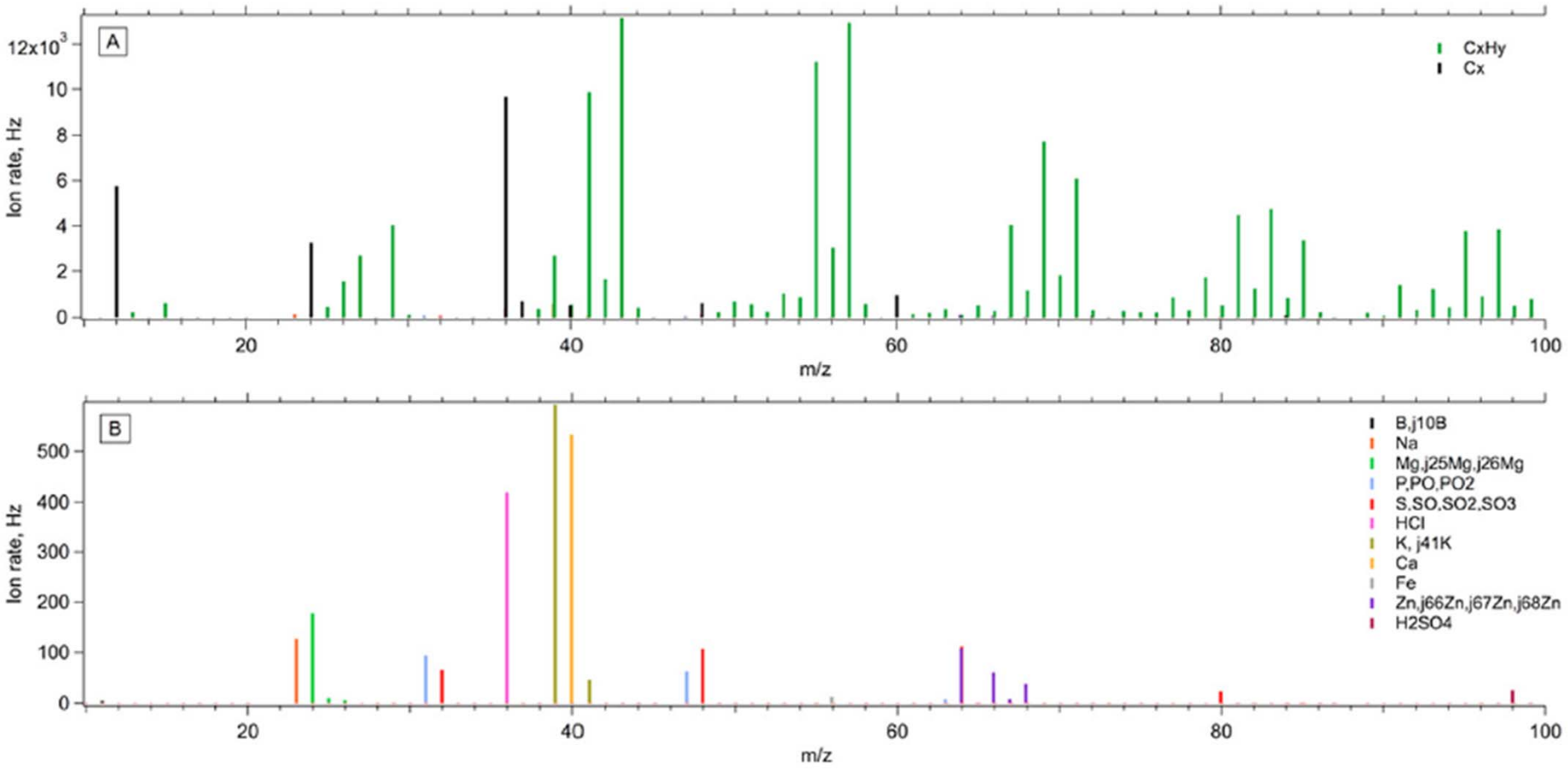
Unambiguous identification of trace metals:
-Exact mass
- Isotopic abundances



[Cross et al., *J. Eng. Gas Turbines and Power*, 2012]

Trace elements in emitted particles

Lubricant components: B, Ca, Mg, P, Zn
Engine-wear markers: Fe, Pb
Others: K, Na, S, Cl



[Cross et al., *J. Eng. Gas Turbines and Power*, 2012]

Summary/conclusions

- New instrument for measuring amount, volatility, and (ensemble) composition of IVOCs and SVOCs in near-real time

- Aircraft emissions: Emissions, composition (alkane/aromatic/oxygenate), and volatility all strongly power-dependent (fuel $\rightarrow$ pyrolysis)

- Diesel engine emissions: Emissions of 0.2-20 mg/kg fuel, depending on engine power; analysis of volatility and composition still in progress

- Follow-on work: Comparison of multiple IVOC/SVOC techniques on the same engine (May-June 2014)

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Eleanor Browne