OSHA

adds value to business, work and life.

Hydrocarbon Exposures During Tank Gauging and Sampling Operations

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OSHA Problem Solving Initiative (PSI)

- Prevent injuries and illnesses and raise S&H awareness of oil employers in Oil and Gas
  - Manual Tank Gauging, Sampling, Fluid Transfer Operations
    - Hydrocarbon exposures compared to Short Term Exposure Limits (STEL), Ceilings (C), and Immediately Dangerous to Life and Health (IDLH)
    - O_2 deficiency
    - Combustible Vapors/Gas

Light Hydrocarbon Exposures During Tank Gauging

- 9 Similar Cases (2010-2014)
- Non H_2S Sites
- Many Workers found collapsed
- Others complaining of adverse health effects
- Common Circumstances
  - Found near tank openings
  - Collapsed on/near catwalk
  - Working alone
  - Limited PPE

Light Hydrocarbon Exposures During Tank Gauging and Sampling

- Manual Gauging
- Sample Collection
- Gauging Tape/Reel/Stick

- Document production rates
- Assess load-out needs
- “Pumpers” gauge multiple locations throughout the day.

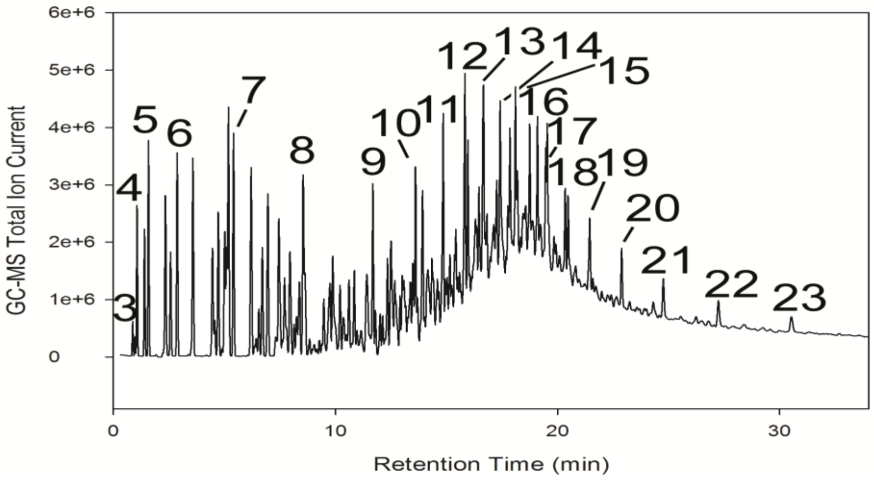
Exposure Activities

Light Hydrocarbon Exposures During Tank Gauging

- Exposure Assessments
  - Non-traditional IH assessment methods
  - Grab Samples
  - PEAK, STEL, IDLH assessments
  - Real-time GC/MS Analysis

Light Hydrocarbon Exposures During Tank Gauging

- Bulk Air Sample
  - Breathing Zone
- Benzene, Cyclohexane, Ethyl Benzene, Heptane, n-Hexane, Pentane, Toluene, Xylene, Propane, Butane



Substance	OSHA 8-hr TWA (ppm)	OSHA Ceiling (ppm)	OSHA Max Peak above Ceiling for 8-hr Shift (ppm)	NIOSH IDLH (ppm)	Cal/OSHA PEL (ppm)	NIOSH REL (ppm)	ACGIH® 2015 TLV® (ppm)
Benzene	10	25	50 (10 min)	500	1 5 (ST)	0.1 1 (ST)	0.5 2.5 (ST)
n-Butane	None	None	None	None {1,900 (10%LEL)}	800	800	1000 (ST)
Cyclohexane	300	None	None	1300 (10%LEL)	300	300	100
Heptane	500	None	None	750	400 500 (ST)	85 440 (ST, 15min)	400 500 (ST)
N-Hexane	500	None	None	1100 (10%LEL)	50	50	50
Pentane	1000	None	None	1500 (10%LEL)	1000	120 610 (C, 15min)	1000
Propane	1000	None	None	2100 (10%LEL)	1000	1000	Appx. F TLV Book
Toluene	200	300	500 (10 min)	500	10 150 (ST) 500 (C)	100 150 (ST)	20
Methylcyclohexane	500	None	None	1200 (10%LEL)	400	400	400

