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.**

**High post collection analysis costs**
Aerosol Mass Spectrometer Measurements
A bulk measurement - limited speciation

Zhang et al, GRL 2007

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

Green: higher time and size resolution
Orange: lower Tradeoff

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

Back-flush

Sampling

Desorption

Transfer

Two 4-port Valco valves, 350C max temperature
Prototype ACM
Connected to a GC/MS detector

see poster presented by Dahai Tang.
Program Cycle

Temperature (-20 to 350C)

Time (~ 1hr)

Standby

Collection (> -50C)

Desorption

Back-flush (< 350C)

Automated cycle controlled by microcomputer
ACM data from a hydrocarbon standard

Decane

Tetradecane

C_{10} to C_{18}

Total Ion Intensity (arb.)

Elution Time, min

Ion Intensity

AMU
ACM Paraffin Candle Soot Sample

Peak assignments from NIST Mass Spectral Library
Octadecane GC/MS Sample

Octadecane (m/z 254)

C_{18}H_{38}
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

Adipic acid

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, Allen H. Goldstein, Dylan B. Millet, Rupert Holzinger, Nathan M. Kreisberg, Susanne V. Hering, Allen B. White, Douglas R. Worsnop, James D. Allan, and Jose L. Jimenez

Only 30-40% of total organic is eluted

Chebogue Point, Nova Scotia, 2004

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

Direct Vacuum Desorption System

High Resolution Mass Spectrometry
Soft ionization schemes

Factor analysis for component classification

Particle beam
ionization region
collector/desorber
cartridge heater
coldfinger

Collaboration with Paul Ziemann, UC Riverside
and Tofwerks, Switzerland
Temperature-programmed desorption (TPD): Separation of organics by volatility

(b) mixture

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(b) mixture
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.
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