Particle Sampler for On-Line Chemical and Physical Characterization of Particulate Organics

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Organic Aerosols

- Sources
  - POA, Primary organic aerosol, vehicles, factories, biomass burning, etc.
  - SOA, Secondary organic aerosol, photochemistry, gas phase precursors.

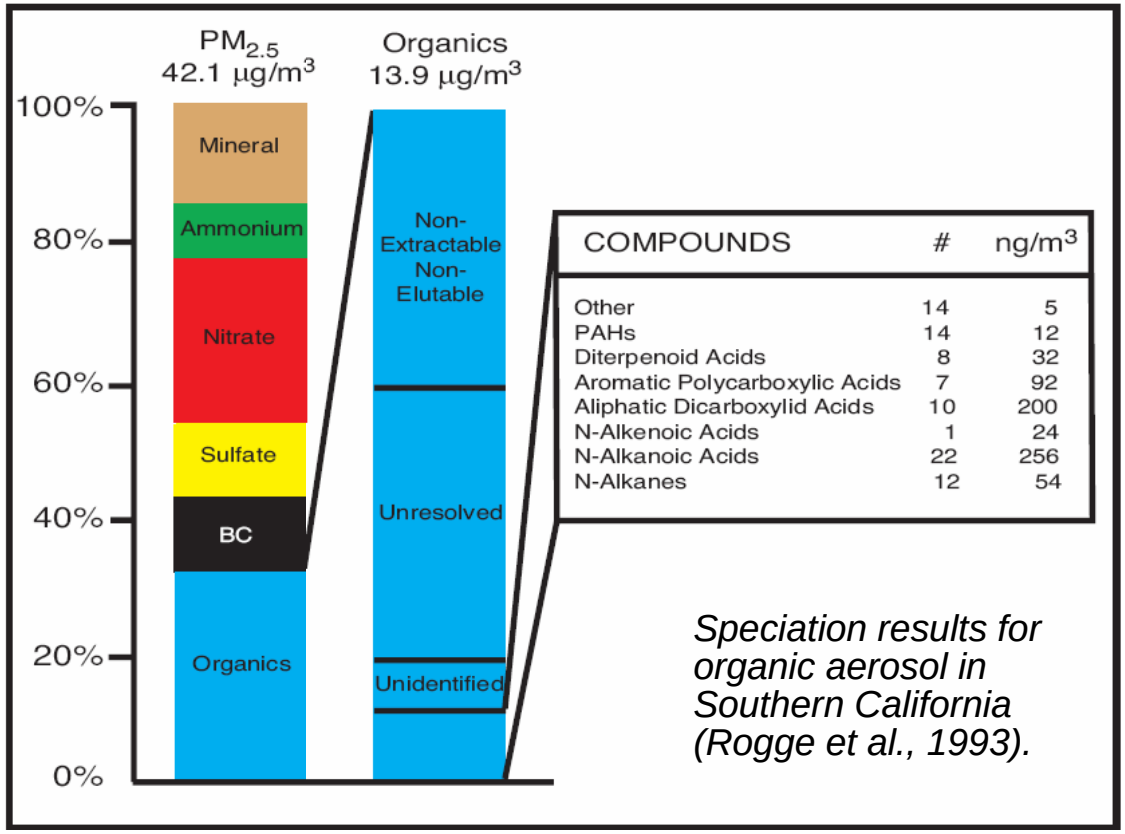
- Can impact
  - Health effects
  - Air quality/visibility
  - Climate change

How much do we know about the organic fraction of ambient aerosol?

- Can be a significant fraction of total aerosol mass.
- Complex mixture of many individual compounds.
- Advances in understanding depend on faster real-time characterization methods.
- There is a trade off between ability to chemical speciate and measure the total aerosol mass.

Filter Based Methods
Organic Aerosol Composition

- *GC-MS of extracted organics.*
- *Identify hundreds of individual molecules, useful as tracers for primary emissions.*
- *Only 10% or so of total organic mass characterized.*
- *Long sampling times, 6-24 hrs.*

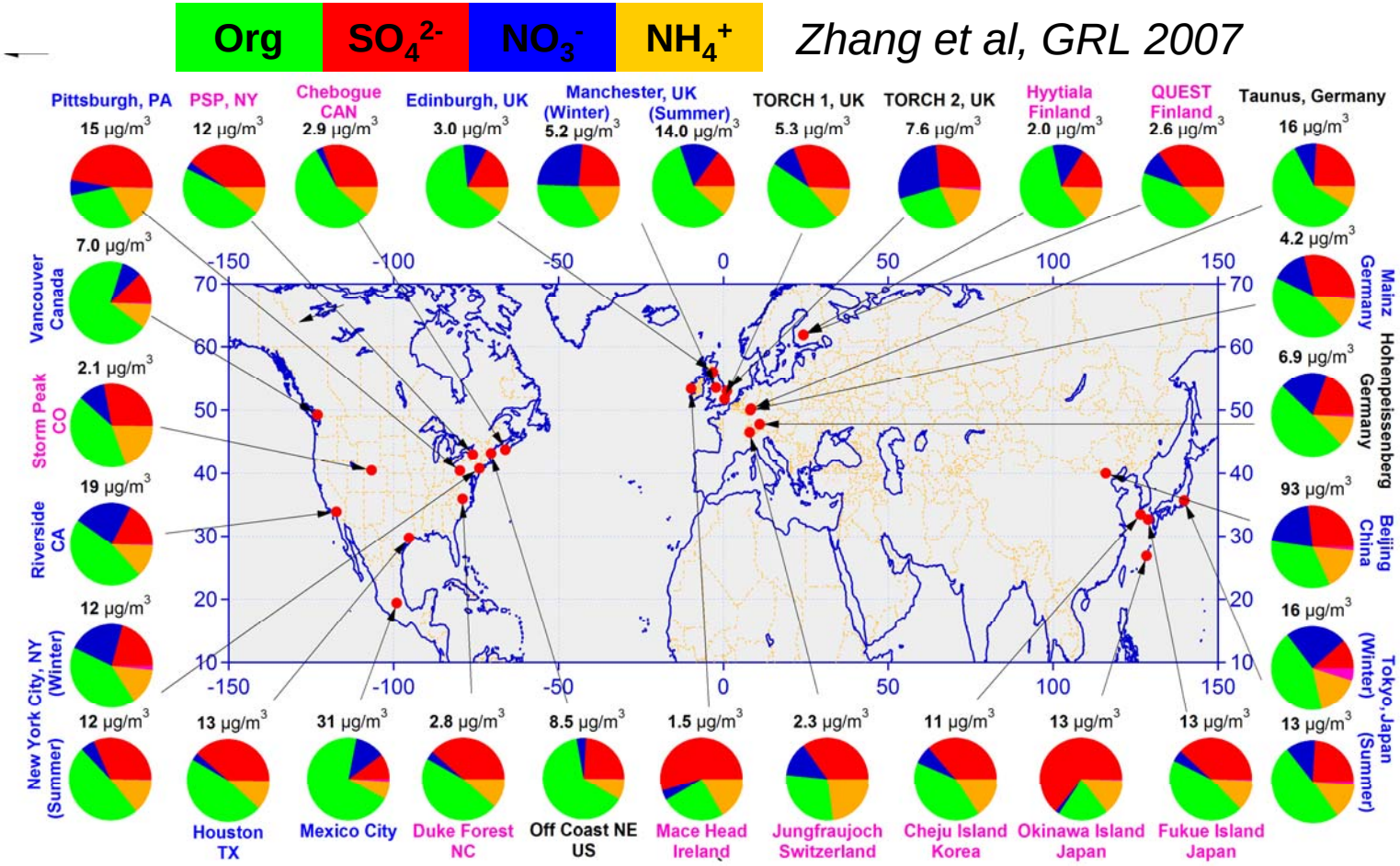


Speciation results for organic aerosol in Southern California (Rogge et al., 1993).

