Field monitoring of ozone precursor type and air toxic compounds with a small, fast GC analyzer: the microFAST GC

Edward B. Overton (ebovert@lsu.edu), Scott Miles, Buffy Ashton, and Scott McDaniel
LSU Dept of Environmental Sciences and Analytical Specialists Inc. (ASI)
Why HRVOC verses VOC Analysis?

Lower tropospheric ozone production

HRVOC → OH → R → H₂O

HRVOC → RO₂ → OH → ROOH → Removal

NO₂ + O₃ → NO₂ + O₂

NO₂ + hv → NO + O³(³P)(phot)

O³(³P) + O₂ + M → O³ + M(fast)

Uses up ozone

Produces ozone

NO₅ + VOCs + cities (cars/trucks)

VOCs + forests

NO₅ + power plants
Important VOCs

Ethane**
Ethene* & **
Propane**
Propene* & **
Butanes**
Butenes*
Pentane**
Pentenes*
Isoprene* & **
Benzene**
Toluene**
Xylenes & Ethyl Benzene**

*biogenic sources ** geogenic and anthropogenic sources
Environmental HRVOC Analysis

On-Site

Laboratory

Traditional analytical scheme

Temp, wind speed, RH → GC, GC-MS

LSU Analytical Scheme

microFAST GC for HRVOCs
Temp, wind speed, RH

and

TD-GC-TOF-MS
HRVOCs are reactive compounds, can be loss in sample transport

**On Site Speciation**
- Larger number of analyses
- Real time feed-back
- No sample loss
- less chance for contamination

**Pros**
- Difficult to do speciation
- Slightly less sensitive

**Cons**
- Slow analysis
- Target compounds
- Possible sample alteration

**Lab Speciation**
- Traditional approach
- Good QA/QC
- Controlled Environment (GC-TOF-MS full scanning)

**HRVOCs** (olefins) have half lives measured in minutes and are important ozone precursors
**VOCs** (NMHC) are stable and less subjected to sample loss, also less important in ozone formation
TD-GCMS
HRVOC Component Identification

1. Ethane
2. Ethylene
3. Propane
4. Propylene
5. Butane (2ppm)
6. 1-butene
7. 1,3-butadiene
8. Pentane (2ppm)
9. 1-pentene
10. Isoprene
11. Hexane (2ppm)
12. 1-hexene
13. Heptane
14. Benzene
15. Isooctane
16. Octane
17. Toluene
18. Nonane
19. Ethylbenzene
20. m,p-Xylene
21. o-Xylene
### microFAST Near-Shore Averages: 76 Samples

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Grand Isle 8/20-22/07</th>
<th>Cameron 9/5-6/07</th>
<th>Port Fourchon 9/17/07</th>
<th>Port Fourchon 10/1-4/07</th>
<th>Green Canyon 6/9/08</th>
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<tbody>
<tr>
<td>Ethane</td>
<td>1.1</td>
<td>1.1</td>
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<td>Ethylene</td>
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<td>Propane</td>
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<tr>
<td>Propylene</td>
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<tr>
<td>Butane</td>
<td>1.5</td>
<td>0.3</td>
<td>11.0</td>
<td>0.0</td>
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<tr>
<td>1-Butene</td>
<td>0.4</td>
<td>0.0</td>
<td>6.5</td>
<td>0.0</td>
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<tr>
<td>Pentane</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>1-Pentene</td>
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<td>0.7</td>
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<td>0.0</td>
<td>0.0</td>
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<tr>
<td>Hexane/Isoprene</td>
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<td>0.1</td>
<td>7.7</td>
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<td>10.0</td>
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<td>0.0</td>
<td>0.0</td>
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<tr>
<td>Benzene</td>
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<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
<td>7.2</td>
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<tr>
<td>Toluene</td>
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<td>0.1</td>
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<td>Xylenes</td>
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<td>0.1</td>
<td>0.1</td>
<td>0.8</td>
<td>8.4</td>
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</tbody>
</table>
microFAST GC set-up at Green Canyon Site

Dual microFAST GC instruments operating on the aft deck in the Green Canyon sampling area
0.5 liter H2 high pressure Storage Cylinder (1500 psi) with required regulator
~ 50 L of Hydrogen