Anesthetic Properties of Light Hydrocarbon Gases and Vapors

- Methane and ethane have anesthetic properties only when O_2 is diluted <18% (simple asphyxiants)
- C_3 and higher hydrocarbons may induce anesthesia at lower concentrations (close to IDLH values for C_3 and C_4)
  - Drummond, L. Light Hydrocarbon Gases: Narcotic, Asphixiant, or Flammable Hazard? Appl. Occup. Environ. Hyg. 8(2):120-125; 1993.
- Concentration needed to produce anesthesia decreases with carbon number: oil/air partition coefficient used to predict anesthetic potency (Meyer 1899, Overton 1901)
  - CH_4 = 0.89
  - C_4H_{10} = 17
  - C_6H_{14} = 87

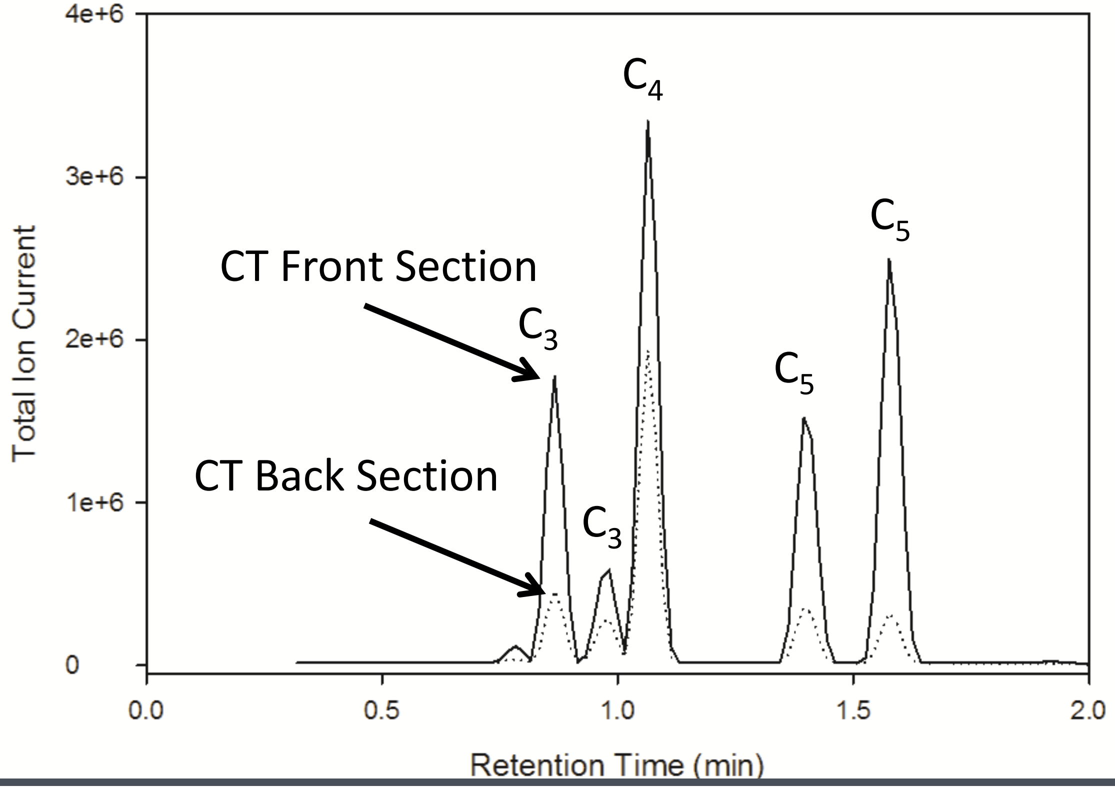
Phase 1 Sampling

Initial Solution for IDLH/Peak Sampling

Collect breathing zone "grab" sample at time of greatest exposure potential

Stabilize VOC analytes on sorbent media for lab analysis using validated methods

