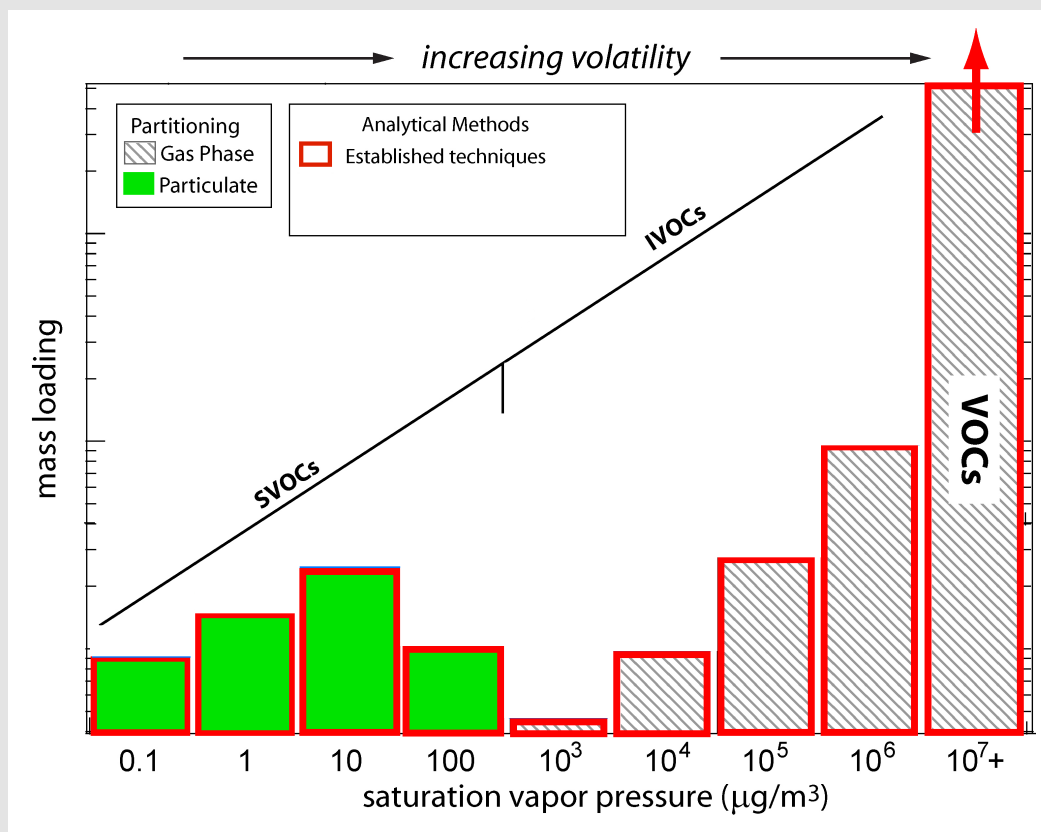


US EPA ARCHIVE DOCUMENT

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

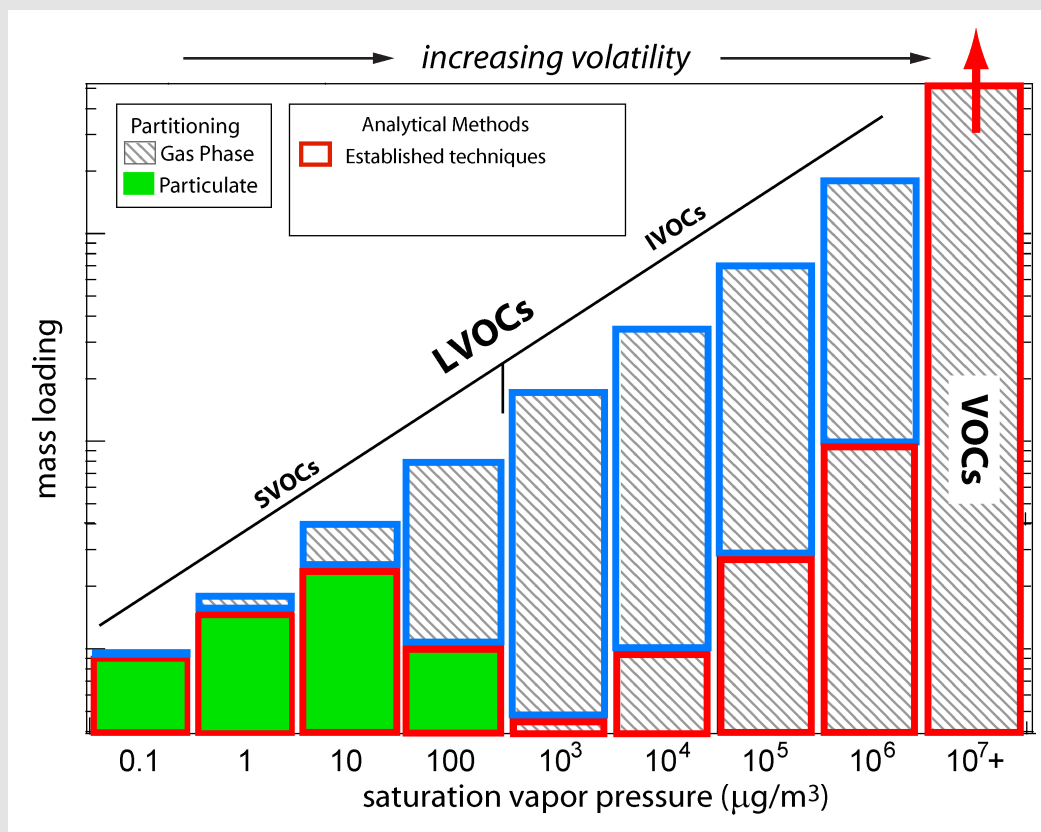
Jesse H. Kroll
MIT CEE and ChE
EPA STAR Kickoff Meeting
16 November 2010

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



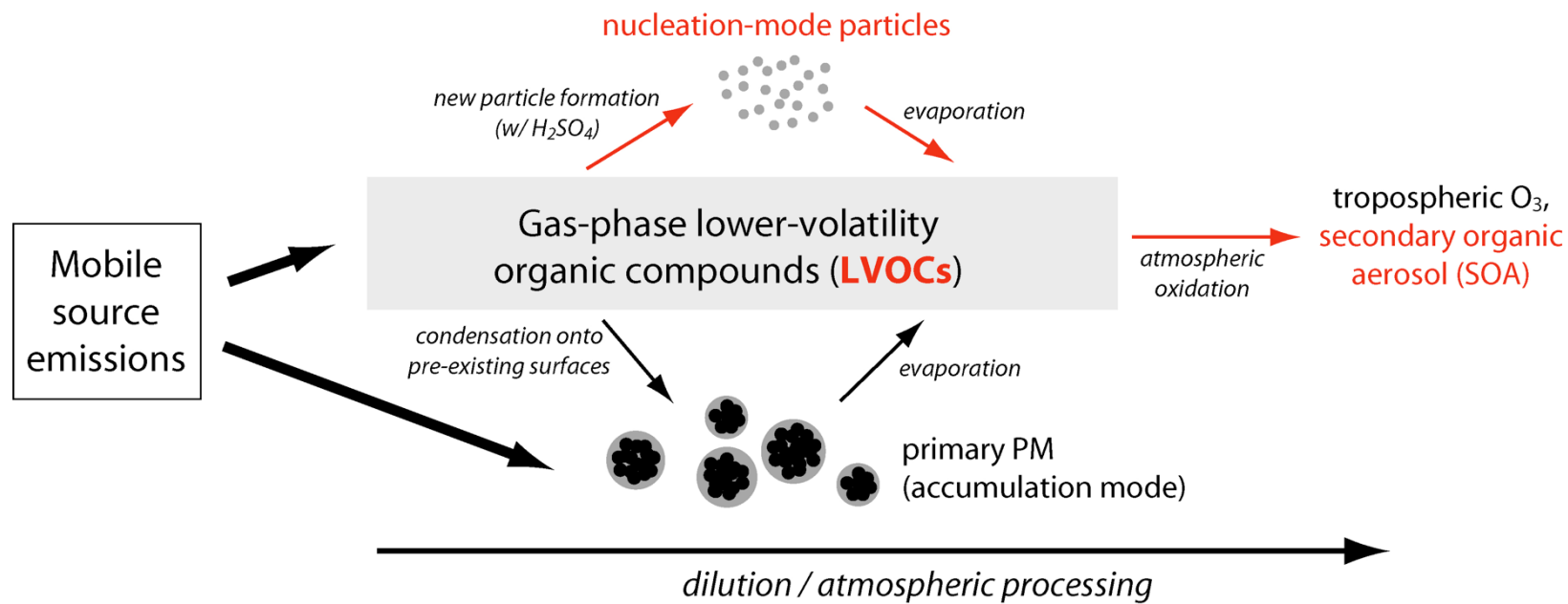
VOC: volatile organic compounds (gas phase)

IVOC: "intermediate volatility" organic compounds (gas phase)

SVOC: semivolatile organic compounds (gas, particle phase)

LVOC: lower-volatility organic compounds (IVOC + gas-phase SVOC)

Importance of LVOCs



Measuring LVOCs: Approaches

1) *Speciated* (e.g., GC-MS)

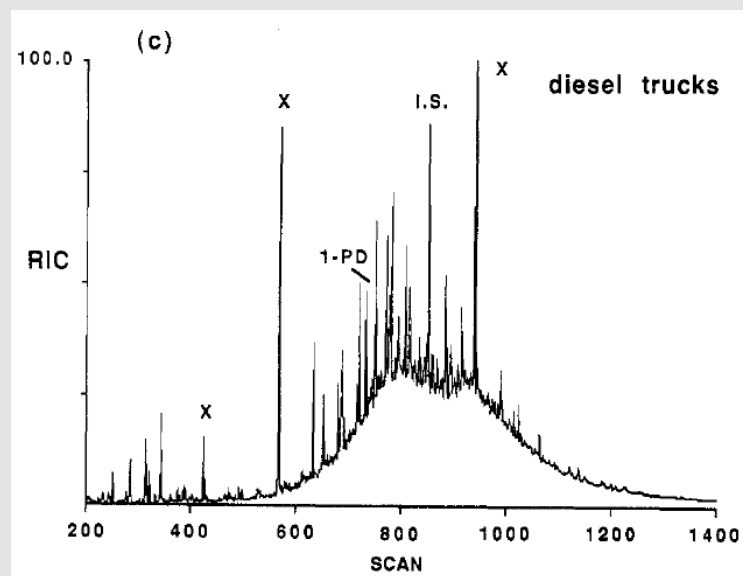
Sensitive and specific
Identifies, quantifies major species

But: *many* minor species
selective?

