A Hybrid Vehicle Mounted Membrane Inlet Mass Spectrometer for Spatial Analysis of Atmospheric Chemical Concerns

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UNT
UNIVERSITY OF NORTH TEXAS™

INFICON
Oil and Gas Well Drilling in DFW

Drilling in the Barnett Shale
The Texas Railroad Commission has issued at least 17,800 permits between 2000 and 2009 to drill in the Barnett Shale.

- Increased urban drilling presence has raised environmental impact concerns
- NOAA led studies have shown that wells emit more fugitive effluent than previously estimated
Potential Environmental Impacts

INDUSTRY’S “FOOTPRINT”

When a mining, oil or gas corporation proposes to mine or drill on pristine public lands, the company often defends its development plans with statistics on the size of the operational “footprint” — the amount of land that will be denuded of vegetation for roads, buildings, concrete well pads, waste pits, processing facilities and other infrastructure.

In reality the footprint is rarely so remarkably contained as industry would have officials believe: government studies document that 40 percent of all Western headwaters are polluted with mine waste, and that in some cases plumes of smog that rival big city pollution will extend hundreds of miles from well fields.

<table>
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<tr>
<th>DISTANCE</th>
<th>IMPACTS</th>
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<tbody>
<tr>
<td>0.5 miles</td>
<td>Noise impacts from oil &amp; gas drilling</td>
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<tr>
<td>0.66 miles</td>
<td>Surface water pollution from gas drilling</td>
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<tr>
<td>5+ miles</td>
<td>Views marred by oil &amp; gas wells</td>
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<tr>
<td>20 miles</td>
<td>Groundwater pollution from mining</td>
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<tr>
<td>55 miles</td>
<td>Soil contaminated by mining dust</td>
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<tr>
<td>75 - 80 miles</td>
<td>Migrating wildlife impacted</td>
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<td>120 miles</td>
<td>Surface water pollution from mining</td>
</tr>
<tr>
<td>200 miles</td>
<td>Air pollution from oil &amp; gas drilling</td>
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</table>
Emissions to be Monitored

BTEX emissions are of great concern to citizens living in the vicinity of urban oil and gas drilling processes.

OSHA PEL:
- Benzene: 1.0 ppmv
- Toluene: 200 ppmv
- Ethylbenzene: 100 ppmv
- Xylenes: 100 ppmv

<table>
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<tr>
<th>Region</th>
<th>Number of Sites Tested</th>
<th>% of Sites with Visible Emissions</th>
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<td>Amarillo</td>
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<td>95</td>
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<td>Midland</td>
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http://www.tceq.texas.gov/airquality/barnettshale/bshale-faq
Fugitive Effluent

MIMS

Quadrupole Rods

Membrane

Vacuum Chamber

Filament

Analyte In

Analyte Out
## Volume Equivalents at LOD

<table>
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<tr>
<th>Compound</th>
<th>Minimum Measured Leak Rate (g/hr)</th>
<th>Volume Equivalent at OSHA PEL (m³)</th>
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<td>Xylenes</td>
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<table>
<thead>
<tr>
<th>Compound</th>
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</table>

http://www.tceq.texas.gov/airquality/barnettshale/bshale-faq
Membrane Response

Benzene

- Time (s) vs. Intensity for Benzene with m/z 77 and m/z 78.

Hexane

- Time (s) vs. Intensity for Hexane with m/z 91, m/z 85, and m/z 86.

Xylenes

- Time (s) vs. Intensity for Xylenes with m/z 91, m/z 92, m/z 105, and m/z 106.

Heptane

- Time (s) vs. Intensity for Heptane with m/z 91, m/z 92, m/z 99, and m/z 100.
INFICON Rack Mount MIMS Eng Prototype w/ MPH

Acknowledgement: Jaime Winfield and Les Volles, INFICON Inc
INFICON Rack Mount MIMS Eng Prototype w/ MPH
Open Source Data

Toluene - Unheated Membrane

21 mL/min Toluene in air
All Electric Mode
- Analysis Mode

Or Hybrid Mode

All Gas Mode
- Drive to location
- Power up Pumps and Peripherals
- Return Home
Mapping Data – Campus
Mapping Data – Campus - Benzene
p-Cymene

m/z 105 Cumene
Deep Well Injection - Benzene
Deep Well Injection – Toluene
Deep Well Injection - Cymene
Deep Well Injection – Cumene
Detection of Simulated Clandestine Laboratory Methamphetamine Precursor Synthesis via Mobile Mass Spectrometry
Phenylacetylcarbinol Synthesis
Dibenzyl Ketone Synthesis

\[
\text{Acetyl} + \text{Acetyl} \rightarrow \text{Dibenzyl Ketone}
\]

\[
\text{Acetyl} + \text{Dibenzyl Ketone} \leftrightarrow \text{Acetyl} + \text{Acetyl}
\]

\[
\text{Dibenzyl Ketone} \rightarrow \text{Acetyl} + \text{Acetyl} + \text{CO}_2 \to \text{Acetyl} + \text{CO}_2
\]
(1E & 1Z)-1-Phenylprop-1-en-2-yl acetate Synthesis
Phenylacetone (P2P) Synthesis

\[
\text{Phenylacetone} + \text{Acetone + Water} \rightarrow \text{Phenylacetone (P2P)}
\]

\[
\begin{align*}
\text{Phenylacetone} & : \text{CH}_3\text{C}_6\text{H}_4\text{CHO} \\
\text{Acetone} & : \text{CH}_3\text{COCH}_3 \\
\text{Water} & : \text{H}_2\text{O}
\end{align*}
\]
Fume Hood Mass Scan Monitoring of Effluent from Synthesis
PCC Reaction Mechanisms