Laboratory Analysis

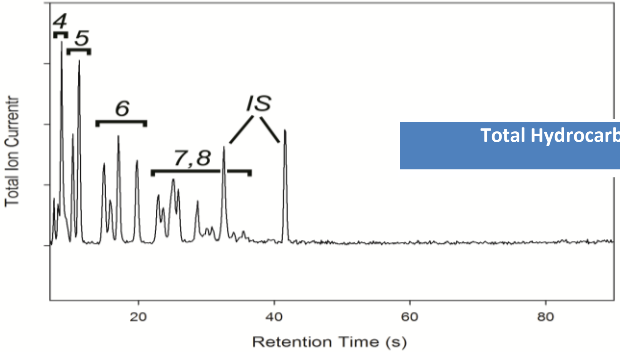


Light Hydrocarbon Exposures During Tank Gauging

- Bulk Samples

Analyte:	Code:	#TN1	#OFBA	#SB4	#SB1
Toluene	2460	0.44%	0.41%	0.40%	0.28%
Methylcyclohexane	1740	1.72%	1.42%	1.52%	0.20%
Hexane	1380	1.81%	2.03%	1.33%	0.10%
3-Methylpentane	M337	0.53%	0.59%	0.39%	ND
Pentane	1990	1.52%	2.33%	0.87%	ND
Heptane	1371	1.93%	1.80%	1.79%	0.20%
2-Methylbutane	R228	0.72%	1.15%	0.37%	0.03%
Cyclohexane	0810	0.63%	0.60%	0.50%	0.12%
Benzene	0320	0.18%	0.24%	0.13%	0.04%
2-Methylpentane	M127	0.99%	1.14%	0.69%	ND

- Personal Air Sampling



Total Hydrocarbons	PK	P	1,460.0 ppm
	PD	P	211.9 ppm

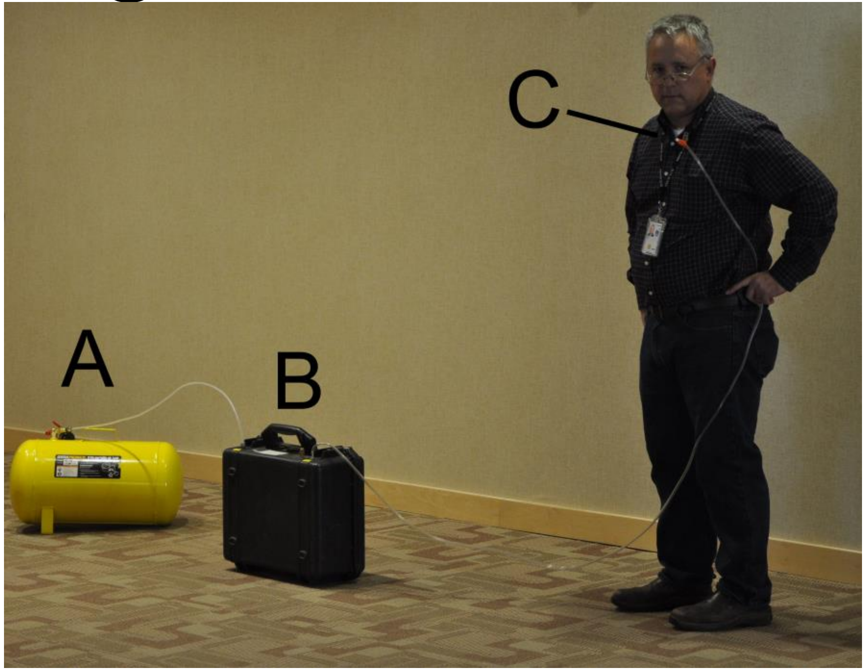
Phase 1: Laboratory Analysis

Breathing zone grab samples from gauging, stabilized on sorbent tubes; breakthrough observed

