Thermal-Desorption Aerosol GC/MS-FID (TAG)

ICARTT 2004

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Major Supporting Data (ICARTT 2004):
Aerodyne Research, Inc.: Doug Worsnop et al.
University of Colorado, Boulder: Jose-Luis Jimenez et al.
University of Manchester, UK: James Allan et al.

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ISSUE

• Organic portion of Atmospheric PM$_{2.5}$ Aerosols (20-60%) is helpful in determining and understanding:
  – Particle sources
  – Particle formation processes

• Past field measurements:
  – In-Situ techniques (no extensive individual organic compound separation)
  – Filter collection (12 to 24-hour time resolution)

• New measurement technique: Thermal-desorption Aerosol GC/MS-FID (TAG)
  – Faster time resolution
  – Automated: No sample handling
  – In-Situ data acquisition
OBJECTIVES

1) Test TAG’s ability to achieve:
   – In-Situ - Automated, semi-continuous measurements
   – 1-hour time resolution in a “remote” location
   – Separation / Identification / Quantification of individual organic marker compounds from particle phase

2) Preliminary Data Analysis (Today’s Focus):
   – Initial focus on resolved marker compounds to determine organic aerosol source regions
**APPROACH**

**TAG:** Thermal Desorption Aerosol GC/MS-FID

1. **Collection technique:**
   - Inertial Impaction (30°C)

2. **Sample transfer:**
   - Thermal Desorption (50-300°C)

3. **Chemical separation:**
   - Gas Chromatography

4. **Compound identification:**
   - Mass Spectrometry (Quadrupole)

5. **Compound quantification:**
   - Flame Ionization Detection

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![Diagram](attachment:diagram.png)
TAG’s First Trip to the Field

• Chebogue Point, Nova Scotia - Canada (ICARTT 2004)
• Hourly data (750 chromatograms x 2 detectors = 1500)
• First look TAG data July 26 – August 15 (~3 weeks)
• Manual calibration with directly applied standards
• Automated filtered and zero air blanks

NOAA http://map.ngdc.noaa.gov/website/al/emissions/Run.htm
Chebogue Point, Nova Scotia. August 7, 2004

Sample time: 0.5 hour
Sample Volume: 0.25 m³
Thermal Desorption: 50-300°C
GC oven temp. range shown here: ~ 45°C to 300°C

Total Organic Aerosol = (Resolved Compounds + Unresolved Compounds + Non-Eluting Compounds)
Compounds collected in Nova Scotia are extremely oxygenated. Difficult to identify using only NIST database, may not be in database.

Berkeley, CA
Winter Evening 2004
Resolved Compounds Matched by NIST library: **80%**

Nova Scotia, Canada
Summer Evening 2004
Resolved Compounds Matched by NIST library: **35%**

The dotted red line represents equivalent abundance between graphs A and B.
- Compounds collected in Nova Scotia are extremely oxygenated
- Difficult to identify using only NIST database, may not be in database

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The dotted red line represents equivalent abundance between graphs A and B.
Some Identified Compounds from Nova Scotia

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7H12O2</td>
<td>5-Hexenoic acid, 5-methyl-</td>
</tr>
<tr>
<td>C10H12O5</td>
<td>5,6-Dihydropyran-2-one, 5-acetoxy-6-(1,2-epoxypropyl)-</td>
</tr>
<tr>
<td>C8H6O4</td>
<td>Phthalic acid</td>
</tr>
<tr>
<td>C10H18O2</td>
<td>2,3-Pinanediol</td>
</tr>
<tr>
<td>C8H15NO</td>
<td>Pelletierine</td>
</tr>
<tr>
<td>C7H8O4</td>
<td>1,6-Dioxaspiro[4,4]nonane-2,7-dione</td>
</tr>
<tr>
<td>C9H18</td>
<td>2,2-Dimethyl-3-heptene trans</td>
</tr>
<tr>
<td>C11H18O3</td>
<td>4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester</td>
</tr>
<tr>
<td>C13H24O3</td>
<td>4s,6s-Dimethyl-7R-acetoxy-3-nonanone (acetyl serricornin)</td>
</tr>
<tr>
<td>C8H14O</td>
<td>Cyclohexanone, 2-ethyl-</td>
</tr>
<tr>
<td>C5H6O2</td>
<td>2(3H)-Furanone, 5-methyl-</td>
</tr>
<tr>
<td>C9H14N2O2</td>
<td>Spiro[1,3-dioxolane-2,2'-[6,7]diazabicyclo[3.2.2]non-6-ene</td>
</tr>
<tr>
<td>C6H8O3</td>
<td>2(3H)-Furanone, 3-acetyldihydro-</td>
</tr>
<tr>
<td>C15H22O2</td>
<td>3,5-di-tert-Butyl-4-hydroxybenzaldehyde</td>
</tr>
<tr>
<td>C14H12O</td>
<td>Dibenz[c,dihydrooxepin]</td>
</tr>
</tbody>
</table>
Reproducible Standards from Nova Scotia (manual injections)

Phthalic 3,4,5,6 acid  C8H6O4
Acenaphthene          C12H10
Hexadecane            C16H34
Eicosane              C20H42
4,4'-Dimethoxybenzophenone C15H14O3
Chrysene              C18H12
Octacosane            C28H58
aaa-20R-Cholestane    C27H48
Oxygenated Standards from Nova Scotia

4,4′-dimethoxybenzophenone

C6H4(COOH)2

Both oxygenated standards have nearly identical response on the FID detector. Future Analysis: may be able to “approximately” quantify oxygenated Nova Scotia compounds.