2) *Bulk* (e.g., FID)

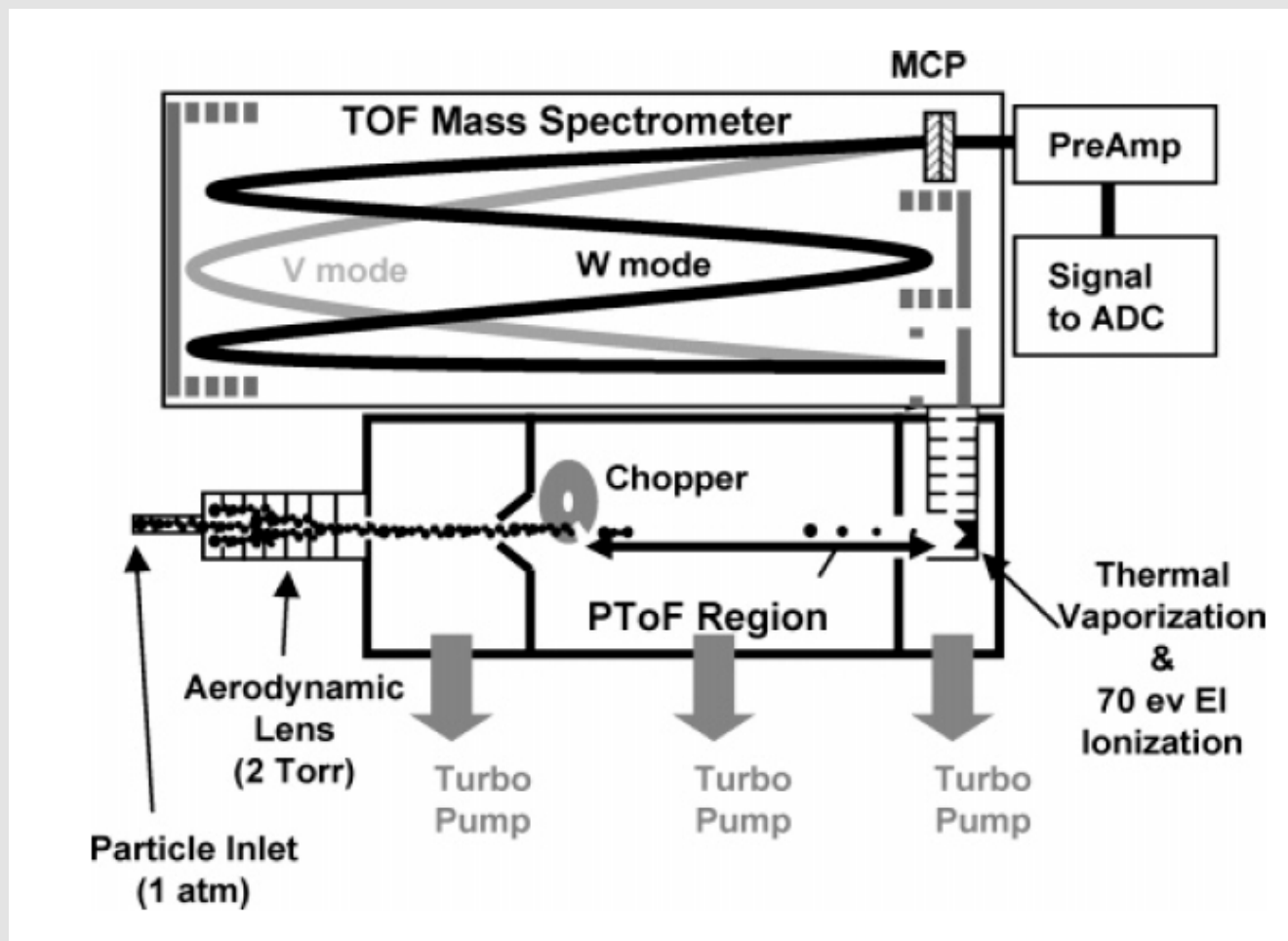
Universal
Detects all carbon

But: no chemical information
no VOC-LVOC differentiation
varying response factors

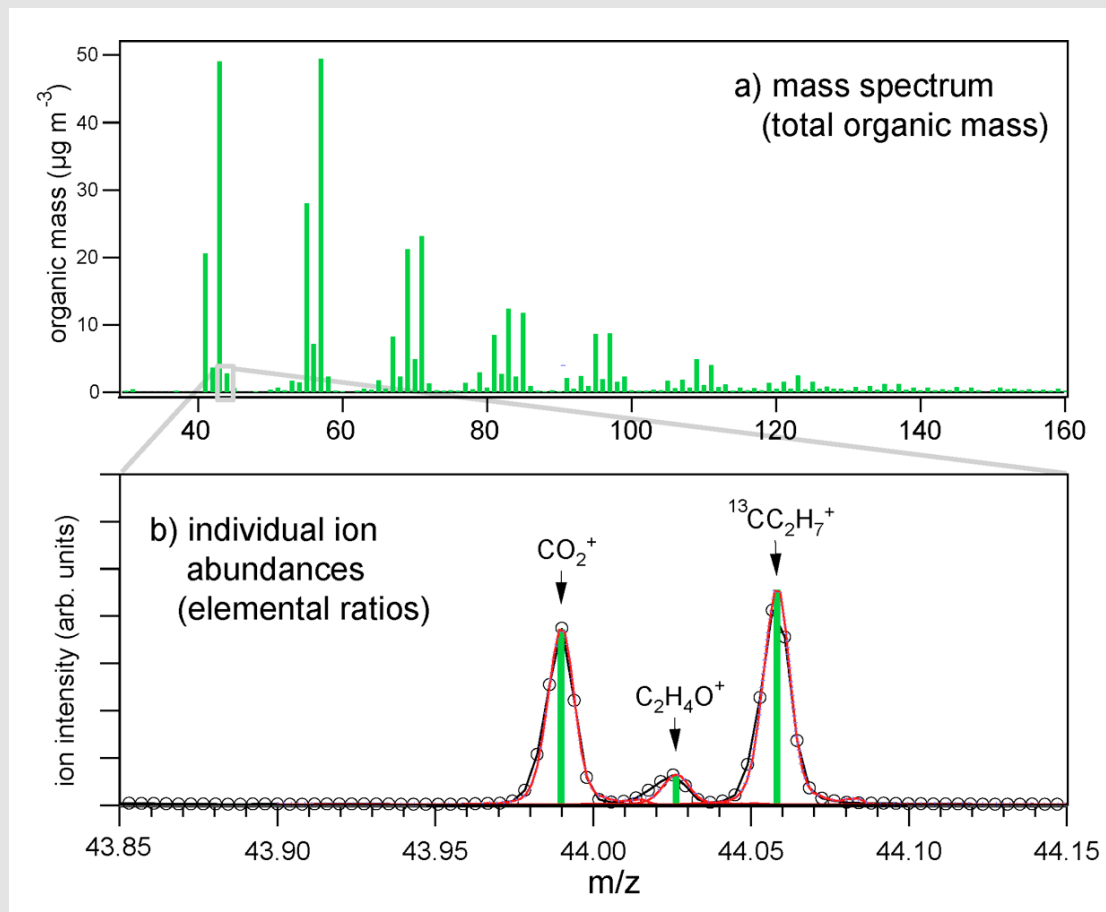


Diesel exhaust PM
(Rogge et al, *ES&T* 1993)