Analyte	Concentration Range	Short-Duration Standard (or IDLH)
n-Pentane	9.6 – 623 ppm	1,500 ppm (IDLH)
2-Methylbutane	2.6 – 408	None
Benzene	1.6 – 4.0	50 (Z-2, Peak)
Cyclohexane	7.2 – 15.6	2,000 (IDLH)
Methyl cyclohexane	5.3 – 14.8	1,200 (IDLH)
n-Hexane	29.2 – 143	1,100 (IDLH)
n-Heptane	9.5 – 16.0	750 (IDLH)
[A] Total Hydrocarbons	212 – 1,460	None

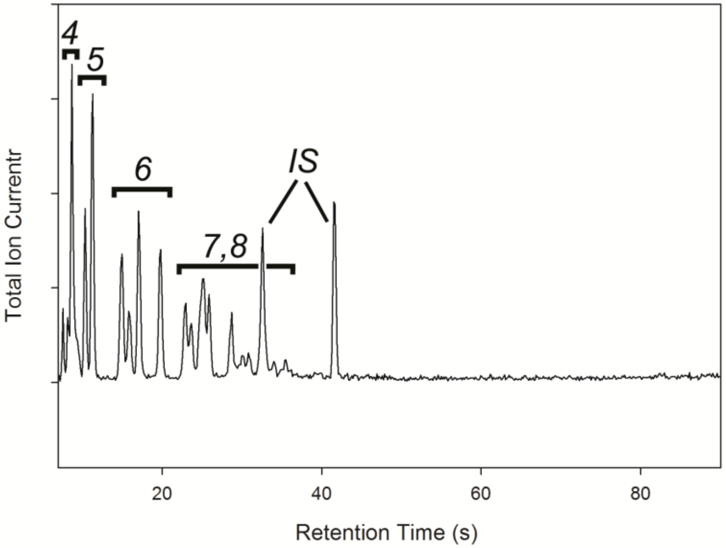
[A] Does not include C_3 and C_4 hydrocarbons

Phase 2: Breathing Zone and Area Grab Sampling Train



Field Analysis Data

- To avoid the loss of light hydrocarbon gases, breathing zone samples were immediately collected onto a tri-bed needle trap for analysis by field-portable GC-MS



Phase 2 Laboratory Results

Area grab samples ~1' above hatch during gauging, only includes analytes measured >1,000 ppm; breakthrough observed

Analyte	Concentration (ppm)	IDLH (ppm)	Severity
Total Hydrocarbons – Plume 1, sum of averages	219,173	None	None
Total Hydrocarbons – Plume 2, sum of averages	179,303		

Phase 2 Laboratory Results

Area grab samples ~1' above hatch during gauging, only includes analytes measured >1,000 ppm; breakthrough observed

Analyte	Concentration (ppm) (Average of 3 Replicate samples)	IDLH (ppm)	Severity
Propane – Plume 1 Propane – Plume 2	41,678± 12,041, RSD=28% Proportion of total hydrocarbons = 19% 44,232 ± 5,801, RSD=13% Proportion of total hydrocarbons = 25%	2,100	~20X
n-Butane – Plume 1 n-Butane – Plume 2	107,836 ± 11,891, RSD=11% Proportion of total hydrocarbons = 49% 91,050 ± 5,511, RSD=6.1% Proportion of total hydrocarbons = 51%	1,900*	~57X

*Based on 10% of LEL

Phase 2 Laboratory Results

Area grab samples ~1' above hatch during gauging, only includes analytes measured >1,000 ppm; breakthrough observed