High post collection analysis costs

Aerosol Mass Spectrometer Measurements

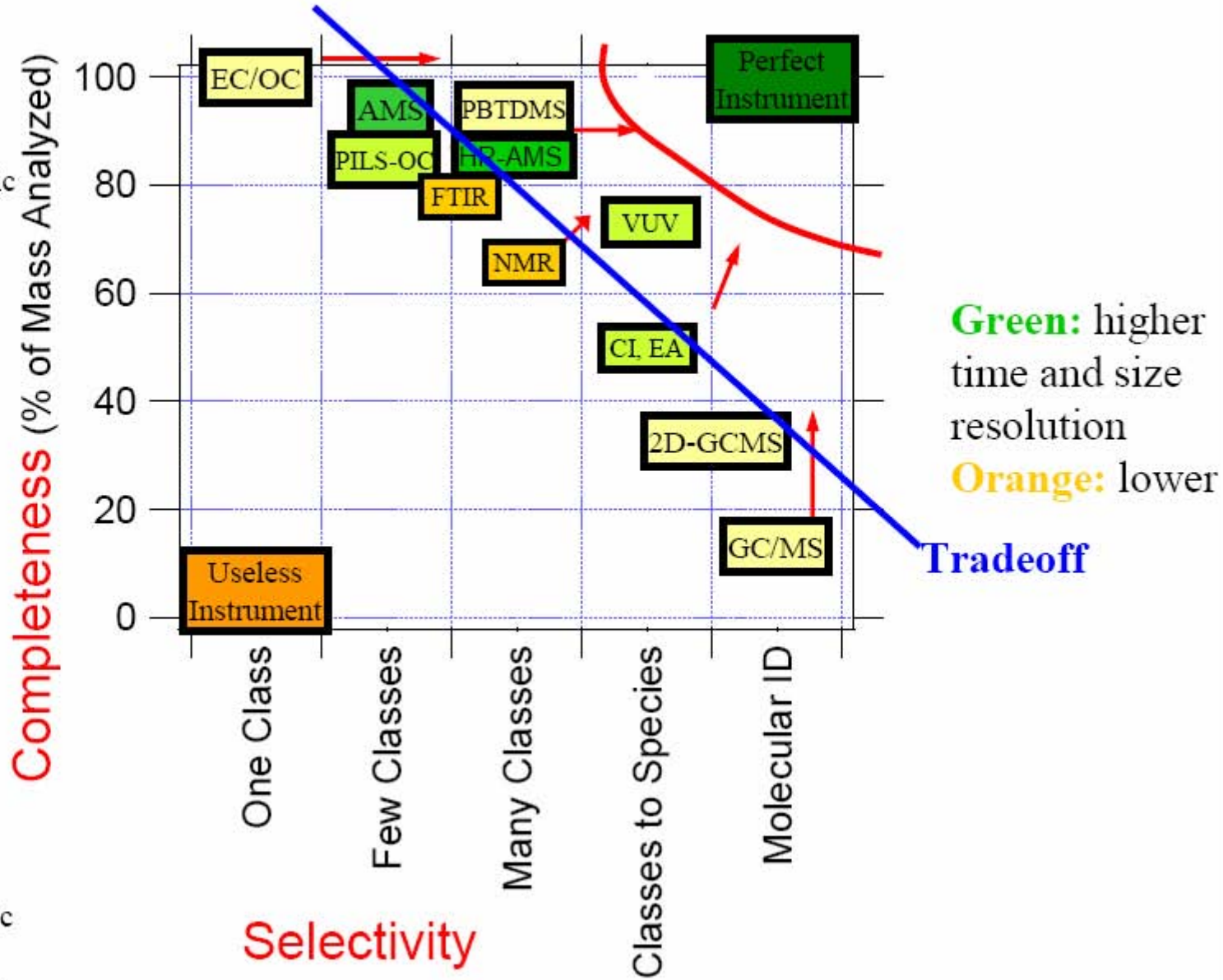
A bulk measurement - limited speciation



Fast time resolution allows correlations with gas phase species…insight into chemical processing.

Organic Aerosol Analysis

AMS=Aerosol Mass Spectrometer
CI=Chemical Ionization
EA= Electron Attachment
EC/OC=Elemental/Organic Carbon
FTIR=Fourier Transform Infrared Spectroscopy
GC/MS=Gas Chromatography/Mass Spectrometry
2D-GCMS=Two-Dimensional Gas Chromatography/Mass Spectrometry
HR-ToFAMS=High-Resolution Time-of-Flight Mass Spectrometer
NMR=Nuclear Magnetic Resonance
PBTDMS=Particle Beam Thermal Desorption Mass Spectrometer
PILS-OC= Particle-Into-Liquid-Sampler for Organic Carbon
VUV= Vacuum Ultraviolet



Produced by J. Jimenez

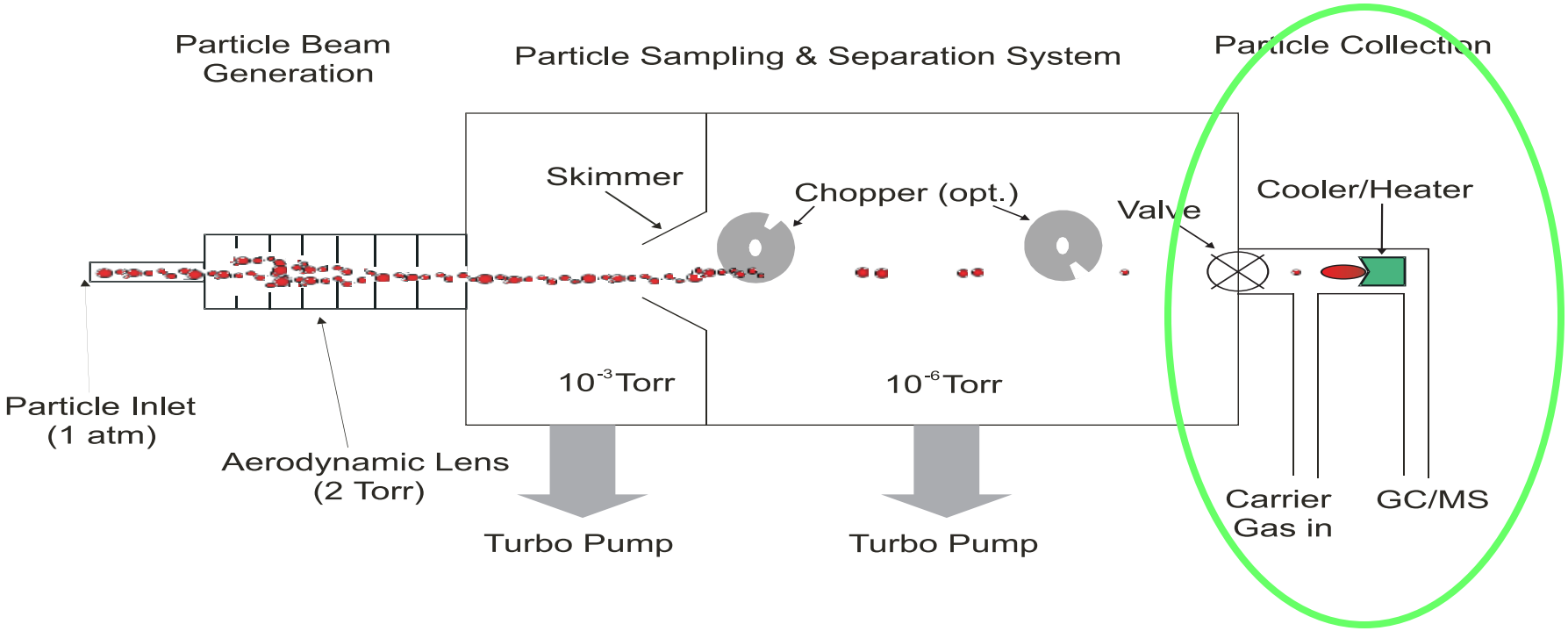
Aerosol Collector Module Concept

- Builds on aerosol lens technology used in the AMS
  - particle concentrator
  - minimize gas phase collection

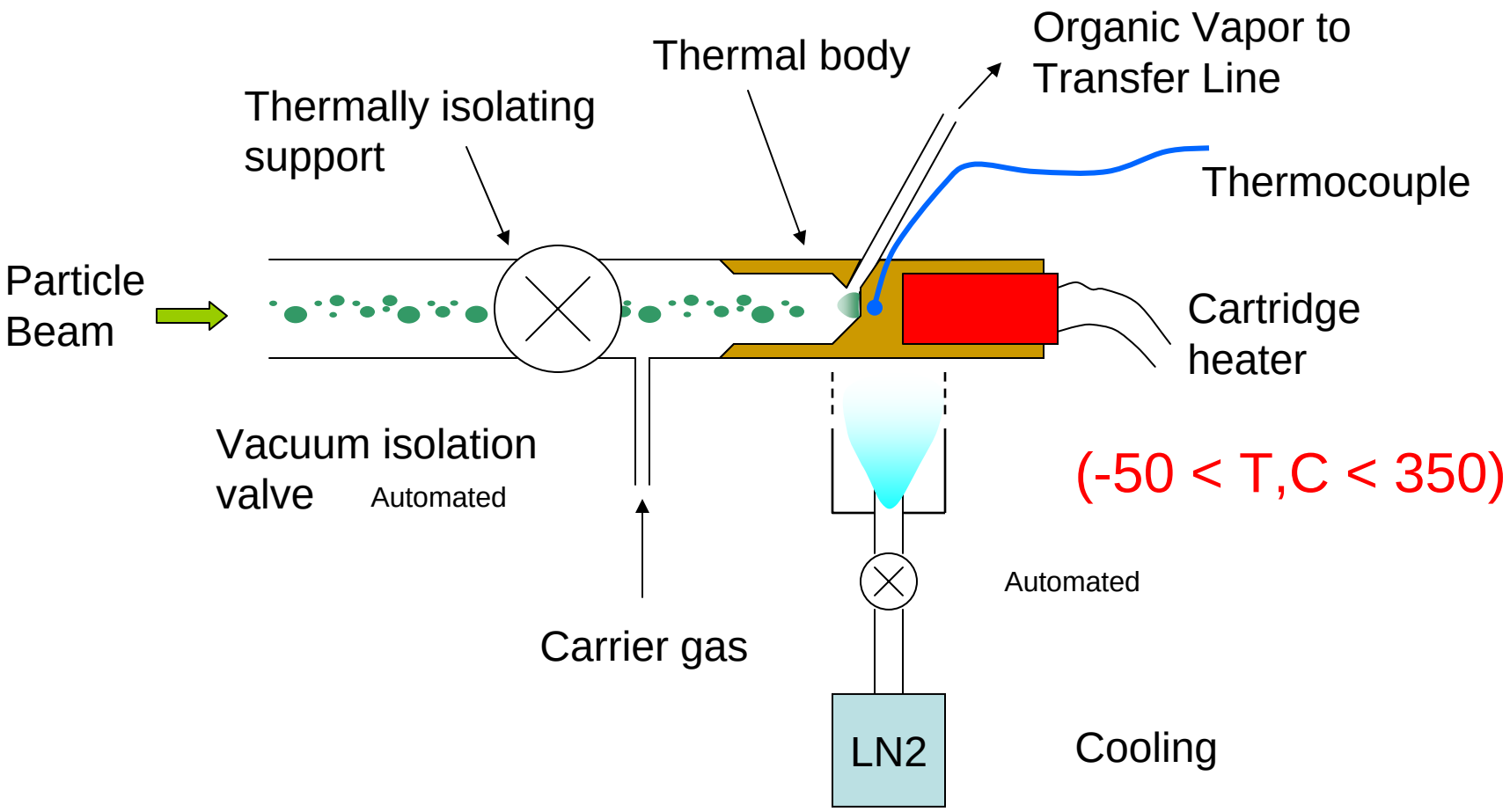
- Size segregated sampling
  – aerodynamic sizing based on particle velocimetry.