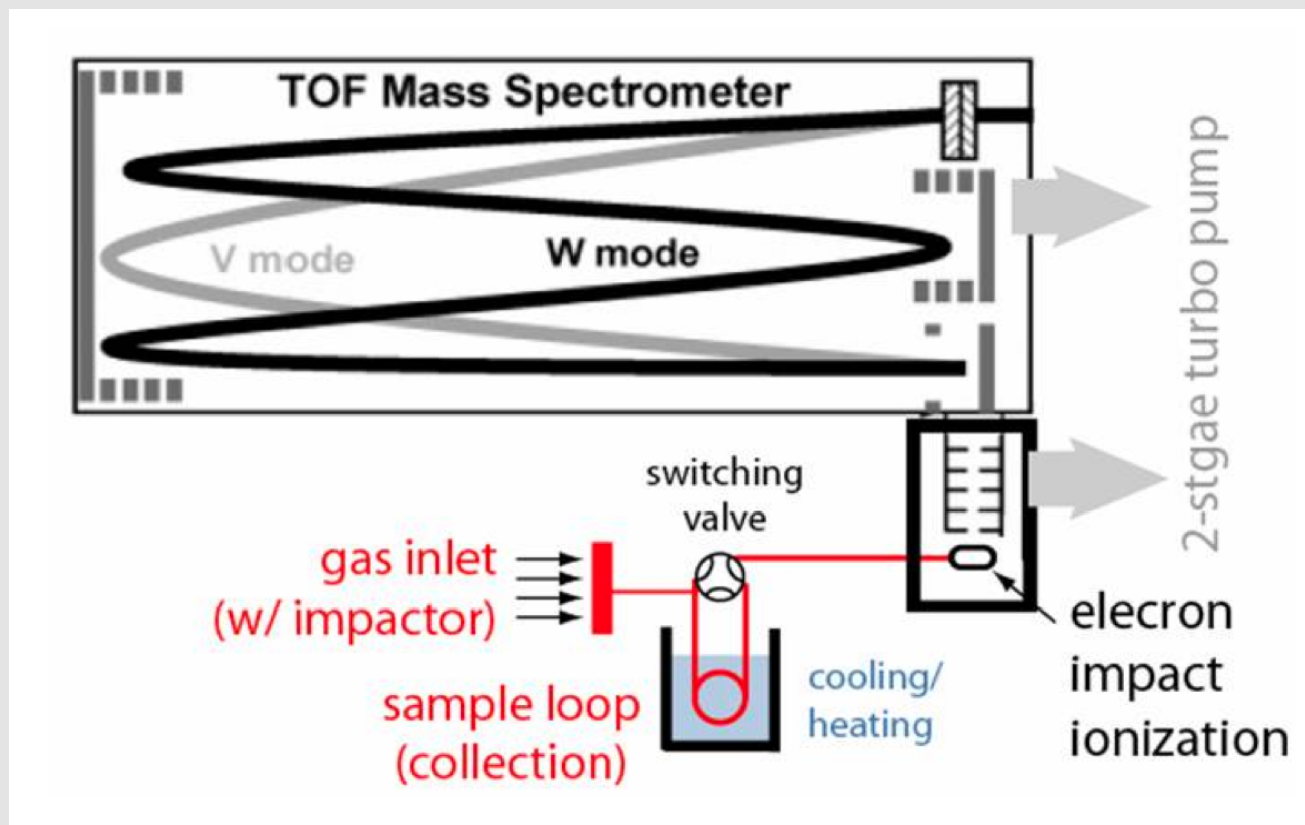
Aerodyne aerosol mass spectrometer (AMS)