Analyte	Concentration (ppm) (Average of 3 Replicate samples)	IDLH (ppm)	Severity
n-Pentane– Plume 1 n-Pentane – Plume 2	35,816 ± 9,476, RSD=27% Proportion of total hydrocarbons = 16% 21,591 ± 5,526, RSD=26% Proportion of total hydrocarbons = 12%	1,500*	~24X
2-Methylbutane – Plume 1 2-Methylbutane – Plume 2	20,692 ± 2,918, RSD=14% Proportion of total hydrocarbons = 9% 14,351 ± 2,426, RSD=17% Proportion of total hydrocarbons = 8%	1,400*	~15X

*Based on 10% of LEL

Phase 2 Laboratory Results

Area grab samples ~1' above hatch during gauging, only includes analytes measured >1,000 ppm; breakthrough observed

Analyte	Concentration (ppm) (Average of 3 Replicate samples)	IDLH (ppm)	Severity
n-Hexane – Plume 1 n-Hexane– Plume 2	5,534 ± 2,185, RSD=39% Proportion of total hydrocarbons = 3% 3,594 ± 1,500, RSD=42% Proportion of total hydrocarbons = 2%	1,100*	~5X
2-Methylpentane – Plume 1 2-Methylpentane – Plume 2	5,268 ± 1,482, RSD=28% Proportion of total hydrocarbons = 2% 3,083 ± 881, RSD=29% Proportion of total hydrocarbons = 2%	1,200*	~4X

*Based on 10% of LEL

Phase 2 Laboratory Results

Area grab samples ~1' above hatch during gauging, only includes analytes measured >1,000 ppm; breakthrough observed

Analyte	Concentration (ppm) (Average of 3 Replicate samples)	IDLH (ppm)	Severity
3-Methylpentane – Plume 1	2,348 ± 644, RSD=27% Proportion of total hydrocarbons = 1%	1,200*	~2X
3-Methylpentane – Plume 2	1,403 ± 376, RSD=27% Proportion of total hydrocarbons = 1%		

*Based on 10% of LEL

Phase 2 Laboratory Results

Area grab samples ~1’ above hatch during gauging

Analyte	Concentration Range (ppm)	Short-Duration OSHA Regulatory Limit or IDLH (ppm)	Recommended Short-Duration Limit (ppm)
Benzene	122– 452	50 (Z-2, Peak, 10 min)	1.0 (15 min, NIOSH)
Cyclohexane	335– 657	2,000 (IDLH)	None
Methyl cyclohexane	126 – 368	1,200 (IDLH)	None
n-Heptane	232 – 723	750 (IDLH)	440 (15 min, NIOSH)
Toluene	22 – 72	500 (Z-2, Peak, 10 min)	150 (15 min, NIOSH)

Phase 2 Laboratory Results

Breathing zone grab samples from gauging, stabilized on sorbent tubes (“unusual” workpractices observed when sampled: multiple hatches opened, workers upwind)

Analyte	Concentration Range (ppm)	Short-Duration OSHA Regulatory Limit or IDLH (ppm)	Recommended Short-Duration Limit (ppm)
Propane	ND – 150.0	2,100 (IDLH)	None
n-Butane	ND – 92.0	None {1,900 (10%LEL)}	1000
n-Pentane	ND – 65.6	1,500 (IDLH)	610
2-Methylbutane	ND – 34.0	None {1,400 (10%LEL)	None
n-Hexane	ND – 41.0	1,100 (IDLH)	None
2-Methylpentane	ND – 30.0	None	None
3-Methylpentane	ND – 20.0	None	None
Benzene	ND – 1.6	50 (Z-2, Peak, 10 min)	1.0 (NIOSH)
Cyclohexane	ND – 7.1	2,000 (IDLH)	None
Methyl cyclohexane	ND – 9.0	1,200 (IDLH)	None
n-Heptane	ND – 16.0	750 (IDLH)	440 (NIOSH)
Toluene	ND – 2.2	500 (Z-2, Peak, 10 min)	150 (NIOSH)