- Can couple to existing gas phase detectors
  – GC/MS, GC-GC/MS, PTRMS

Aerosol Collector Module Schematic - ACM

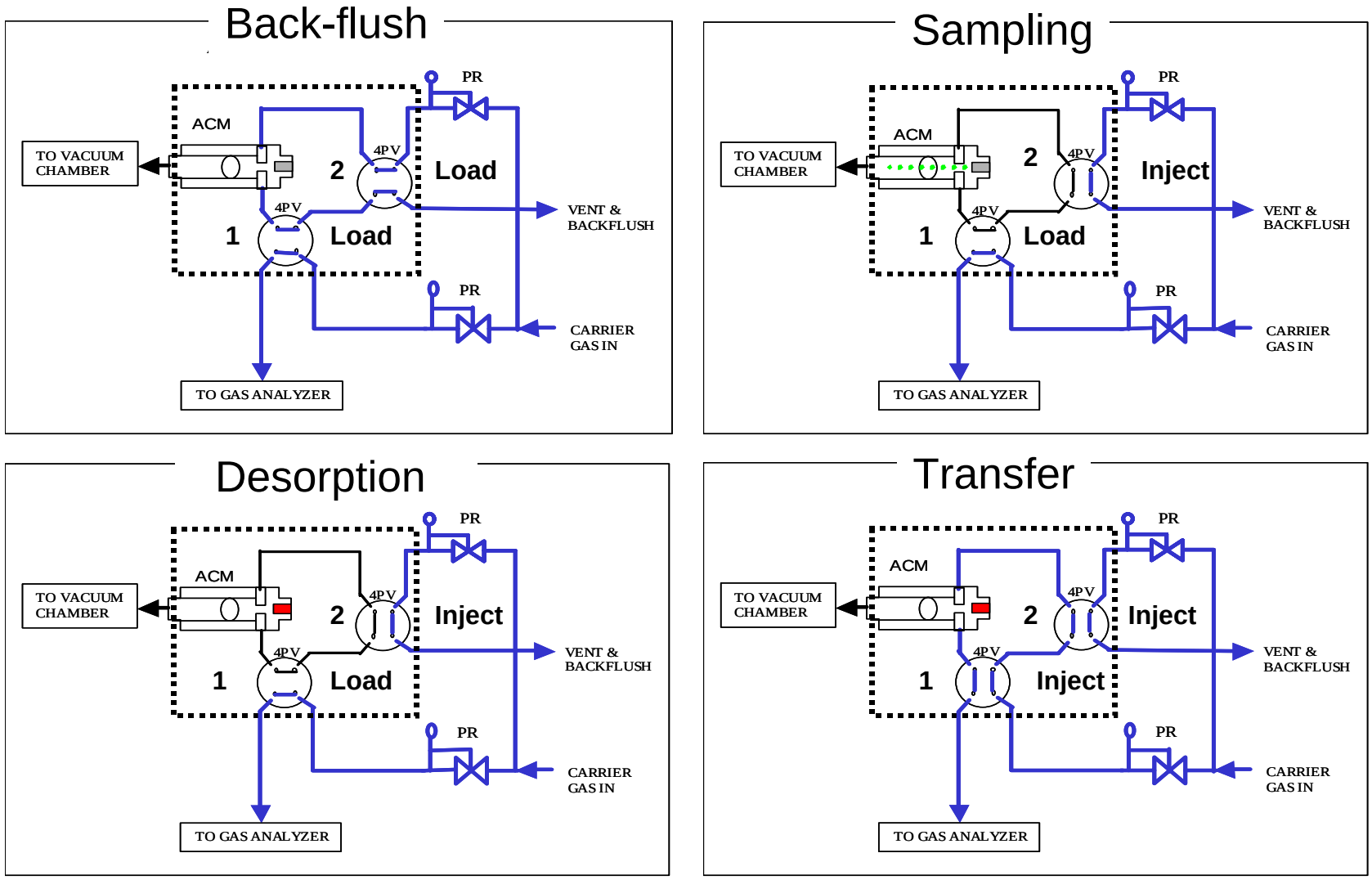


Schematic of Aerosol Collector



Particle collection under high vacuum conditions minimizes gas phase contaminates

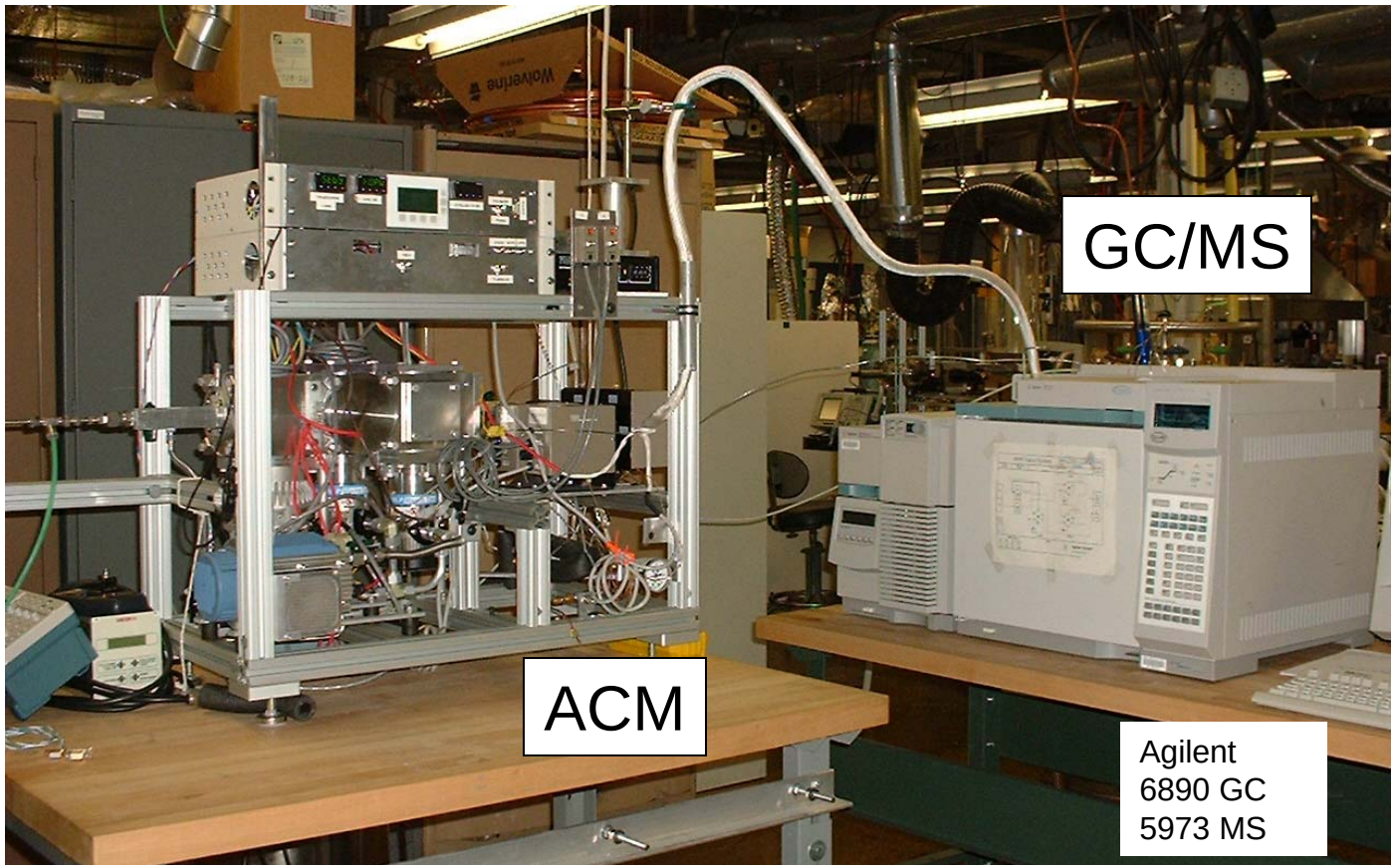
Volatilized Aerosol Sample Transfer System