High-resolution electron impact mass spectrometry

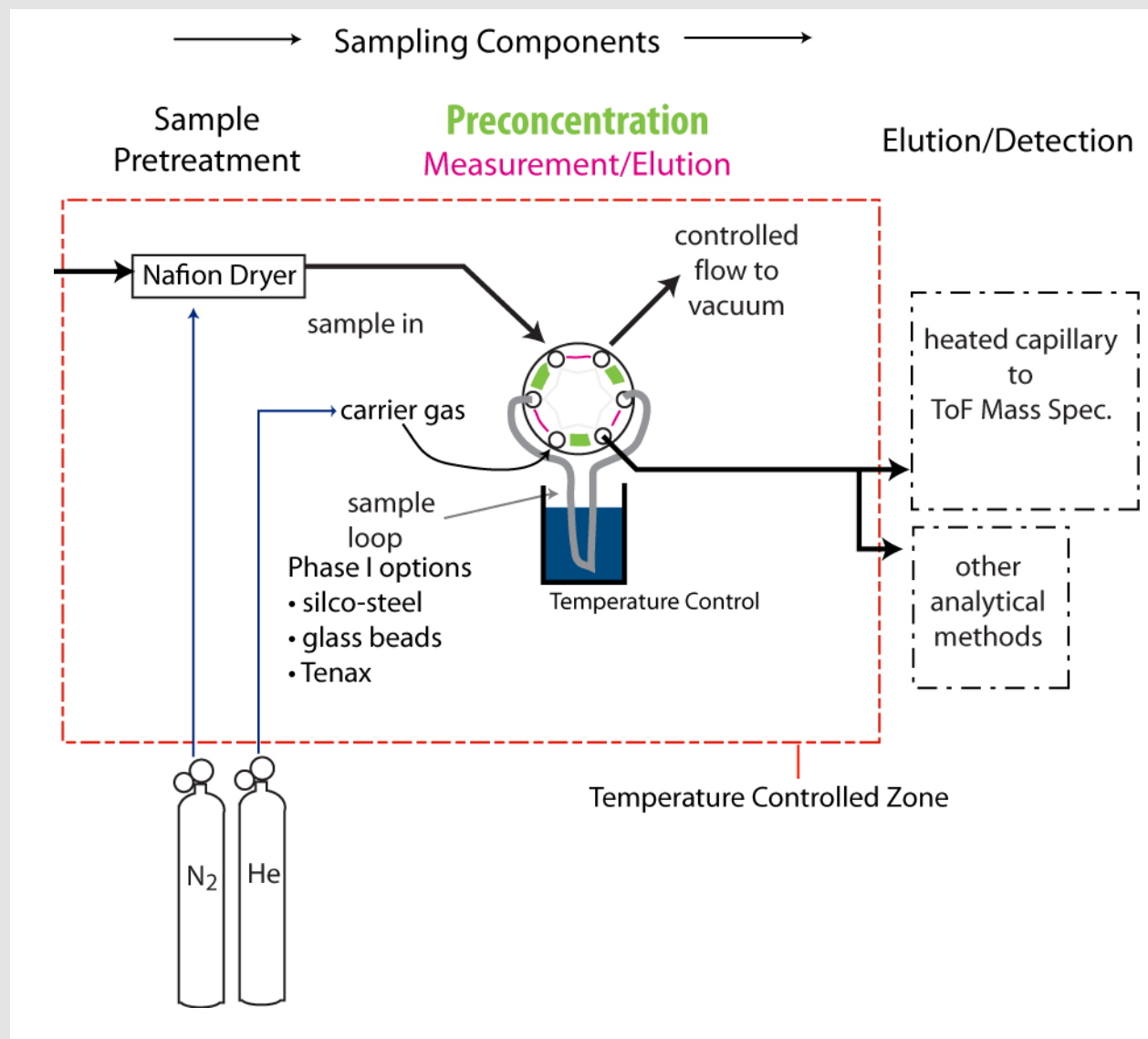


Total Gas-Phase Organics (TGO) instrument

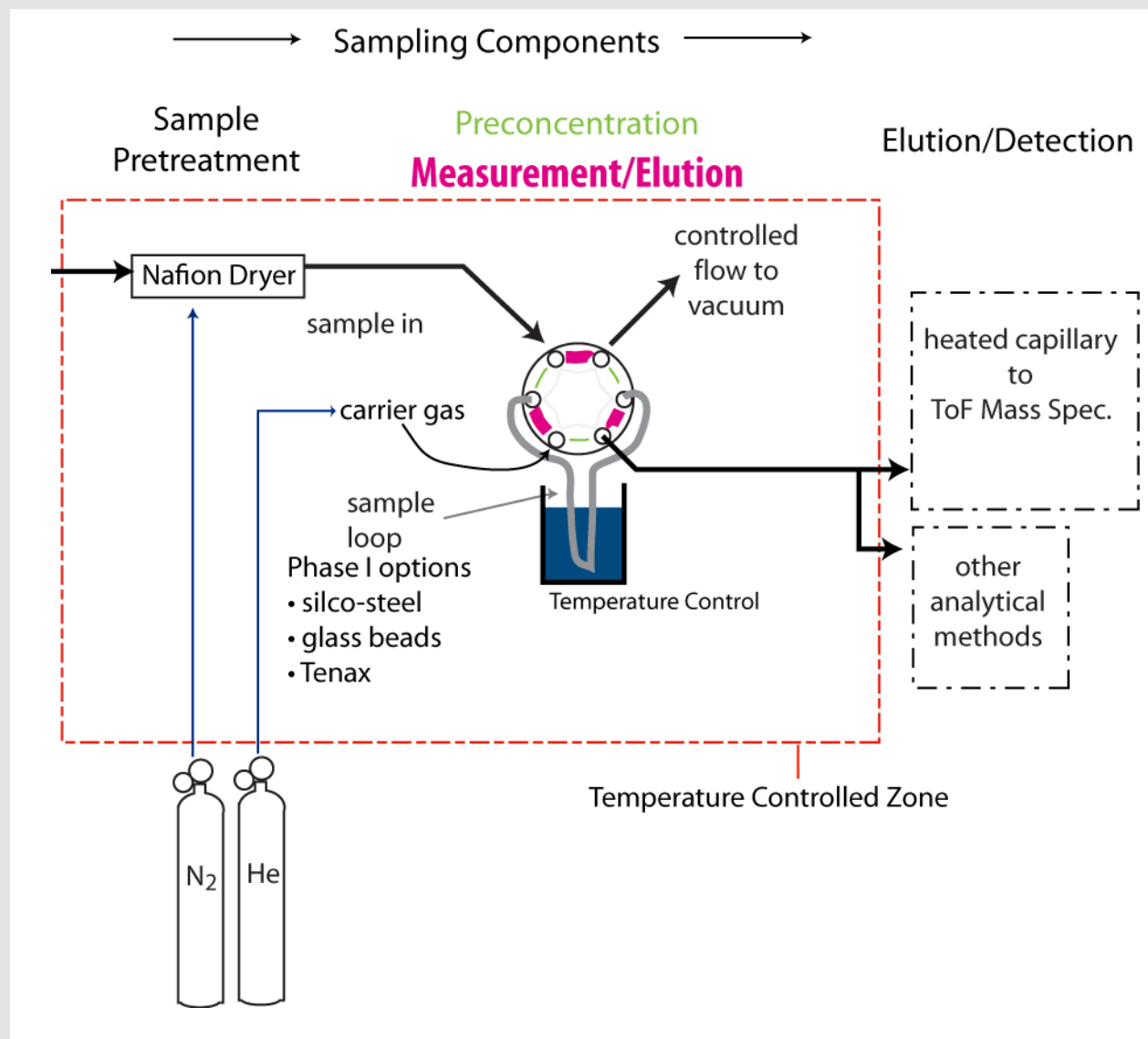


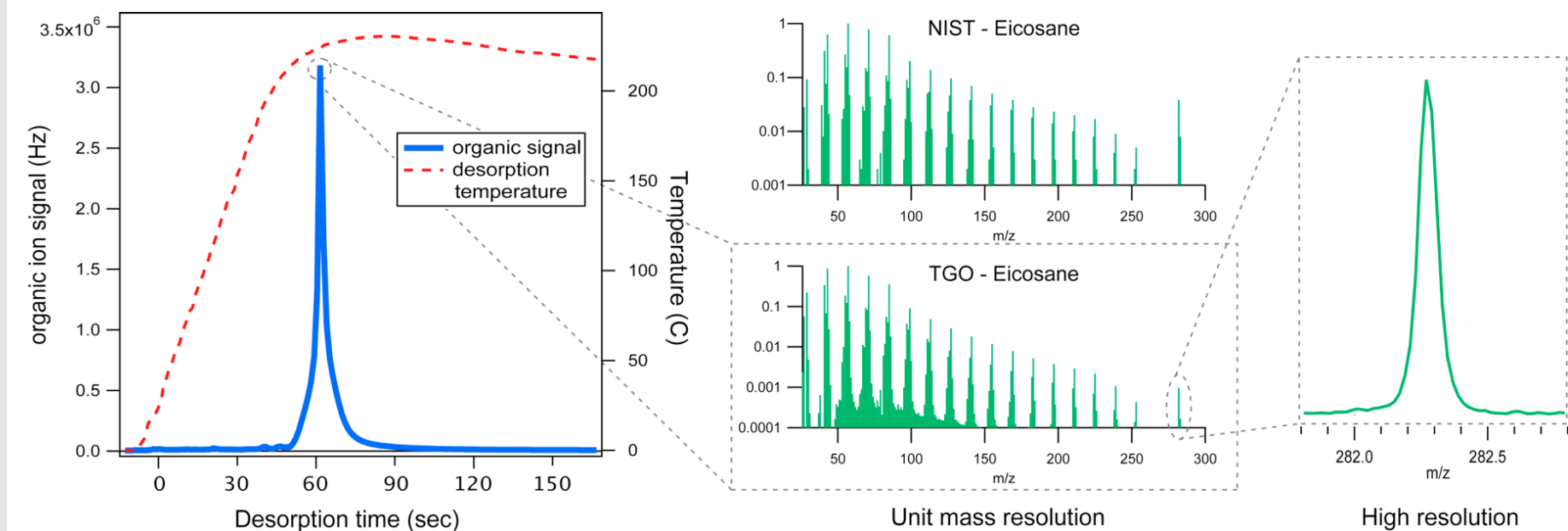
Developed in collaboration with Aerodyne Research, Inc.

TGO front end

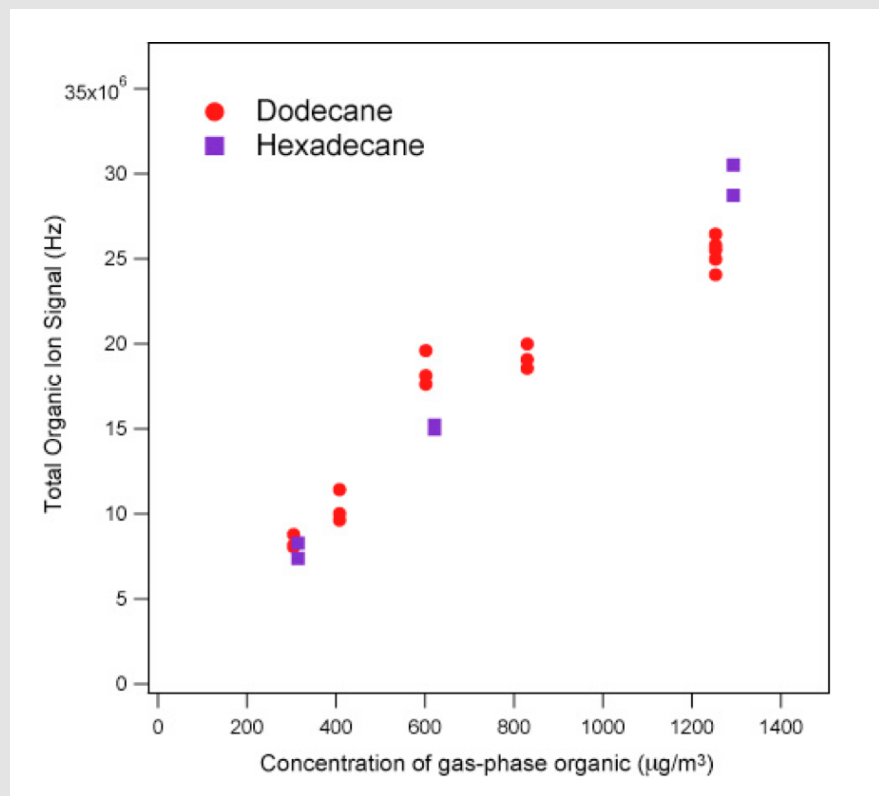


TGO front end



IVOC: eicosane ($C_{20}H_{42}$)

Calibration, linearity



Objective 1: Volatility-resolved organics

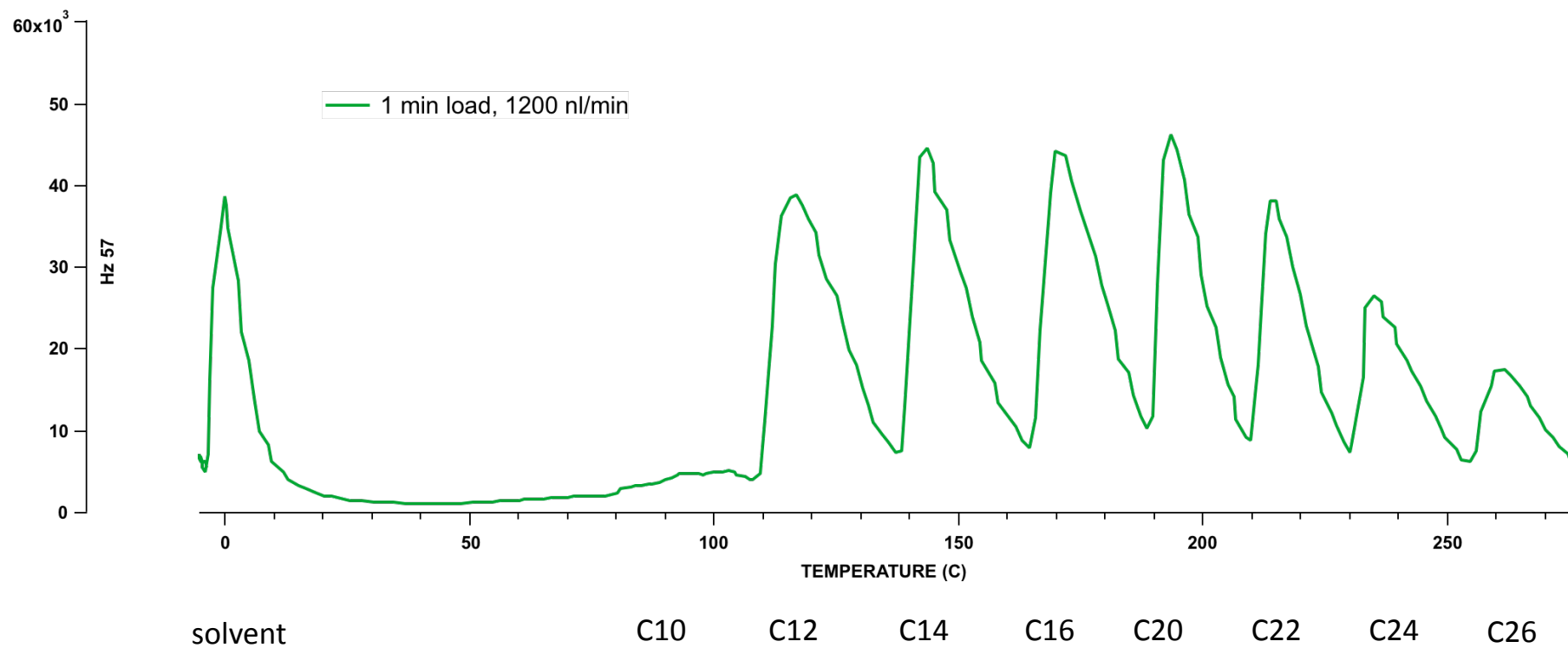
Collected organics will desorb at different temperatures according to their vapor pressures