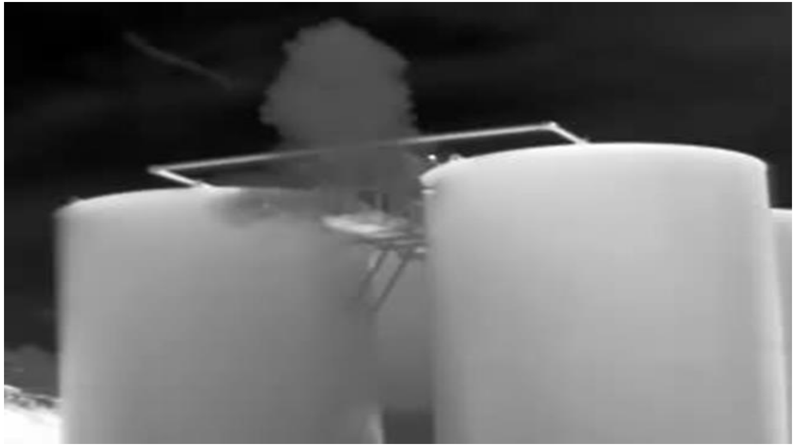
Oxygen Deficiency

- Because O_2 represents only about 1/5 of the total volume of air, every 5% of a displacing gas reduces the $[O_2]$ by only 1%.
- 219,173 ppm total hydrocarbons ~ 22%
- 22%/5 = 4.4%
- $[O_2]$ = 20.9 – 4.4 = 16.5% (calculated maximum value as this only considers displacement by reported hydrocarbon results)

Observations and Findings

Light Hydrocarbon Exposures During Tank Gauging

- Uncontrolled venting
- “Fluttering”
- Vapors easily escape tank headspace
- Worker exposures can reach IDLH



Photos: CDC/NIOSH

Poor work practices routinely observed

Configuration Matters

Vapor Emissions During Hatch Openings

Hatch closed

Hatch open

Findings

- During interviews <u>all</u> employees described cases where chemical exposures caused light-headedness and weakness of knees requiring the need to sit down and rest until symptoms disappeared.
  - Increased incidents when hatches are “fluttering” due to higher gas pressures

Findings

- Did not observe any use of respiratory protection
  - Supplied-air respiratory available where H_2S exposure is possible, although incorrect supply hose combinations were found(not NIOSH-certified when parts are substituted)
- Did not observe use of multi-gas meters for measuring LEL, O_2
  - Occasional use of single gas H_2S meters

Findings

- Potential to exceed OELs and IDLH for hydrocarbons, particularly lighter hydrocarbons (C_3-C_6)
- Potential for O_2 deficient atmospheres
- Flammability hazards
  - Correct use of meters for vapor exposures and O_2 deficient atmospheres.

Flammability Hazards

Recommendations

- Conduct hazard communication training of workers
- Conduct hazard assessment to determine proper PPE, particularly respiratory protection
- Examine and implement engineering controls
- Develop administrative and work practice controls
  - SOPs for hatch opening to reduce exposures and potential for flash fires

Recommendations

- Conduct additional chemical exposure assessments of tank gauging, tank sampling and fluid transfer operations
  - Solo operations (drivers)
  - Pumpers (gauging multiple tanks)
  - Effects of environmental conditions (wind speed, wind direction, inversions, temperature, humidity)
- Examine potential correlation between hydrocarbon exposures and motor vehicle accidents (anesthetic/CNS effects)

Recommendations

- Conduct outreach to medical examiners and coroners on forensic testing for “suspect” cases
- Develop guidance on use, maintenance, and calibration of multi-gas meters for O_2 and LEL measurements
  - Infrared vs. electrocatalytic technology
  - Impacts of “high gas concentrations” on instrument performance (contamination and poisoning)
  - Impacts of anoxic environments
  - Sensitivity coefficient between calibration gas and measured gas

Recommendations

- Improve sampling and analytical methods to more accurately assess exposures
  - Solvent desorption based methods problematic for gas analytes
  - Thermal desorption based methods preferred
  - Collection of "instantaneous" samples for accurate assessment against STEL and C exposure limits

Questions?

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