Volatile Organic Chemical Exposure in Oil and Gas Extraction: Monitoring for Both Low and High Exposure

Michael J. Kosnett, MD, MPH
Associate Clinical Professor
Division of Clinical Pharmacology & Toxicology
Department of Medicine
University of Colorado School of Medicine, and
Department of Environmental and Occupational Health
Colorado School of Public Health

730 17th St, Suite 925 F
Denver, CO 80202-3537

Michael.Kosnett@ucdenver.edu
303.571.5778
Biological Monitoring for Low Level Inhalation Exposure to Benzene

- 8 hr TWA benzene exposures of approximately 0.2 ppm (640 µg/m³) noted during crude oil tank gauging:

- Corresponds to excess cancer risk of ≈ 3 x 10⁻⁴ if regularly performed over a 30 year working lifetime*

* Based on EPA Inhalation Unit Risk of 5 x 10⁻⁶ adjusted for 30 working years

Is there a suitable method of biological monitoring for this level of exposure?
Urinary S-Phenylmercapturic Acid (SPMA) is a relatively specific biomarker for benzene exposure – from all sources, not just the workplace.

\[
\begin{align*}
\text{benzene} & \xrightarrow{\text{CYP2E1}} \text{benzene oxide} \leftrightarrow \text{benzene oxepin} \\
\text{S-phenyl mercapturic acid (S-PMA)} & \xrightarrow{\text{GST + GSH}} \text{gly} \quad \text{gly} \\
\end{align*}
\]

\( T \frac{1}{2} \) (first component) 9 – 13 hr
Correlation between environmental and biological monitoring of exposure to benzene in petrochemical industry operators
[Carrieri M et al. Tox Lett 192:17-21; 2010]

Urinary SPMA measured in end-of-shift spot urine samples from 20 non-smoking refinery workers (97 samples over 9 days), and 9 smoking refinery workers (48 samples over 9 days).

SPMA analysis used a new technique of strong acid hydrolysis.

Full shift breathing zone benzene measured by personal diffusive samplers one air sample corresponding to each end-shift urine sample.

Benzene in air (n=145)
Mean 0.014 ppm; Median 0.003 ppm; Range < 0.001 – 0.280

TLV = 0.5 ppm; NIOSH REL = 0.1 ppm
Graph is data from non-smoking workers.

Median SPMA in non-smokers’ urine specimens = 0.48 µg/gCr

Smoking refinery workers had 5-fold higher urinary SPMA

*The contribution of smoking to urine SPMA greatly overwhelms the contribution of low dose occupational benzene.*
Urinary S-phenylmercapturic acid as a key biomarker for measuring occupational exposure to low concentrations of benzene in Chinese workers: a pilot study

(Lv B et al. JOEM 56:319-25; 2014)

- End of shift urinary SPMA compared to full shift personal air benzene sample in shoe factory workers (n=55)
- Urine SPMA measured using strong acid hydrolysis
- No data on smoking – subjects “requested to abstain” from smoking for at least one day before urine collection
Case Report: Fatal occupational exposure to low molecular weight petroleum hydrocarbons and an oxygen deficient atmosphere during crude oil tank gauging and sampling.

59 yo man employed as an oil tanker truck driver beginning in May 2014 in Weld Co. Colorado

PMH remarkable for type II Diabetes, elevated blood cholesterol and triglycerides, hypertension. On meds for lipids and DM.
Tanker truck drivers gauged and sampled on average 3 sites per work day
Following the worksite death of another tanker truck driver in March 2014 and an OSHA inspection, the trucking company began to equip its workers with a continuous real-time 4 gas monitor – the Drager X-am 2500
Drager X-am 2500 was programmed for real-time monitoring, and data-logging of 1 minute maximum values, for 4 gases:

- Oxygen
- Carbon monoxide
- Hydrogen sulfide
- Lower explosive limit (LEL) (factory calibrated to methane)

Programmed for visible, audible, and vibratory alarms A1, A2, and “blocking alarm” (for >100% of LEL).
On June 25, 2014, the 59 yo tanker truck driver was discovered by a co-worker “standing in a daze” unresponsive to conversation, on the cat-walk of a tank site, near an open thief hatch.

The worker was assisted off the catwalk and allowed to sit down in fresh air. He became attentive, and was transported to a local ED. He later recalled only becoming dizzy after detecting a “gasoline smell.”

He was discharged from the ED after documentation of normal findings. Diagnosis: Gas exposure and dizziness. Cleared to return to work the next day.

Drager not interrogated at that time.
Approximately a week later, the worker requested PPE and was provided with a half-face respirator with North 7583 P100L filtration (organic vapor and acid gas cartridge with a P100 particulate filter). No record of respirator training or fit testing.