Two 4-port Valco valves, 350C max temperature

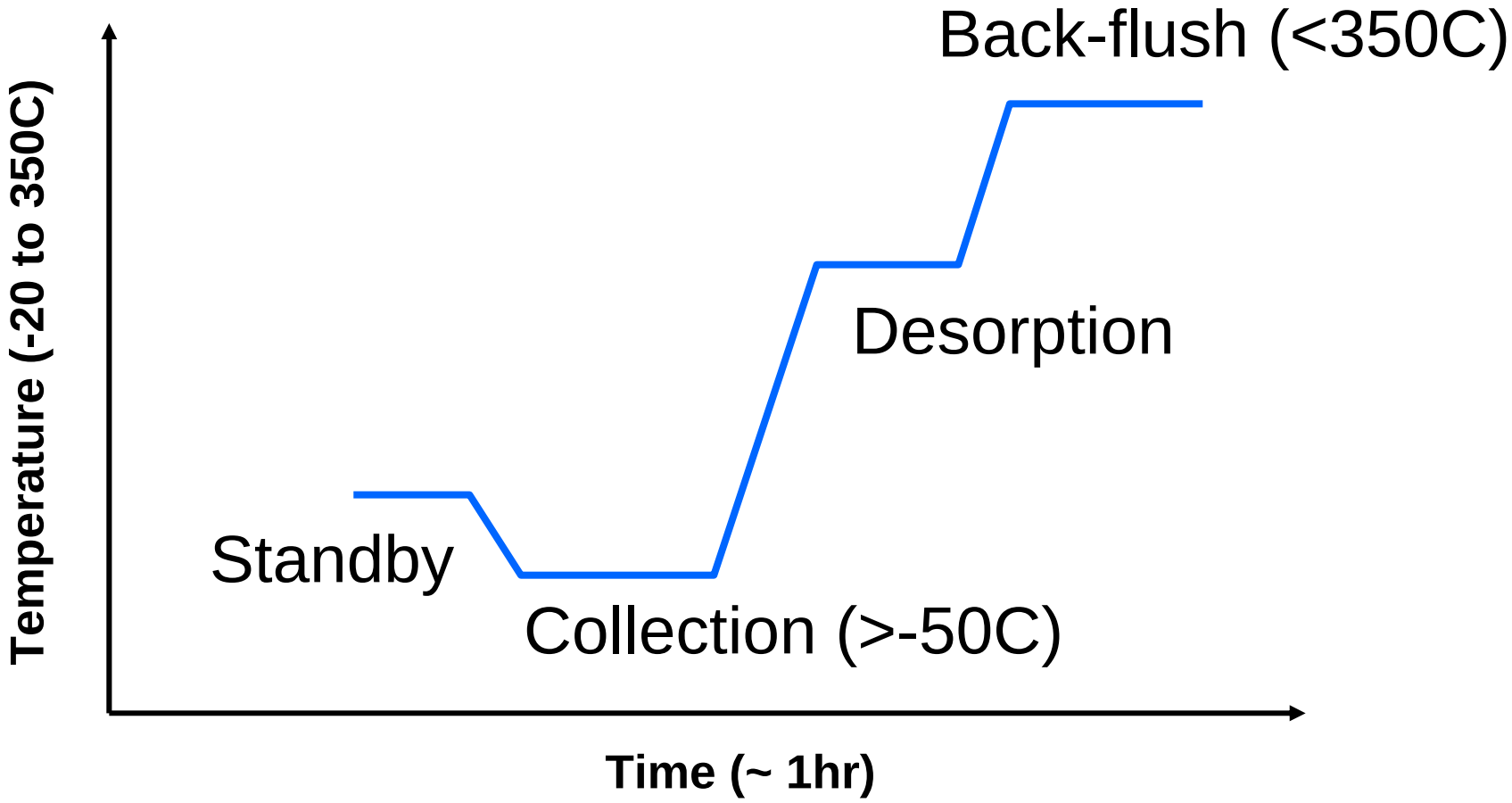
Prototype ACM

Connected to a GC/MS detector



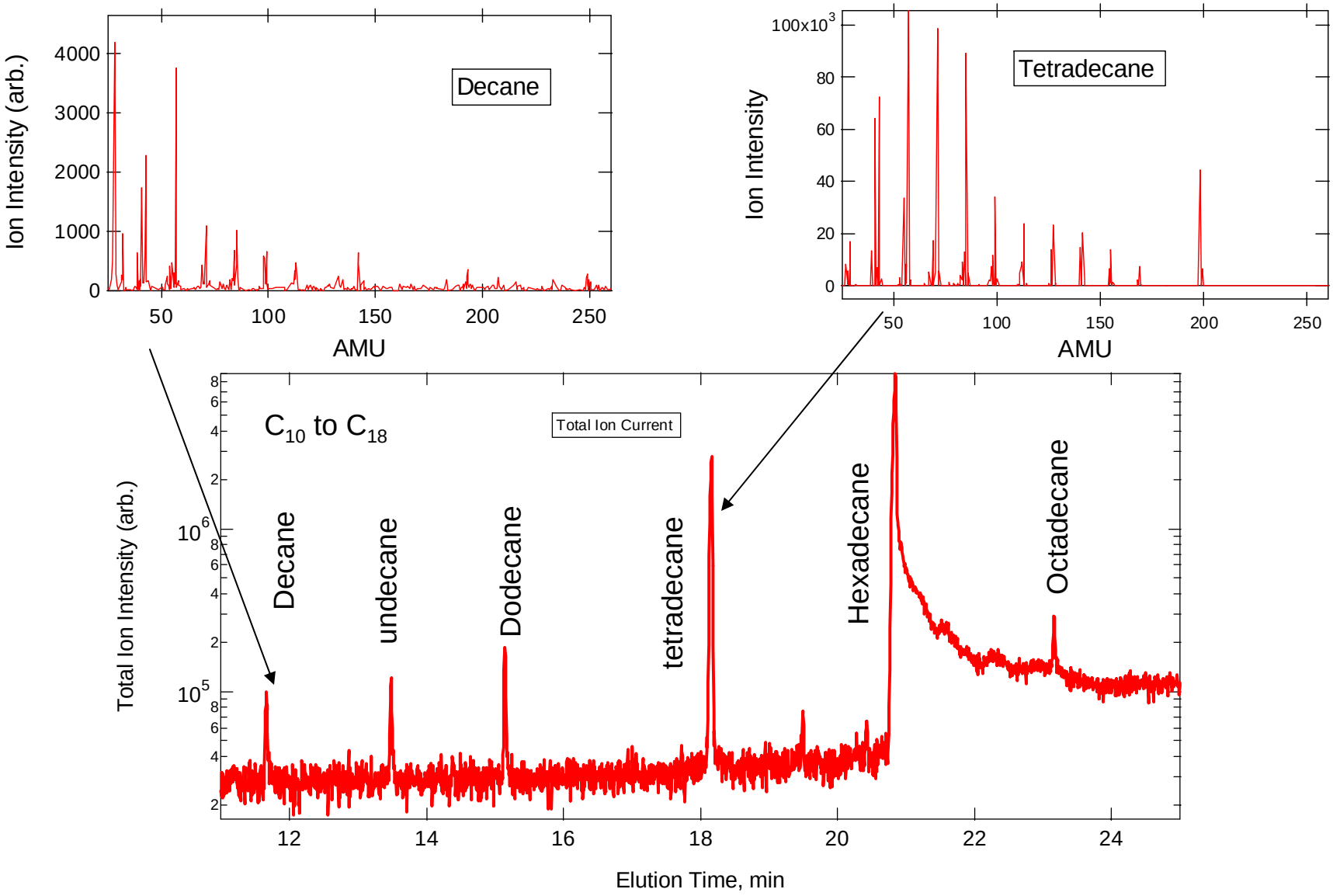
see poster presented by Dahai Tang.