50L H Bank Hydrogen Storage Cylinder
delivery pressure of ~50 psi

for microFAST GC PortaPack
HRVOC Installation
Soil Gas Sampling and Analysis

In 15 minutes or less
microFAST GC Analysis of Soil Gas Across Baton Rouge Fault

![Graph showing GC analysis](image)
The **microFAST GC** rapidly analyzes compounds using:

- two short, narrow bore capillary columns (1 -3 meters)
- ultra fast temperature programming (5-25°C/sec)
- high velocity hydrogen carrier gas flows with FIDs
- rapid injection via desorption from a focusing micro trap

The sophisticated sequence of **method-driven** events that enable the wide dynamic range of **microFAST GC** analyses includes the following steps:

- Sampling of air, liquid extracts, SPME, or aqueous solutions
- Purging the trap and injector of residual air or solvent
- Equilibrating the pressure within the injector and trap zones to the pressure at the head of the columns
- Rapidly heating the trap under no flow conditions
- Transferring thermally desorbed analytes from the trap to the head of the columns in a narrow plug
- Rapid temperature programming the separation columns and detecting eluting compounds
- Cleaning out of the trap simultaneously with the chromatographic separation process
- Cooling down the columns and trap in preparation for the next analysis
**microFAST GC**

**analytical columns**

**assembly**

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Column Types:
- 100 to 320 micron ID
- 1 to 3 meters in length
- either open tubular or PLOT

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**Low Thermal Mass Heater & 2 Cap Columns**

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- **column #1**
  - 100 micron ID
  - DB-5

- **column #2**
  - 100 micron ID
  - DB-1701

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**ultra fast**

**temperature programming up to**

25°C/second
microFAST™ GC’s Column Temperature Verses Heating Rates
# GC Inlet Systems

<table>
<thead>
<tr>
<th>Method</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>flash evaporative injectors</strong></td>
<td>neat liquids, organic solvent extracts of liquid and solid samples</td>
</tr>
<tr>
<td><strong>sample loops</strong></td>
<td>permanent gases gases under high pressure</td>
</tr>
<tr>
<td><strong>solid sorbent traps</strong></td>
<td>dilute gases, Industrial Hygiene Samples Purge and Trap VOCs, Static/Dynamic Headspace VOCs</td>
</tr>
<tr>
<td><strong>Solid Phase Micro Extractions (SPME)</strong></td>
<td>primarily VOCs in liquid and head-space samples</td>
</tr>
<tr>
<td><strong>microFAST GC's flash evaporative solid sorbent trap injection system</strong></td>
<td>all of the above, plus SCF and pyrolysis extracts and direct aqueous samples</td>
</tr>
</tbody>
</table>
Sorbent Trap Based Injector

Sample Valve for Continuous Sampling of VOCs/HRVOCs
Human Breath Volatile (HBV) Analyses

GC Dynamic Ranges

Carbon Number Range
(RI = Carbon # times 100)

- Permanent Gases
  - >250mmVP
  - % to ppm
  - Micropacked GC column, loop injector

- VOCs
  - 250 to 0.1mm VP
  - ppm to high ppb
  - Thick film capillary sorbent trap injector

- SemiVOCs
  - 0.1 to .000001mmVP
  - Low ppm to low ppb
  - Thin film capillary sorbent trap or flash heated injector

HBV-challenging
Dr. Phillips’ Analytes

HBV-straight-forward
Single Trap or Dual Trap microFAST GC Analysis?
Diagram of microFAST GC as a dual trap, dual column Air Analyzer

Dual trap HBA

Placing Trap #1 in MFGC
Step 1: collect breath sample on sampling trap

Dual-Bed Sampling Trap

Bed 1-Tenax GR

Connection to Tee Sampler

Bed 2-Carboxen

Connection to vacuum pump

Dual bed traps sample a broader range of compound volatilities than can be sampled using a single bed trap, but dual bed traps are also easier to contaminate than single bed traps.
Step 2: place sampling trap into heated injection port of the microFAST GC

Place sorbent trap into the heated injection port of the microFAST GC
Step 4

Run analytes desorbed from sampling trap using the microFAST GC, with cycle times of 5 minutes per analysis and with fast, dual column GC separations of Breath Volatiles