**2 CAUTIONS AND LIMITATIONS**

A- Not for use in atmospheres containing less than 19.5 percent oxygen.
B- Not for use in atmospheres immediately dangerous to life or health.
C- Do not exceed maximum use concentrations established by regulatory standards.
H- Follow established cartridge and canister change schedules or observe ESLI to ensure that cartridges and canisters are replaced before breakthrough occurs.
<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS #</th>
<th>Synonym</th>
<th>IDLH (ppm)</th>
<th>OEL (ppm)</th>
<th>Odor Threshold (ppm)</th>
<th>Respirator (to 10x OEL)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>106-97-8</td>
<td>n-Butane, Methylethyl methane</td>
<td>16000</td>
<td>STEL=1000</td>
<td>204</td>
<td>SA</td>
<td>Short OV service life</td>
</tr>
</tbody>
</table>

SA = supplied air respirator

Short “organic vapor” cartridge service life
On July 13, 2014, the worker arrived at an oil tank battery at approximately noon. Climbed onto a catwalk and opened a blow down valve and a thief hatch to gauge tank and then collect samples.

At 1:15 pm, a co-worker arrived at site to pump oil from an adjacent tank. At 1:30, he observed worker “hunched over the tank, with his face partially inside the tank.”

He was unresponsive, wearing respirator, with large quantities of visible mucous at airway. Appeared to be deceased. 911 on scene within 10 minutes, postmortem hypostasis noted.
Autopsy performed within 24 hours confirmed presence of coronary artery disease without acute thrombosis or infarction.

Petroleum distillates panel C1-C7 & hydrocarbon/oxygenated volatiles panel

- Benzene 0.10 mcg/ml (environmentally exposed average 0.0002 mcg/ml in non-smokers and 0.004-0.006 mcg/ml in smokers)
- Ethane 7.6 ppm
- Propane “present”
- Butane 32 ppm
- Pentane 15 ppm
- Hexane 6.2 ppm
- Methane: None detected
- Thiosulfate: 2.7 mcg/ml (basal serum, plasma, and blood concentrations of thiosulfate are < 2 mcg/ml)
The Drager X-am gas monitor worn by the decedent was first interrogated for data from the June 25, 2014 incident and the July 13, 2014 (fatal) incident after his death.
Dräger GasVisi X-am 2500 data from 11:00:07 am to 12:17:14 pm on 6/25/14

From 11:51 am to 12:03 pm, the oxygen level is below 19.5%.

11:51 am
LEL > 100%
Oxygen 16.4%

11:54 am
Oxygen 9.1%

12:00 pm
Oxygen 9.9%

% Oxygen

% Lower explosive limit (LEL)

Time

Percent oxygen concentration

"OVR" > 100%
Dräger GasVisi X-am 2500 data from 11:30:41 am to 12:15:56 pm on 7/13/14

Percent oxygen concentration

Percent lower explosive limit

% Oxygen

Dräger alarm 19.5% oxygen
Air contains approximately 21 percent oxygen. Therefore for every 1 molecule of oxygen displaced from air, 4 molecules of another gas (mainly nitrogen) are also displaced.

A 1% decline in oxygen corresponds to ≈ 5 percent displacement of the air by another gas.

This is equivalent to 50,000 ppm (i.e. 5%) of that other gas.

Measurements conducted in the breathing zone above open thief hatches have found at least 50,000 to 100,000 ppm butane.

Butane and other LMW petroleum hydrocarbons at a total concentration of 500,000 ppm could account for a decrease in oxygen to ≈ 10%
A comparison of hypoxemia and exercise electrocardiography in coronary artery disease

Diagnostic precision of the methods correlated with coronary angiography

D. G. Kassebaum, M.D.
K. I. Sutherland, M.D.
M. P. Judkins, M.D.
Portland, Ore.

Am. Heart J.
June, 1968

Twenty-four of 36 patients with coronary artery disease developed electrocardiographic evidence of myocardial ischemia (ST segment depression) while breathing 10% oxygen at sea level at rest (Kassebaum et al, 1968).

Influence of Altitude Exposure on Coronary Flow Reserve

Christophe A. Wyss, MD*; Pascal Koepfli, MD*; Gregory Fretz, MD; Magdalena Seebauer, PhD;
Christian Schirlo, MD; Philipp A. Kaufmann, MD

(Circulation. 2003;108:1202-1207.)

8 of 8 patients with coronary artery disease displayed ST segment depression on the electrocardiogram, and 7 of 8 developed angina, while breathing 16.5% oxygen during exercise at sea level (Wyss et al, 2003).
Acute hypoxia reduces oxygen delivery to the heart, which can result in ischemia-induced ventricular fibrillation, especially in a person with pre-existing CAD.