Slow temperature ramp: volatility-resolved measurements

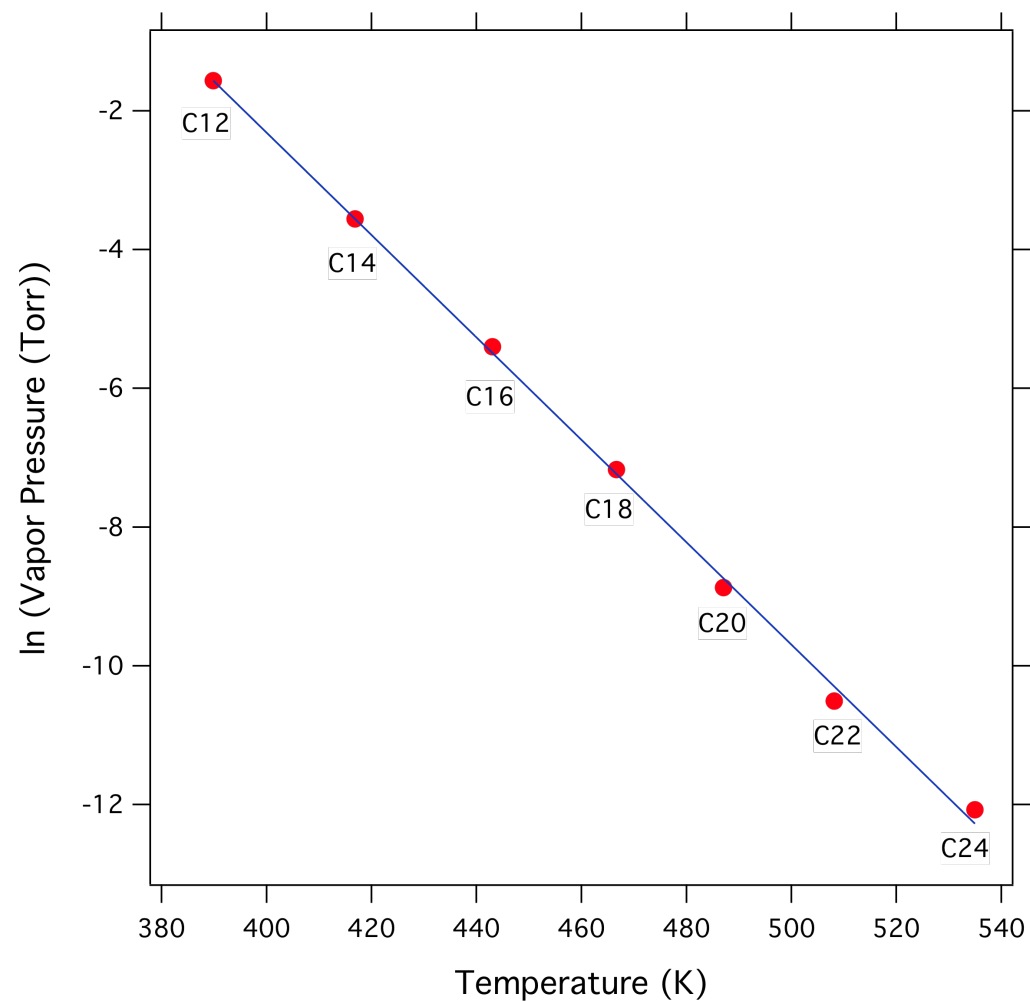
→ Distribution of organics (VOCs vs. IVOCs vs. SVOCs) rather than a bulk average