Program Cycle

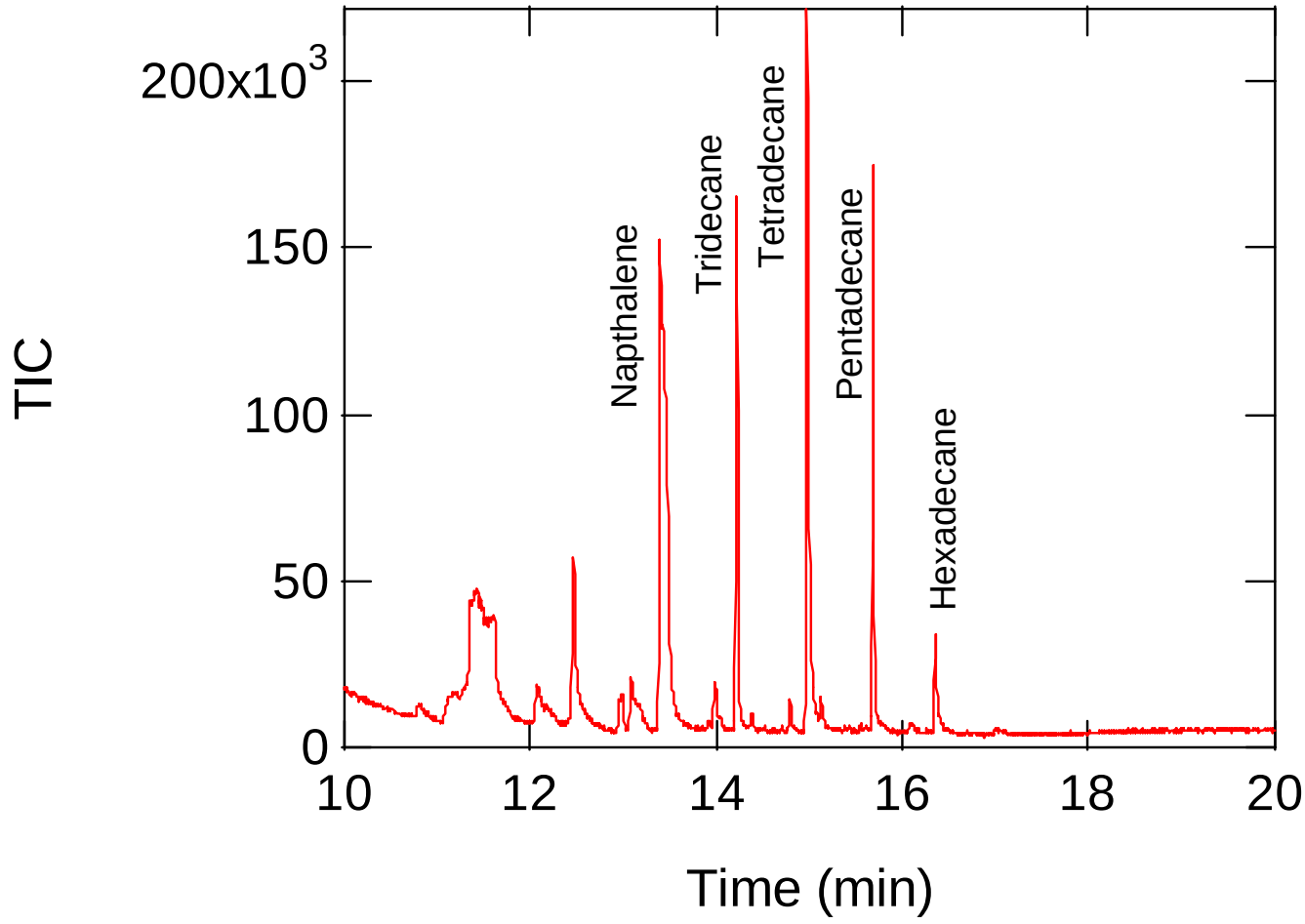


Automated cycle controlled by microcomputer

ACM data from a hydrocarbon standard

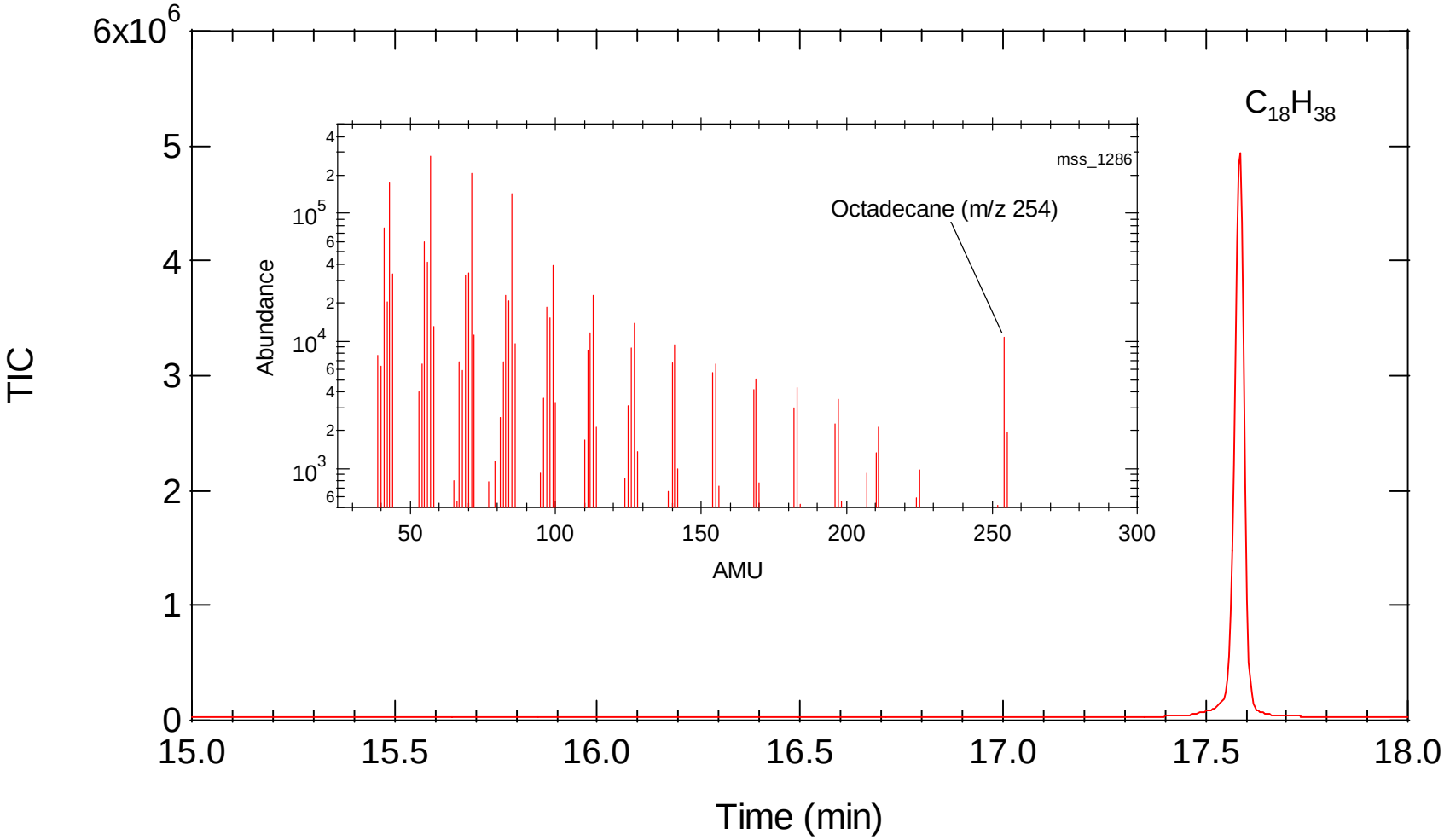


ACM Paraffin Candle Soot Sample

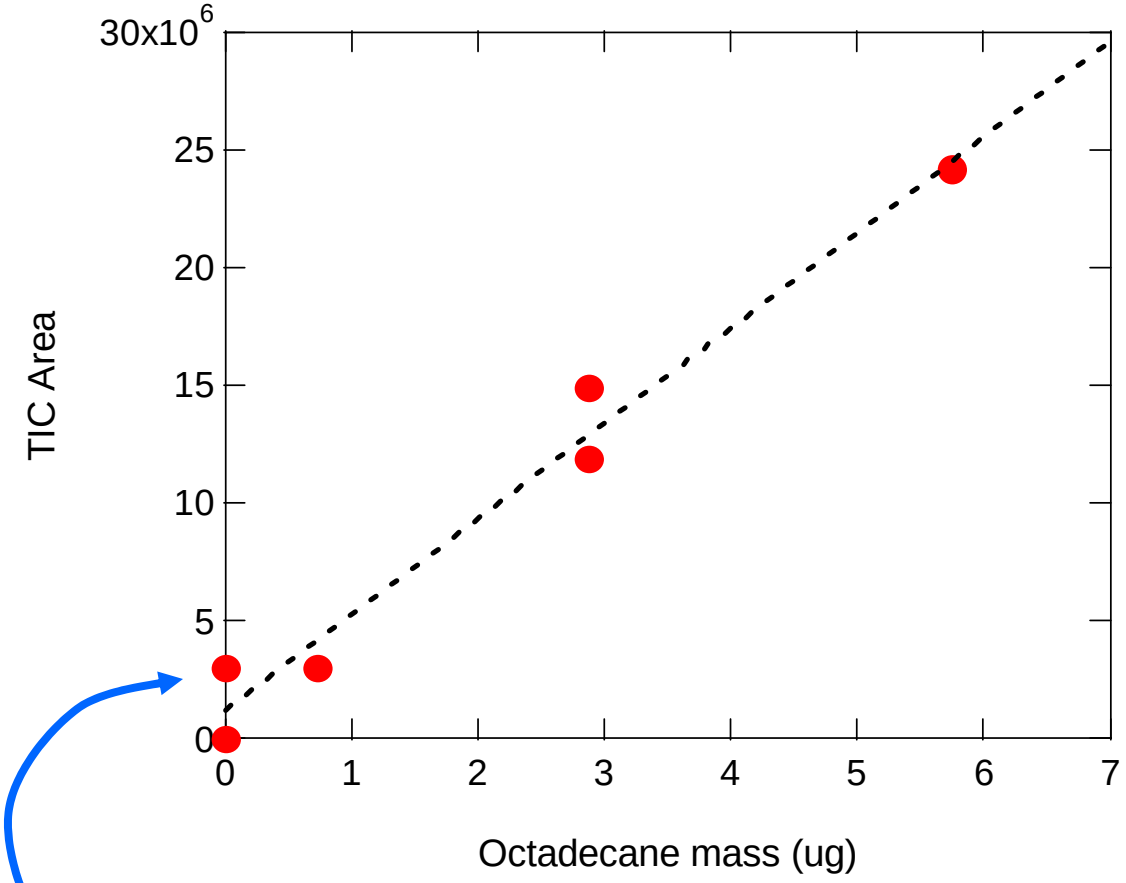


Peak assignments from NIST Mass Spectral Library

Octadecane GC/MS Sample



Detection Linearity

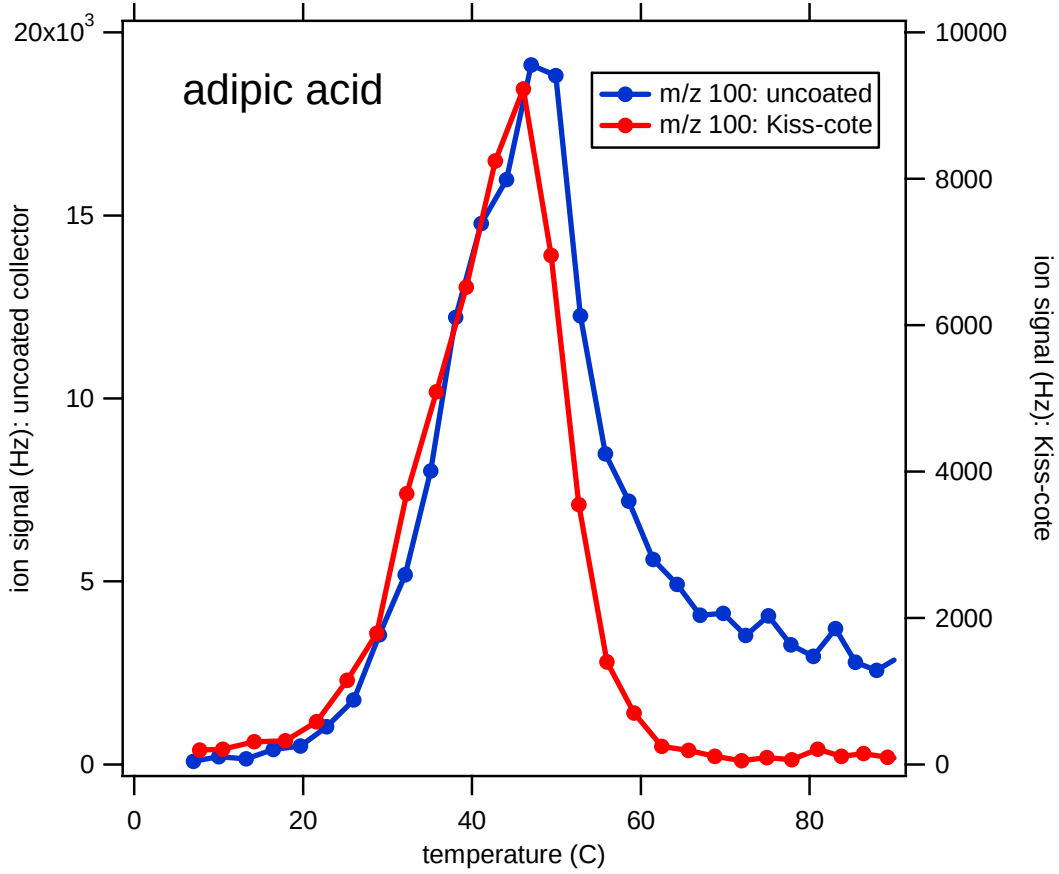


Aerosol loadings generated using DMA and CPC.

Blank/memory effect

Glass coated transfer line and coatings on collector help reduce memory effects, but not eliminated.