Thus far, I have only used relative abundances.
Timeline of Individual Ion Areas

Temporarily refer to Chebogue Point, NS compounds by letter

**Compound: A**

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester (C11H18O3)

**Compound: B**

1,6-Dioxaspiro[4,4]nonane-2,7-dione (C7H8O4)

Chebogue Point, Nova Scotia
4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester (C11H18O3)

**Compound: A**

- AMBIENT
- FILTERED

**Compound: B**

7/28 8/02 8/07 8/12
2004
Compound: A

TAG Individual Compound vs. AMS Total Organics and Total SO4

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester (C11H18O3)

AMS Total Organics

TAG Compound A

AMS SO4

Different Scales

Event Type 1
No SO4

Event Type 2
SO4

AMS Total Organic, Total SO4 data (Aerodyne Research, Inc.: Worsnop et al.)
AMS data supports the fact that these two compounds represent two different events.

AMS data (Aerodyne Research, Inc.: Worsnop et al.)
FACTOR ANALYSIS

• Preliminary Data
  – 28 resolved compounds (using MS single ion peak area)
  – O3, CO, Radon
  – AMS (Organic carbon, SO4, NO3, NH4)
  – Black carbon, CPC data

• See how these 37 elements vary with each other
  – Factor analysis finds some underlying process or source type
Factor 1 = Organic Only Factor
- Majority of TAG compounds (including Compound A)
- AMS Organic aerosol
- Radon

Factor 2 = Organic + SO4 Factor
- A few TAG compounds (including Compound B)
- AMS SO4, NH4, NO3, Organic aerosol
- O3, CO, Elemental Carbon

Factor 3 = Biogenic Oxidation Factor
- Four TAG compounds

AMS data (Aerodyne Research, Inc.: Worsnop et al.)
Radon data (U.Washington, Bothell: Dan Jaffe)
Factor 1
Organic Only

Factor 2
Organic + SO4

Factor 3
Biogenic Oxidation

AMS data (Aerodyne Research, Inc.: Worsnop et al.)
Radon data (U.Washington, Bothell: Dan Jaffe)
Total Organics are mostly split between Factors 1 and 2

AMS data (Aerodyne Research, Inc.: Worsnop et al.)
Potential Reason for Fewer Factor 2 Compounds

Integrated total FID signal and used oxygenated standards to find approximate mass

- Organics present during SO4 events may not elute through our GC column?
- On average, only getting ~ 1/8 of all organics through column, I would expect more to make it through in an urban environment.
TAG instrument successfully deployed
First in-situ hourly measurements of speciated ambient organic aerosol composition
Preliminary analysis of 28 compounds
– See 3 distinct source types w/ different organic marker compounds
There are many “non-eluting” compounds in a remote environment

CONCLUSIONS

In the near future:
Quantify resolved compounds
Add more parameters to factor analysis
Analyze Unresolved Complex Mixture to bring out information on aerosol oxidation level
Take TAG to an urban environment
ACKNOWLEDGEMENTS

AMS Data (ICARTT 2004):
- Aerodyne Research, Inc.
- University of Manchester, UK
- University of Colorado, Boulder
- Allan, Cross, DeCarlo, Northway, Canagaratna, Huffman, Jimenez, Coe, Worsnop

Radon Data (ICARTT 2004):
- U. Washington, Bothell
  - Dan Jaffe

Funding:
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- Department of Energy – Small Business Innovative Research grant
- National Oceanic and Atmospheric Administration
Factor Analysis

F1: U.S.
F2: Local combustion
F3: Alkanes
F4: OVOC
F5: Terpenes
F6: Biogenic OX

Factor 1 (16% of variance)
- co
- iprano2
- buono2
- ch2cl2
- benzene
- c2cl4
- etono2
- npron02
- nh4.ams
- o3

Factor 2 (12% of variance)
- pxylene
- ethylbenzene
- mxylene
- oxylene
- toluene
- heptane
- hexane
- propene
- 1-butene
- isopentane

Factor 3 (9% of variance)
- butane
- pentane
- isopentane
- isobutane
- hexane
- propane

Factor 4 (8% of variance)
- meoh
- acetone
- ch3cn
- ch3cho
- mek
- etoh
- cpc.ams

Factor 5 (7% of variance)
- apinene
- carene
- bpinene
- co2
- propene

Factor 6 (5% of variance)
- mvk
- macr
- o3
- radon
- isoprene
Organic Aerosol Chemical Composition

Multiple regression of OC species with 6 factors:

Tentative Compound ID:

- 1,6-dioxaspiro[4,4]nonane-2,7-dione (C$_7$H$_8$O$_4$) ?
- 7-anti-methyl-2-oxo-bicyclo[2.2.1]heptane-7-carboxylic acid (C$_9$H$_{12}$O$_3$) ?
- 2,3-pinanediol (C$_{10}$H$_{18}$O$_2$) ?

U.S. Alkanes Terpenes Local comb OVOC