Volatility-resolved measurements

Volatilized C10-C30 *n*-alkanes in gas phase

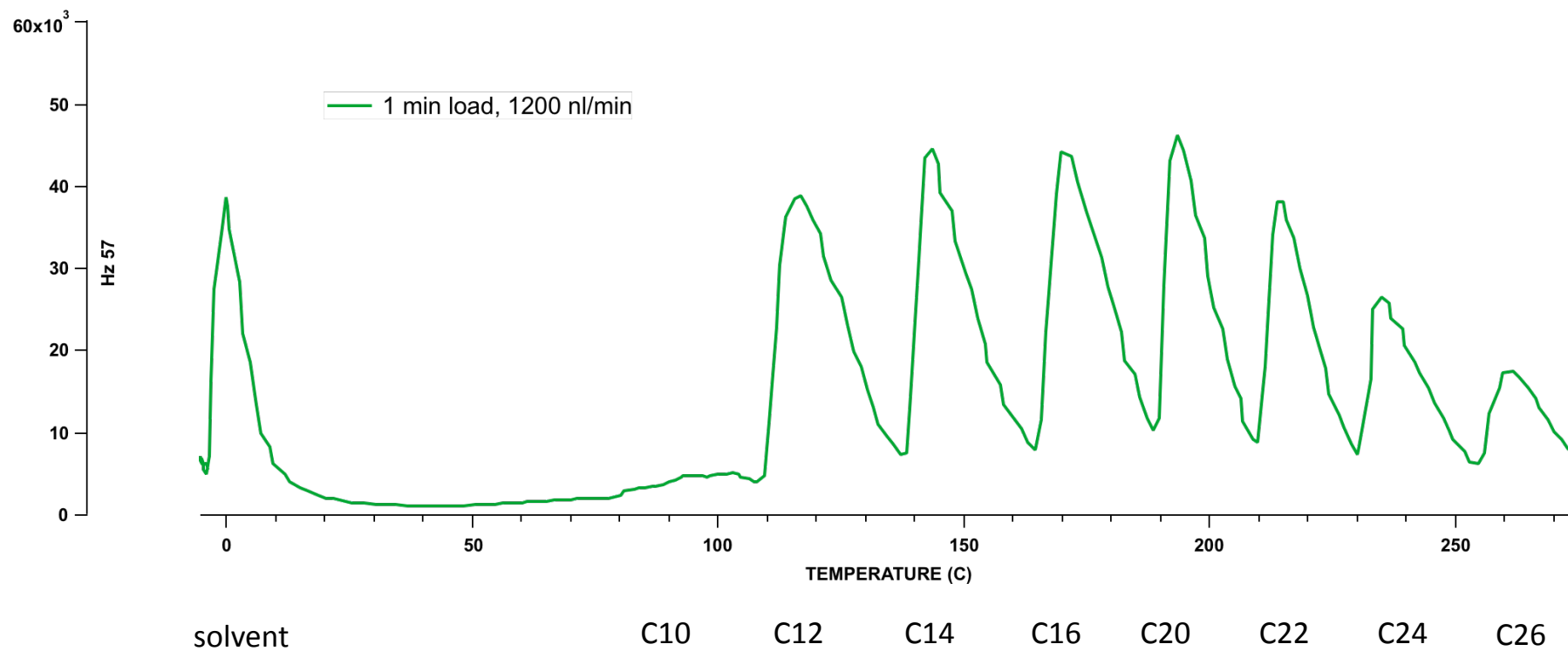


Vapor pressure vs. temperature



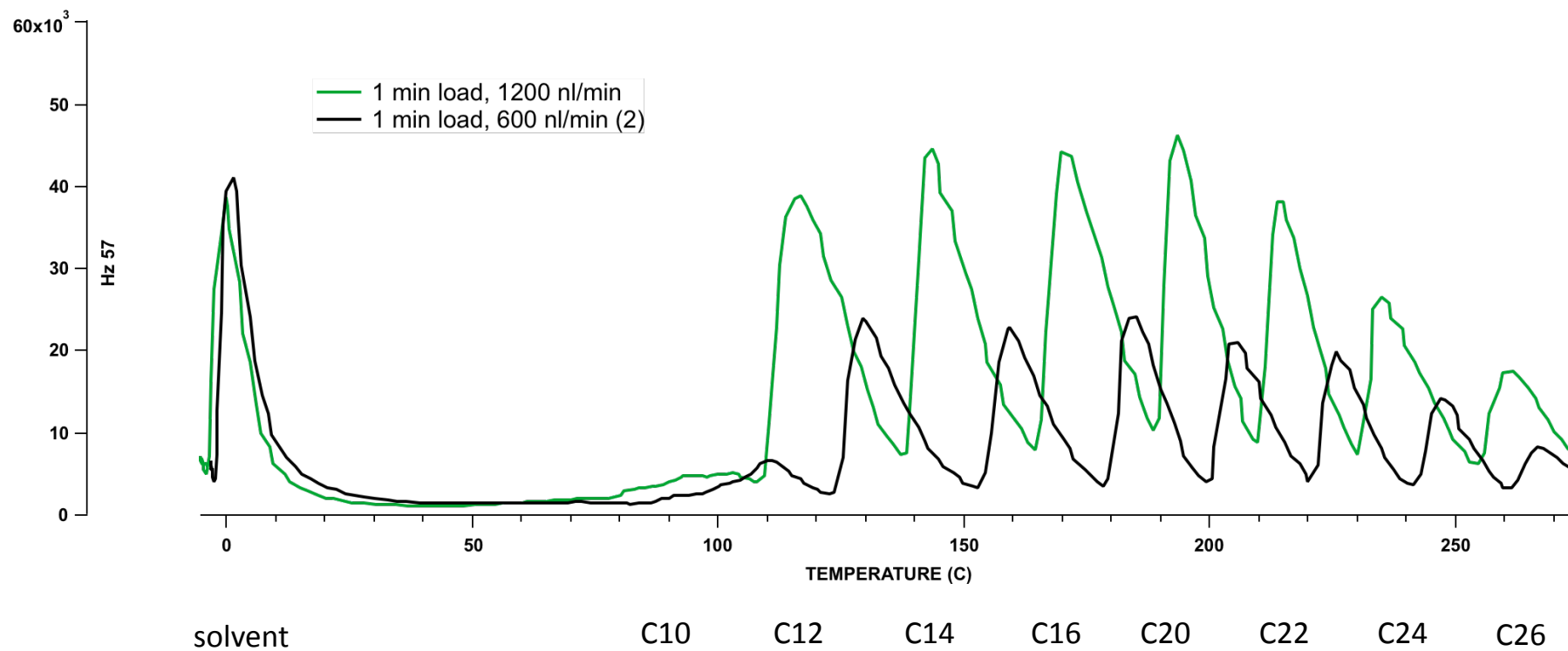
Volatility-resolved measurements

Volatilized C10-C30 alkanes in gas phase



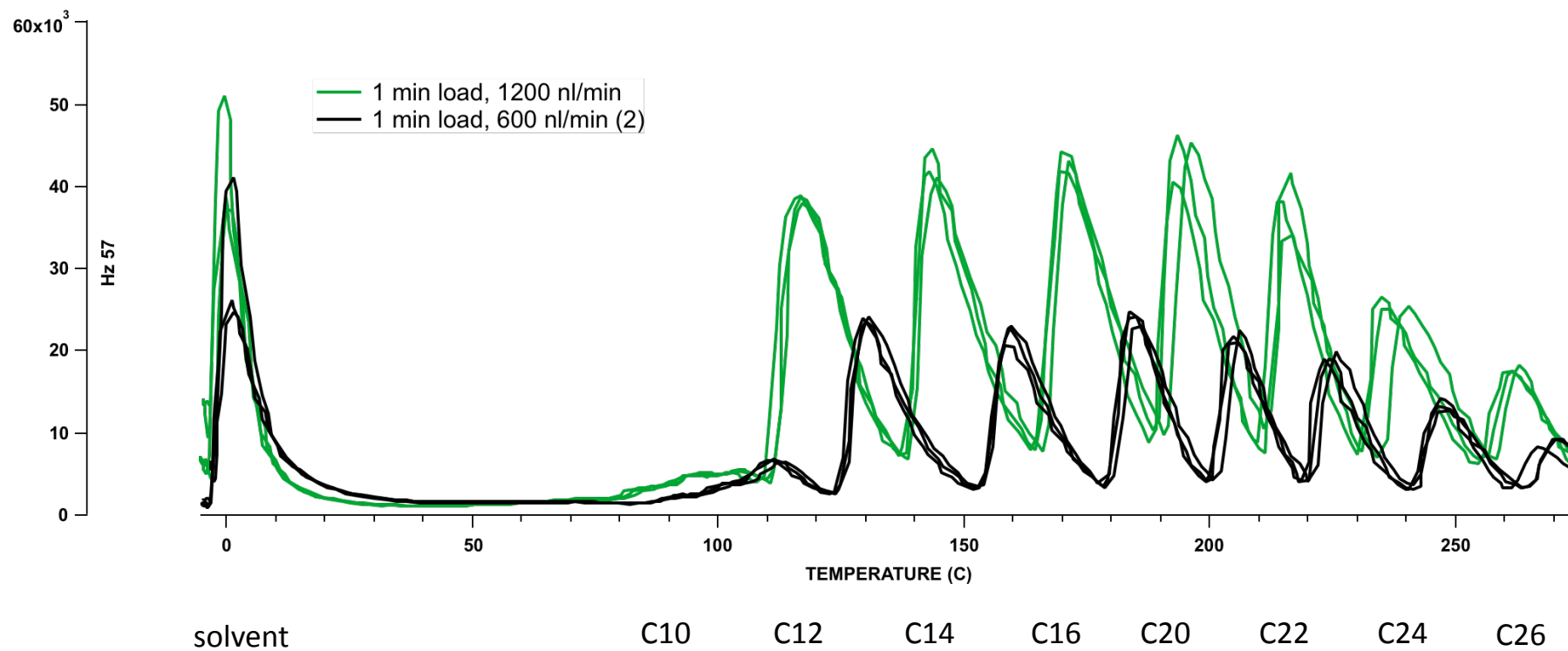
Volatility-resolved measurements

Volatilized C10-C30 alkanes in gas phase



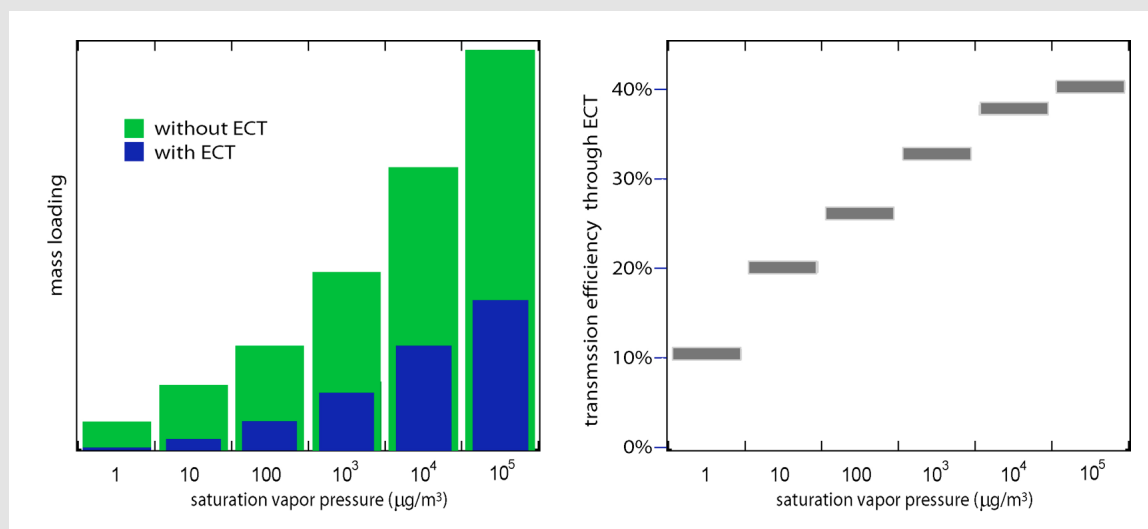
Volatility-resolved measurements

Volatilized C10-C30 alkanes in gas phase



Objective 2: measurements of LVOCs from engines

LVOCs before and after emissions control technology:



Function of

- after-treatment technology: **DPF**, SCR, etc.
- engine type: **heavy-duty diesel**, spark ignition, HCCI
- engine load/cycle (25%, 50%, 75%, 100%, DPF regeneration)
- fuel (diesel, biodiesel, F-T)

Engine lab studies



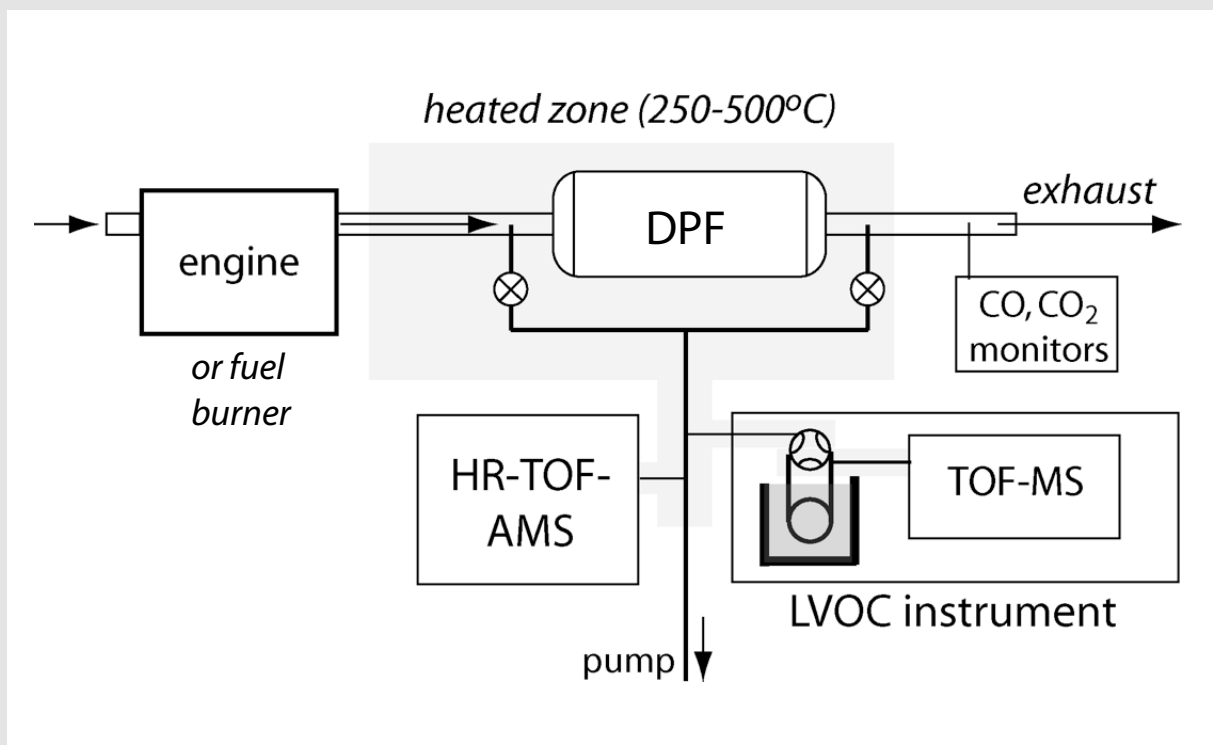
SLOAN AUTOMOTIVE LABORATORY

Founded in 1929 (grant from Alfred P. Sloan, Jr., GM CEO)

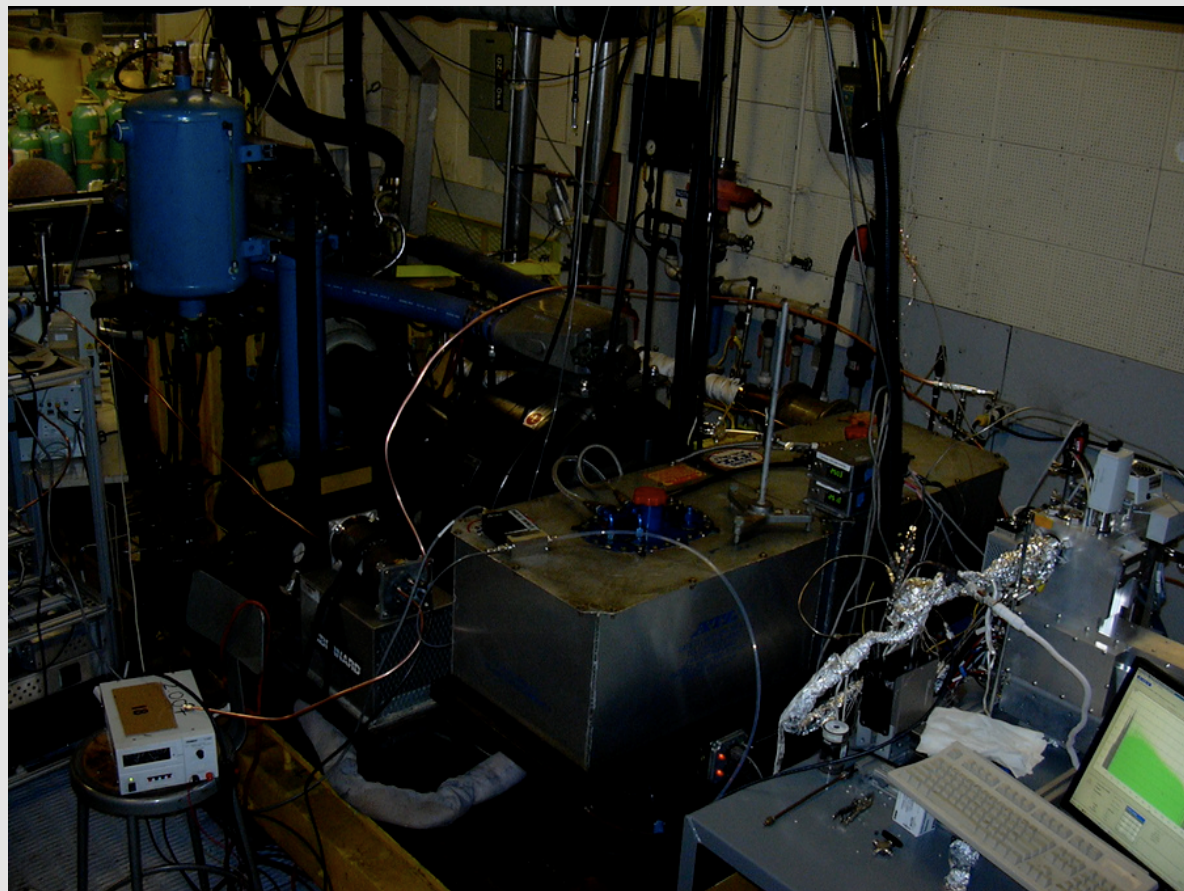
Laboratory objective: "To contribute to future developments in automotive technology through fundamental and applied research on propulsion technology and fuels."