Effect of collector coating

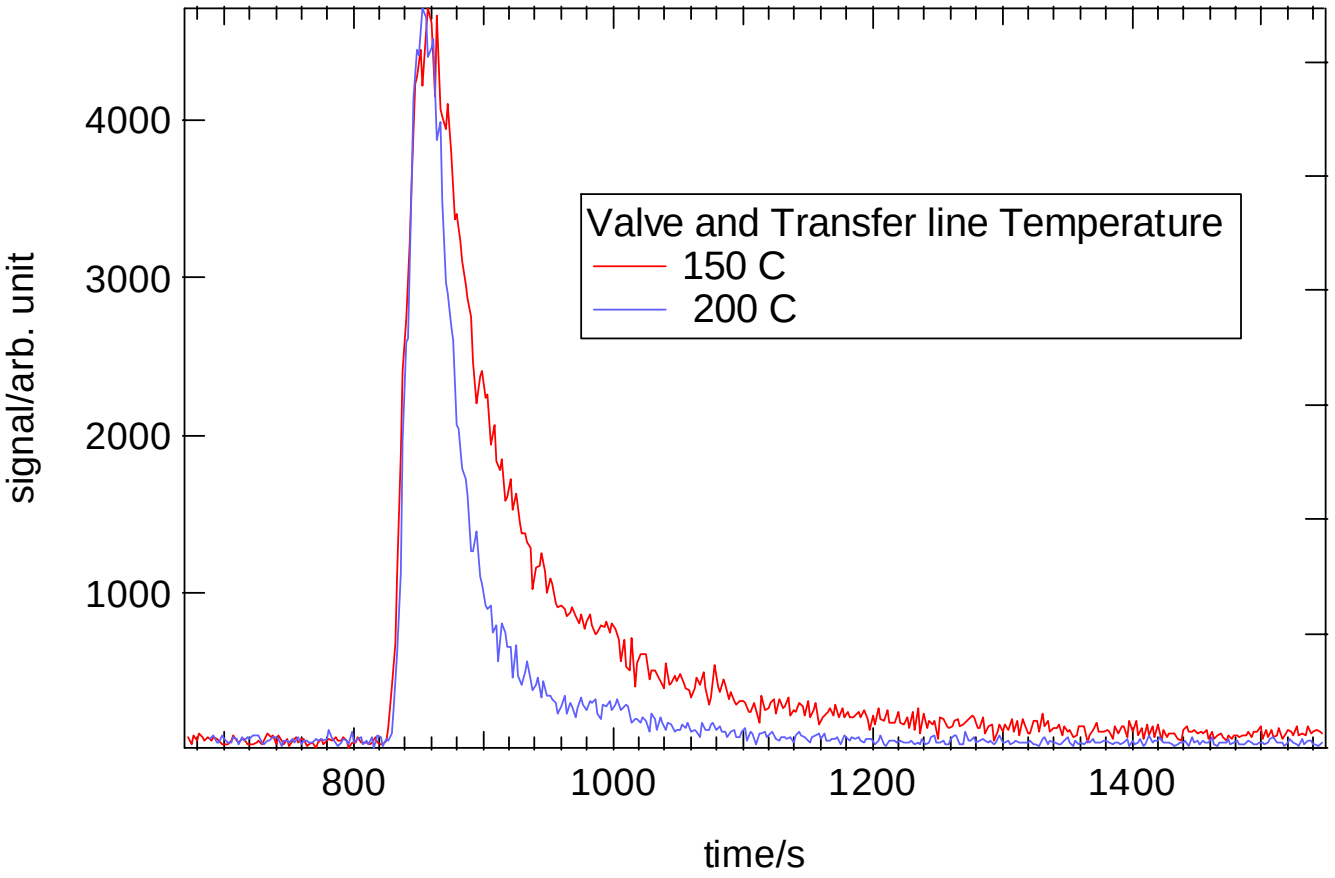


Coating reduces “tailing”

Effect of Temperature on Transfer of Volatilized Sample

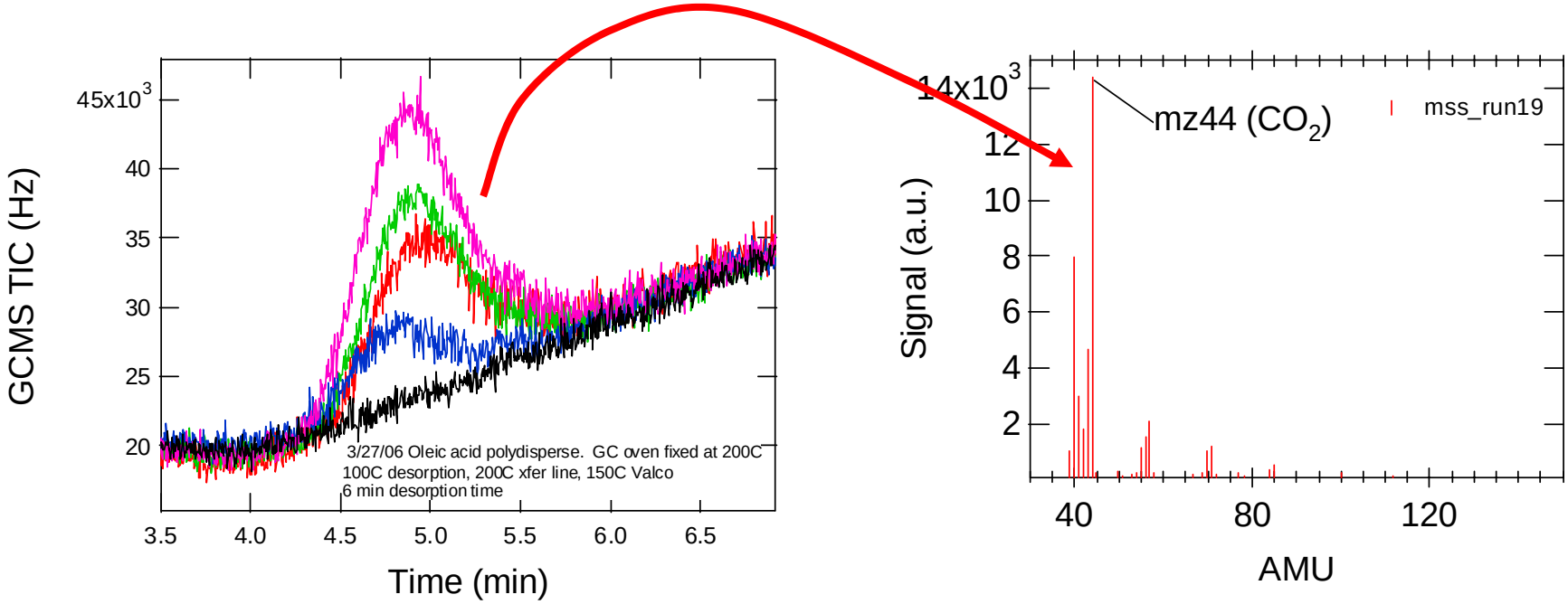
Proton Transfer Reaction Mass Spectrometer (PTRMS)

Motor Oil Sample



Higher transfer line and valve temperatures improve transfer times…*coatings are important*.

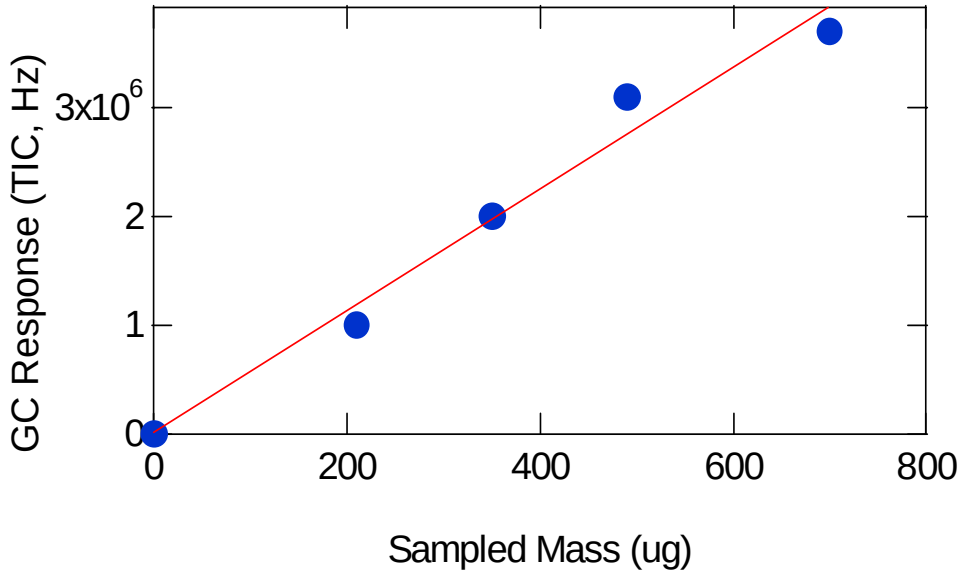
High temperatures can degrade oxidized aerosol