(PCC) 1-piperidinyl cyclohexanecarbonitrile
Cyclohexanone
Piperidine
Baseline
Pyridine
79 m/z
Phenylacetyl carbinol
107 m/z
Variable Wind ← ↙ ↓
Dibenzyl Ketone

C_{21}H_{18}O
118.0549 Da
C_{4}H_{16}O^\cdot 118.0412 Da
C_{15}H_{7}
91.0548 Da

Variable Wind ← ↙ ↓
Variable Wind ← ↙ ↓

P2P Phenylaceton-2-one
### Hourly Weather Conditions Denton Regional Airport

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<th>Humidity</th>
<th>Sea Level PressureIn</th>
<th>VisibilityMPH</th>
<th>Wind Direction</th>
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Tests occurred between 5:00 and 8:00 PM
Future Directions

Atmospheric Chemistry
István Lagzi
Róbert Mészáros
Györgyi Gelybó
Ádám Leelőssy

\[ H_e = \text{Effective stack height} = H_s + \Delta h \]
\[ \Delta h = \text{plume rise} \]
Meth Lab May Have Sparked Bartlesville Building Fire Last Month

Posted: Sep 14, 2009 1:07 PM CDT

By Chris Wright, The News On 6
QUIC-PLUME

QUIC-PLUME is a Lagrangian random-walk dispersion model for computing concentration fields around buildings.

http://www.lanl.gov/projects/quic/quicplume.shtml
SITE DATA:
- Location: DALLAS, TEXAS
- Building Air Exchanges Per Hour: 0.56 (unsheltered single storied)
- Time: July 23, 2015 & 1519 hours CDT (using computer's clock)

CHEMICAL DATA:
- Chemical Name: BENZENE
- Molecular Weight: 78.11 g/mol
- AEGL-1 (60 min): 52 ppm
- AEGL-2 (60 min): 800 ppm
- AEGL-3 (60 min): 4000 ppm
- IDLH: 500 ppm
- LEL: 12000 ppm
- UEL: 80000 ppm
- Carcinogenic risk - see CAMEO Chemicals
- Ambient Boiling Point: 175.3° F
- Vapor Pressure at Ambient Temperature: 0.17 atm
- Ambient Saturation Concentration: 175,206 ppm or 17.5%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)
- Wind: 5 miles/hour from W at 5 meters
- Ground Roughness: open country
- Cloud Cover: 0 tenths
- Air Temperature: 90° F
- Stability Class: A
- No Inversion Height
- Relative Humidity: 50%

SOURCE STRENGTH:
- Direct Source: 100 grams/hr
- Source Height: 0
- Release Duration: 60 minutes
- Release Rate: 0.00367 pounds/min
- Total Amount Released: 0.22 pounds

THREAT ZONE:
- Model Run: Gaussian
- Red: 61 yards --- (.01 ppm)
- Orange: 86 yards --- (.005 ppm)
- Yellow: 193 yards --- (.001 ppm)
1ppb Benzene, 5mph winds, 50% Humidity, Distance in Yds
The CAMEO® Software Suite

ALOHA®

Benzene
Toluene
Xylene
Ethylbenzene

yards

0 50 100 150
0 50 100 150

greater than 1 ppm
greater than 0.5 ppm
greater than 0.1 ppm
wind direction confidence lines
1ppb BTEX from 100g/hr, 5mph winds, 50% Humidity, Distance in Yds

Point 1

Point 2

Point 3

Graphs showing concentration of benzene, toluene, ethylbenzene, and xylenes at different points and distances.
Allow the signal of Pyridine to initiate search, MS then starts looking to Heavier constituents.
As car travels into stream, decision is made for direction
MS - Methyl salicylate

- **C₇H₆O₂**: 59.0133 Da
- **C₈H₈O**: 93.034 Da
- **C₈H₆O**: 64.0313 Da
- **C₈H₆O₂**: 71.0133 Da
- **C₉H₇O**: 17.0027 Da
- **C₉H₇O₂**: 31.0184 Da
- **C₉H₇O₂**: 121.029 Da

**Intensity**

- 2.50E-10
- 2.00E-10
- 1.50E-10
- 1.00E-10
- 5.00E-11
- 0.00E+00

**m/z**

- 50
- 100
- 150
- 200
DMMP - Dimethyl methylphosphonate
Demeton-S-methyl-sulfon
Demeton-S'-methyl

![Graph showing the mass spectrum of Demeton-S'-methyl with peaks at various m/z values and corresponding intensity values.](image)
Funding:
Inficon, Syracuse, NY
UNT
Eagle Ford Preservation Fund