Collaboration: Victor Wong, Alex Sappok

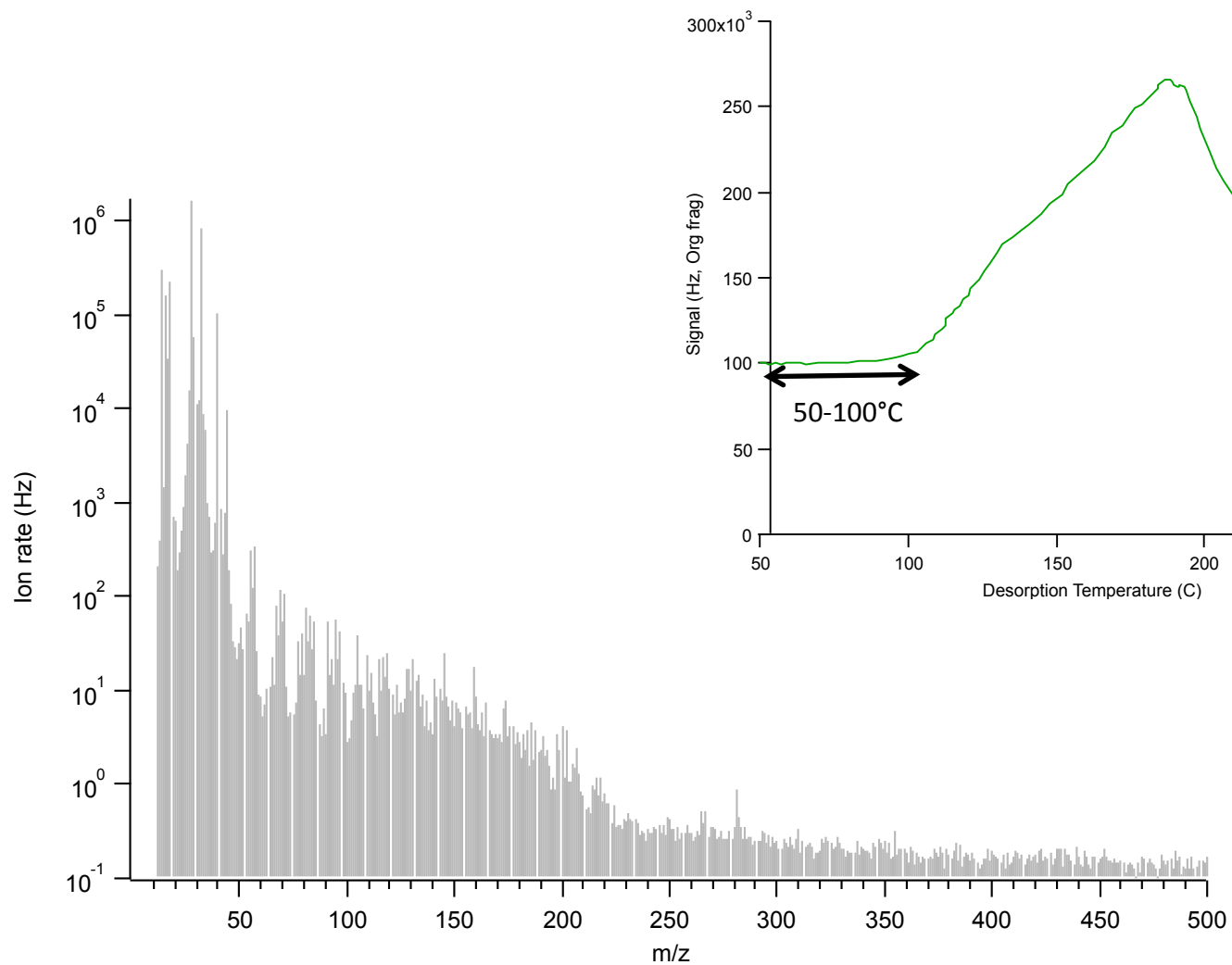
Experimental setup: Schematic



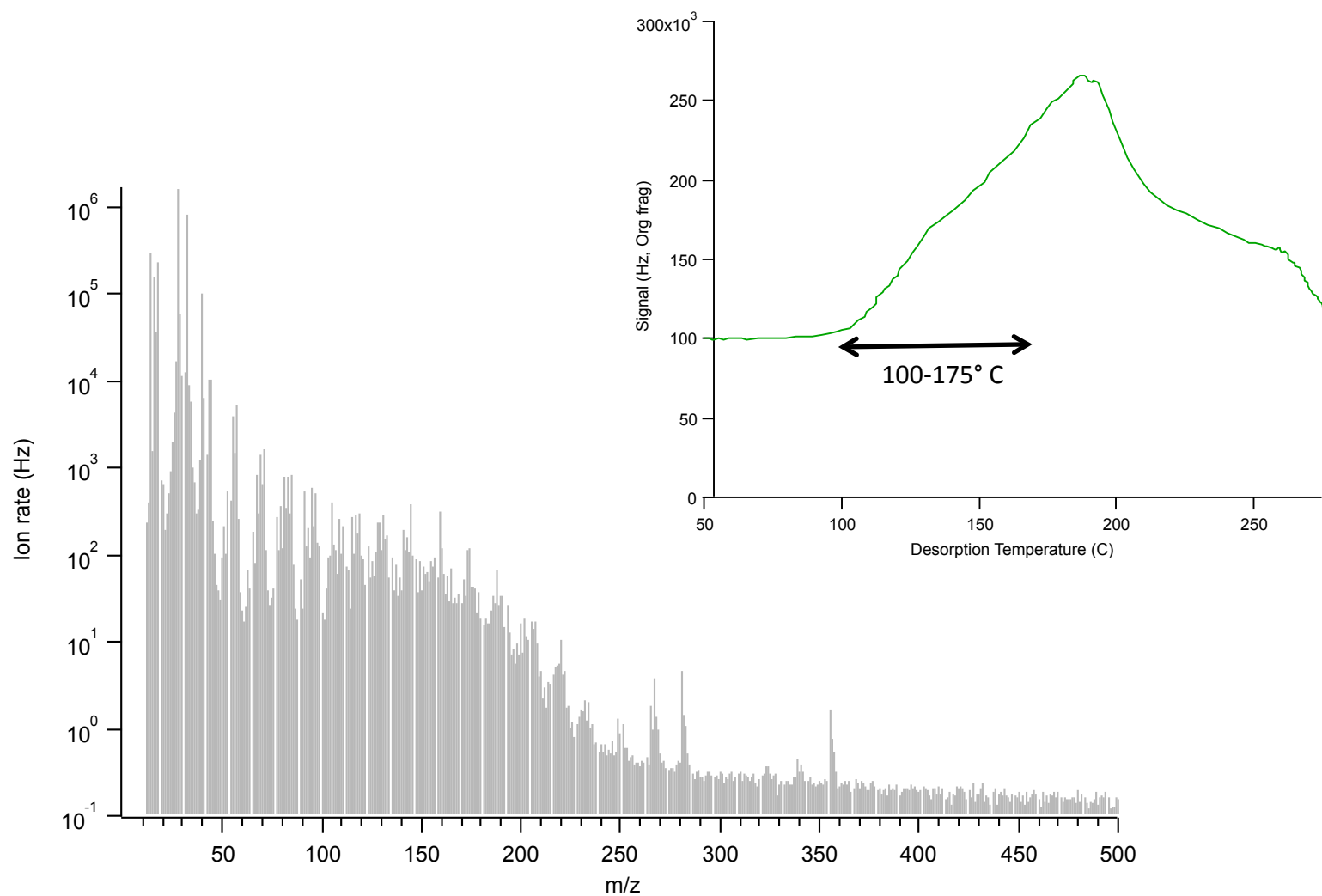
Experimental setup: Reality



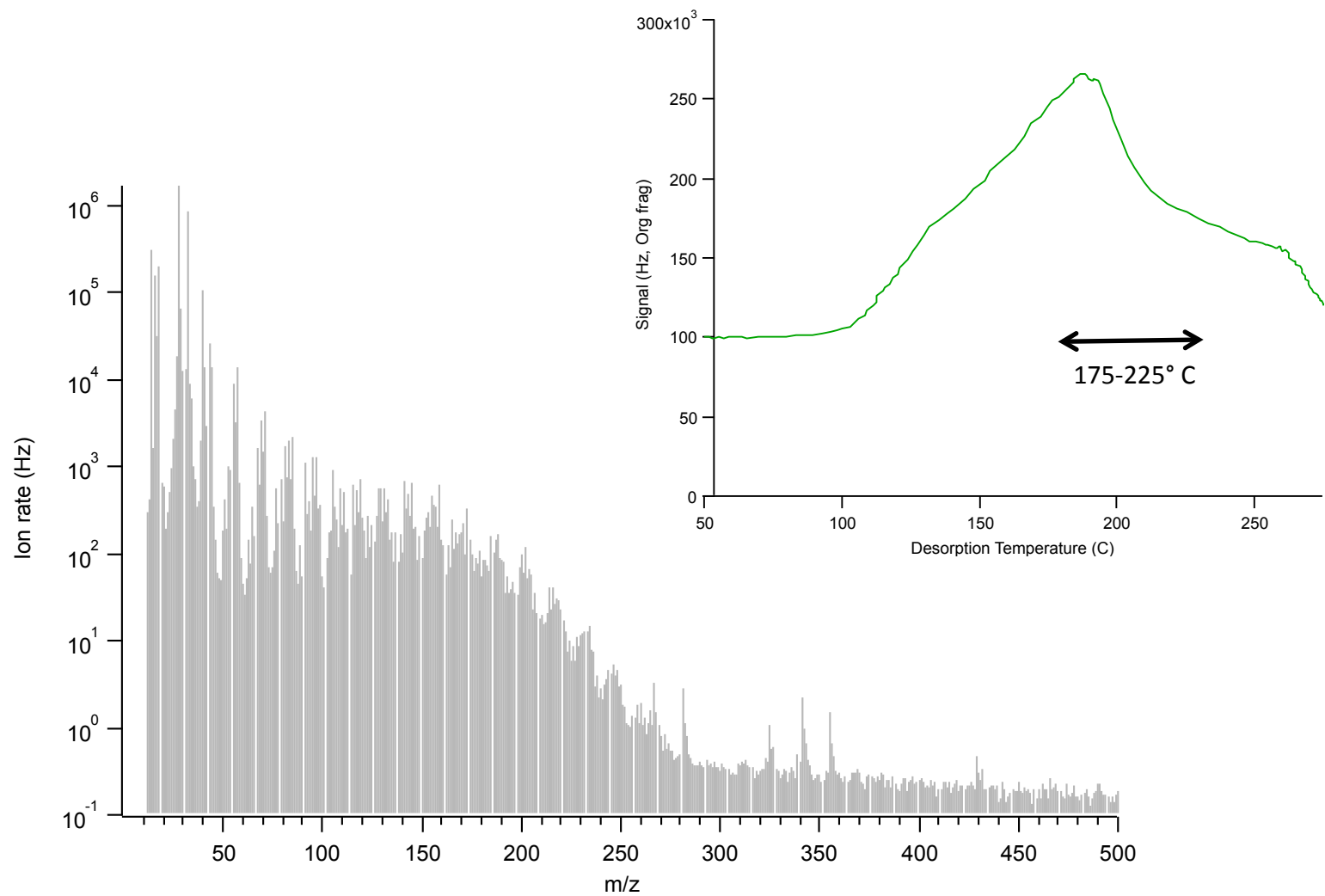
Volatility-resolved LVOCs



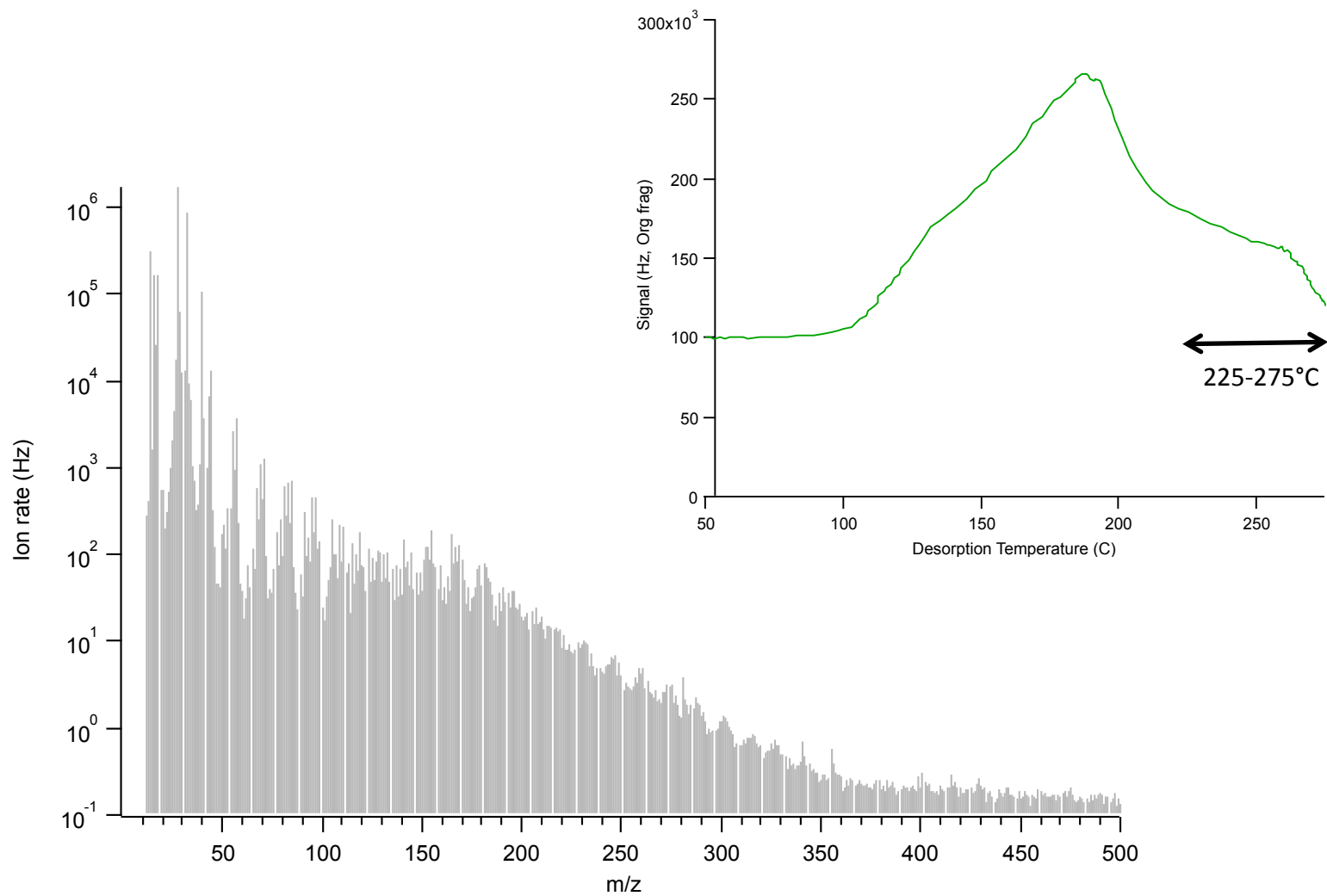
Volatility-resolved LVOCs



Volatility-resolved LVOCs



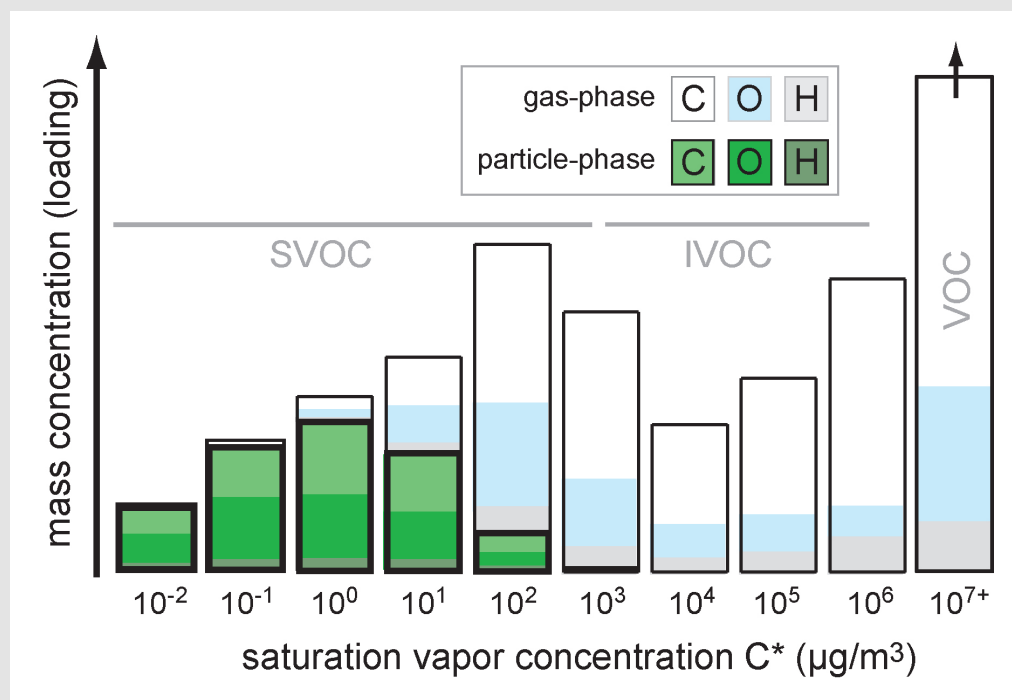
Volatility-resolved LVOCs



Objective 3: Ensemble emissions profiles

From laboratory data, can determine key characteristics of emitted LVOCs *as a function of volatility*:

- mass loadings (emission indices)
- elemental ratios (O:C, H:C)
- aromatic vs. aliphatic character
- approximate carbon number?



Objective 4: Field measurements

roadside measurements of LVOCs, to measure bulk emissions from in-use vehicles

- Aerodyne mobile lab: instruments for CO, CO₂, VOCs, OA, BC
- LVOC instrument closes major gap in these measurements: *all* emitted carbon

Real driving conditions vs. laboratory simulations

Gas-particle partitioning