Oleic Acid

$C_{18}H_{34}O_2$

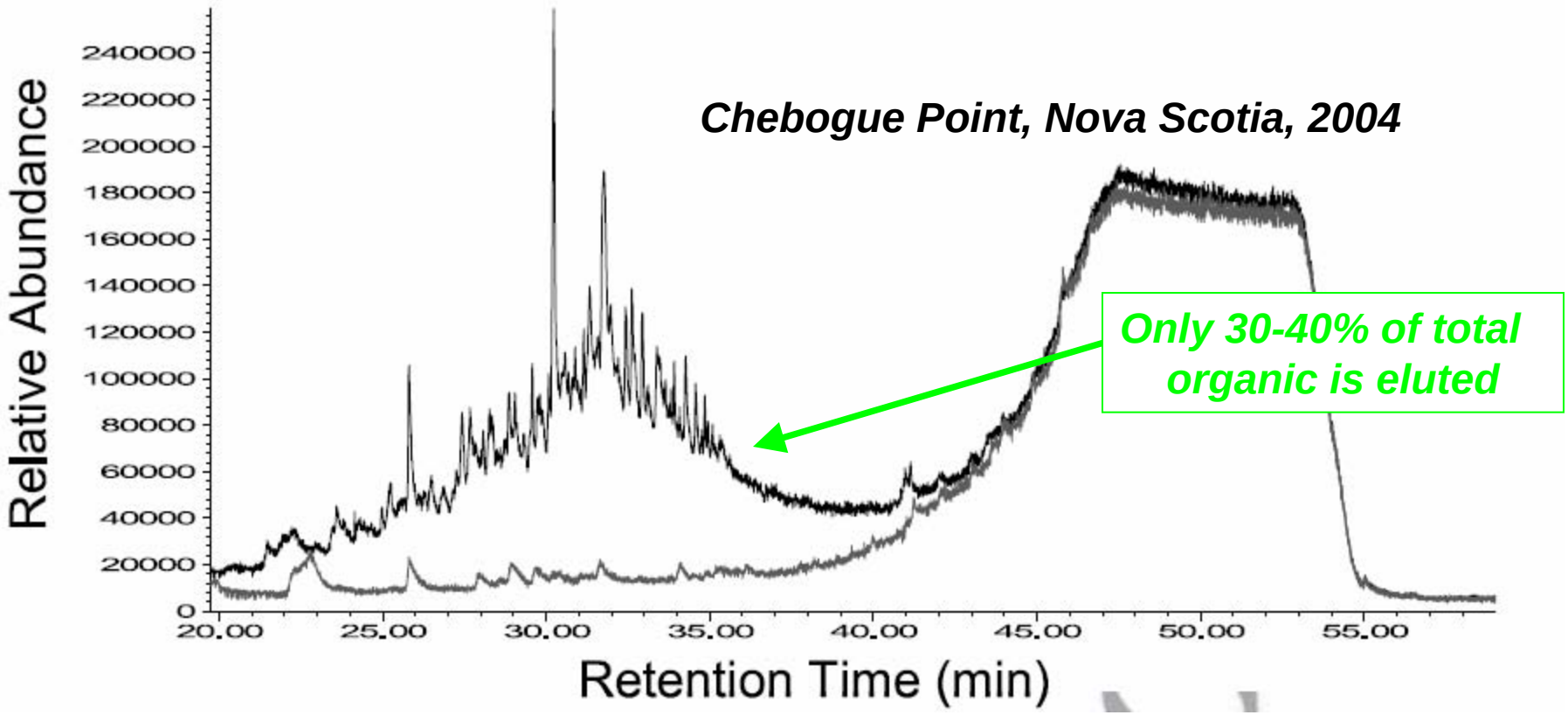
MW 282.47



- *Molecular identification is compromised.*
- *Response is still linear…*

Chemical speciation of organic aerosol during the International Consortium for Atmospheric Research on Transport and Transformation 2004: Results from in situ measurements

Brent J. Williams,[1] Allen H. Goldstein,[1] Dylan B. Millet,[1,2] Rupert Holzinger,[1,3] Nathan M. Kreisberg,[4] Susanne V. Hering,[4] Allen B. White,[5] Douglas R. Worsnop,[6] James D. Allan,[7] and Jose L. Jimenez[8]



TAG: semi-continuous GC-MS of impacted aerosol

Brent Williams, Allen Goldstein, Susanne Hering

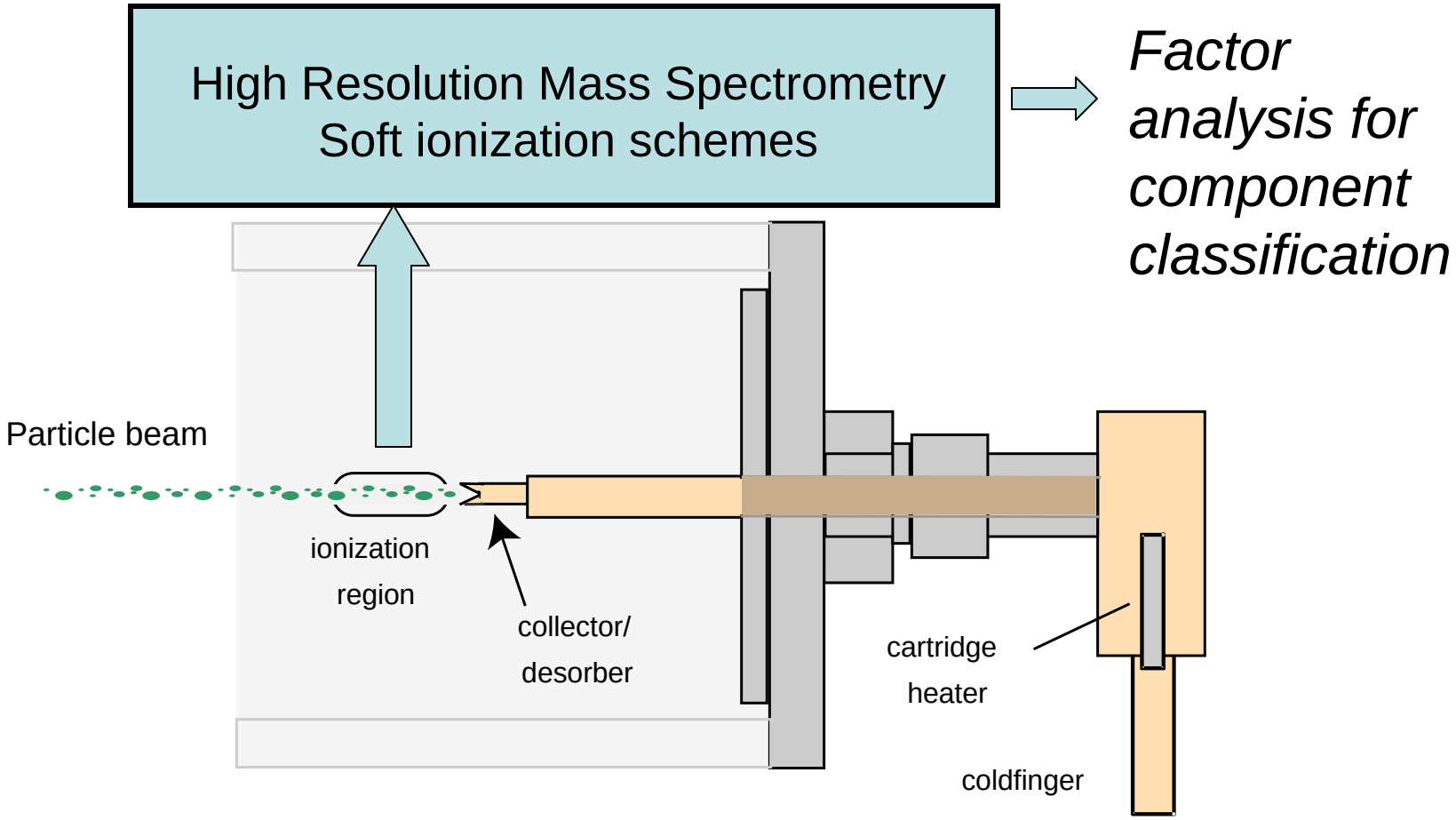
Direct Vacuum Desorption

Aerosol Collection and volatilization directly inside ionizer of mass spectrometer.

- No transfer line issues, minimize thermal degradation.
- No sample dilution, desorb directly into ionization volume.
- Similar to PBTDMS by Ziemann

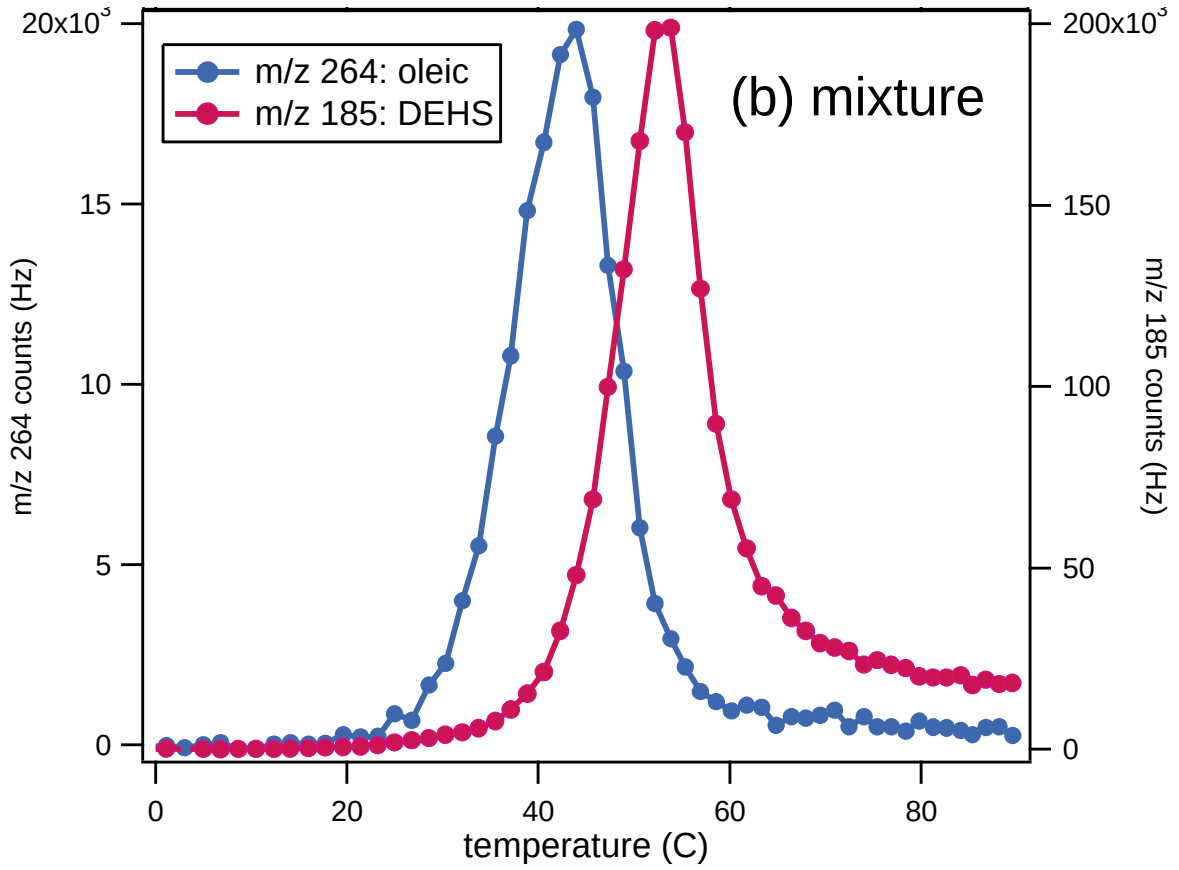
Herbert J. Tobias and Paul J. Ziemann. Compound Identification in Organic Aerosols Using Temperature-Programmed Thermal Desorption Particle Beam Mass Spectrometry. Anal. Chem.1999, 71, 3428-3435.