Significant hypoxemia is sensed within the circulation by the carotid bodies, which in turn leads to increased levels of circulating catecholamines, such as epinephrine (adrenalin).
VENTRICULAR FIBRILLATION INDUCED BY HYDROCARBONS AND EPINEPHRINE*

MAYNARD B. CHENOWETH

From Medical Research Laboratory, Medical Division, Edgewood Arsenal, Md.

Fig. 3. Two experiments on one dog using butane as the sensitizing hydrocarbon. "Epin" represents the injection of 0.01 mgm./kgm. epinephrine except at 16 minutes (experiment A) where the dose was 0.02 mgm./kgm.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Methane</td>
<td>This report</td>
</tr>
<tr>
<td>2. Cyclopropane</td>
<td>(2)</td>
</tr>
<tr>
<td>3. Butane</td>
<td>This report</td>
</tr>
<tr>
<td>4. Hexane, c.p.</td>
<td>This report</td>
</tr>
<tr>
<td>5. Petroleum ether (b.p. 35–60° C.)</td>
<td>This report</td>
</tr>
<tr>
<td>6. Heptane, c.p.</td>
<td>This report</td>
</tr>
<tr>
<td>7. Gasoline, 65 octane</td>
<td>This report</td>
</tr>
<tr>
<td>8. Benzene, C₆H₆, c.p.</td>
<td>(8), (13)</td>
</tr>
<tr>
<td>9. Xylene, c.p.</td>
<td>This report</td>
</tr>
<tr>
<td>10. Toluene, c.p.</td>
<td>This report</td>
</tr>
<tr>
<td>11. Methyl chloride</td>
<td>(5), (6)</td>
</tr>
<tr>
<td>12. Methylene chloride</td>
<td></td>
</tr>
<tr>
<td>13. Chloroform</td>
<td></td>
</tr>
<tr>
<td>14. Carbon tetrachloride</td>
<td></td>
</tr>
<tr>
<td>15. Ethyl chloride and bromine analogues of 11 to 15</td>
<td>(9)</td>
</tr>
<tr>
<td>16. Bis-2,2‘ parachlorophenyl 1,1,1 trichloro ethane (&quot;DDT&quot;)</td>
<td></td>
</tr>
</tbody>
</table>
The Epinephrine and Hydrocarbon-Epinephrine Disturbance in the Cat

Walter F. Riker, France Depierre, J. Jay Roberts, B. B. Roy
and Joseph Reilly

Department of Pharmacology, Cornell University Medical College, 1300 York Avenue,
New York 21, New York

TABLE 3

Arrhythmia production by epinephrine and isopropyl norepinephrine alone and in
combination with hydrocarbon

<table>
<thead>
<tr>
<th>Number of Trials</th>
<th>Procedure</th>
<th>Rhythm Disturbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NR No.</td>
</tr>
<tr>
<td>79</td>
<td>Epinephrine</td>
<td>69</td>
</tr>
<tr>
<td>98</td>
<td>Petroleum ether + epinephrine</td>
<td>87</td>
</tr>
<tr>
<td>11</td>
<td>Chloroform + epinephrine</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>Isuprel</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Petroleum ether + Isuprel</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>Chloroform + Isuprel</td>
<td>7</td>
</tr>
</tbody>
</table>

FR = fibrillatory rhythm = ventricular fibrillation
BUTANE SNIFFING CAUSING VENTRICULAR FIBRILLATION

Sir,—The harmful effects of volatile substance abuse include sudden death, which has been linked with cardiac arrhythmia. We present a case of ventricular fibrillation (VF) after butane sniffing.

Resuscitation 37 (1998) 43–45

Case report

Ventricular fibrillation following butane gas inhalation

D.R. Williams *, S.J. Cole

Journal of Electrocardiology 45 (2012) 164–166

Ventricular fibrillation after exposure to air freshener—death just a breath away☆,☆☆,★,★★

Subramanian Senthilkumaran, MD,a,* Ramachandran Meenakshisundaram, MD,b
Revised autopsy report on worker issued by medical examiner on February 11, 2015 stated that the decedent, “died of sudden cardiac death due to inhalation of hydrocarbons and toxic gases and displacement of oxygen by those same agents in the presence of severe hypertensive atherosclerotic cardiovascular disease. Diabetes and hypertriglyceridemia, as well as tobacco use were contributory. This exposure was unintentional and the manner of death is best characterized as accident.”

*Co-occurrence of an oxygen deficient atmosphere, high levels of hydrocarbons, and pre-existing coronary heart disease is the perfect storm for sudden death.*
Potential steps to mitigate or eliminate the risks associated with manual gauging and sampling of crude oil tanks

- **Re-engineer the process completely to allow for remote and automated gauging and sampling**
- Thorough hazard training of workers and supervisors
- Buddy systems that avoid performance of solo work
- Use of real-time gas monitors
- Supplied air respirators
- Worksite availability of automated external defibrillators