Direct Vacuum Desorption System



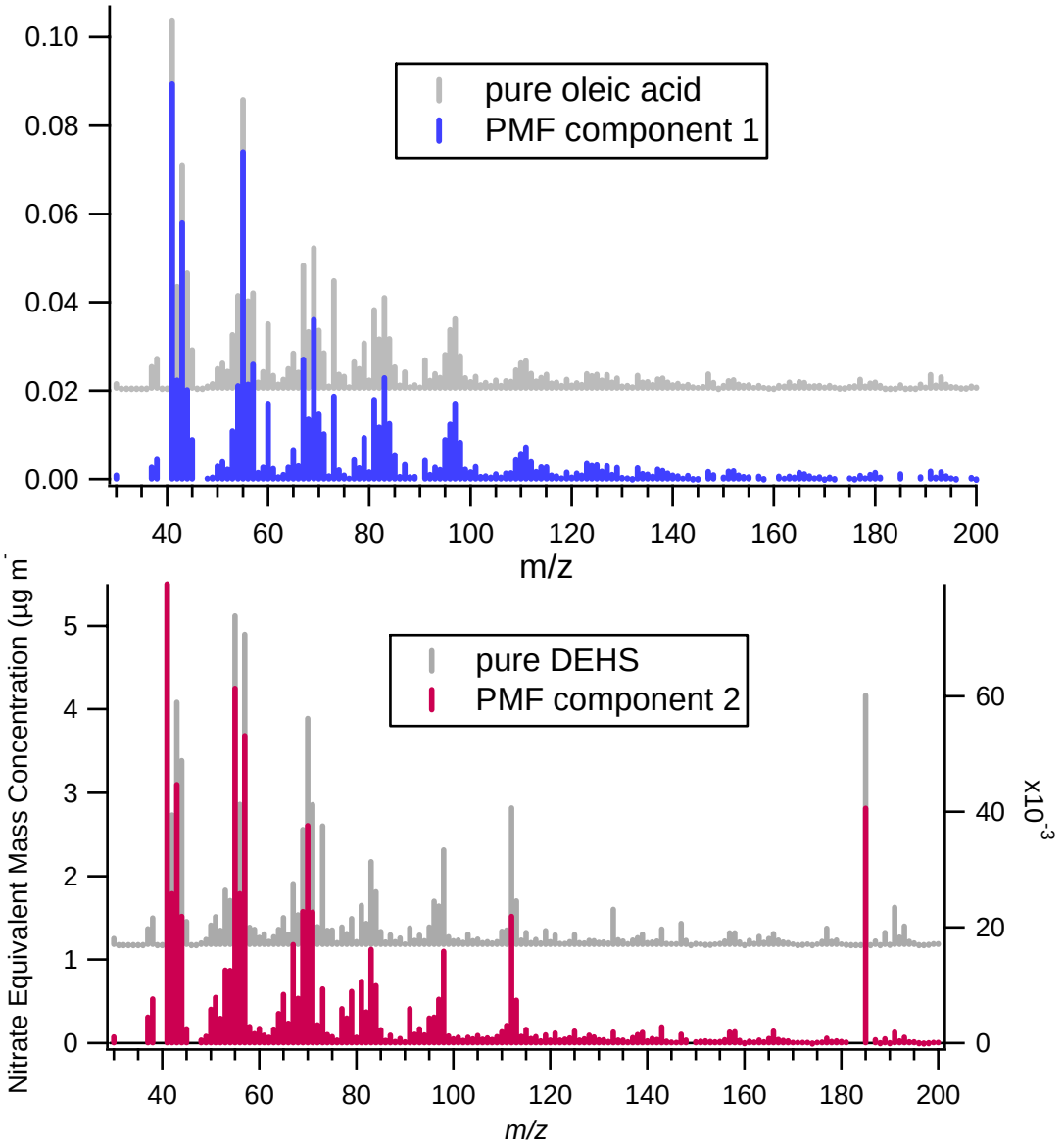
Collaboration with Paul Ziemann, UC Riverside and Tofwerks, Switzerland

Temperature-programmed desorption (TPD): Separation of organics by volatility



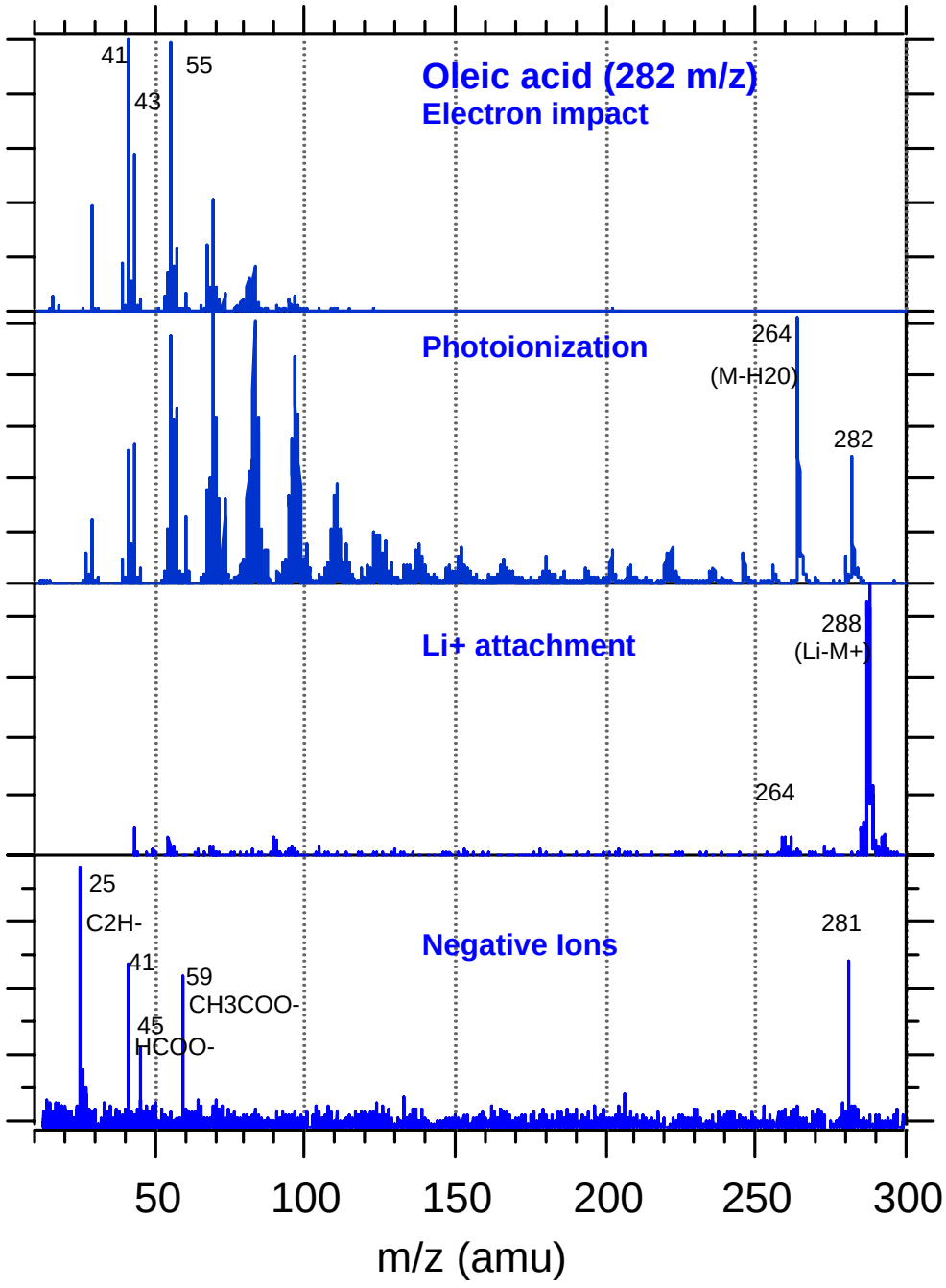
Factor analysis for component classification

- Positive Matrix Factorization - PMF to deconvolve spectra into components.
- Can also be applied to GC/MS spectra.



Soft ionization schemes for improved molecular identification.

Comparison of mass spectra of oleic acid obtained with four different ionization methods.



Summary

- An Aerosol Collector Module was built and evaluated using a GC/MS and a PTRMS.
  - Coatings and transfer lines control throughput and molecular identification, *thermal degradation.*
  - Current detection levels are useful for lab studies.
  - Evaluation is ongoing.
- Direct vacuum desorption
  - Avoids valves and transfer lines.
  - No sample dilution.
  - High resolution spectrometry and soft ionization schemes.

Future Direction

- Plan to do more with ACM-GC/MS
  - Collaboration with Glenn Fyrsinger, USCG, 2D-GC/MS.
- Further explore vacuum desorption
  - Minimize transfer line losses and thermal degradation.
  - Higher time resolution.
  - Higher sensitivity, no sample dilution by carrier gas.
    - *takes full advantage of particle concentration, i.e. air removal*
  - Utilize high-resolution mass spectrometric methods and alternate soft ionization schemes for molecular ID.
    - *e.g. PTRMS, chemical ionization.*
- Integrate particle velocity selector for size resolved measurements.
- PM2.5 aerodynamic lens development.
  - See poster by Dahai Tang.

Acknowlegdements

EPA STAR program

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Paul Ziemann, Allen Goldstein, Susanne Hering, Tofwerks