Capabilities, Limitations and Proper Use of Multi-sensor Confined Space Entry Gas Detectors

Intermediate | 4 Hours

Course Description:

The course will provide an overview of confined space regulations, the atmospheric hazards associated with confined space entry, and the capabilities and proper use of gas detection instruments during entry procedures. The course will focus on choosing and using the best technology for combustible gas and VOC vapor measurement. The course will also explain selection and use of electrochemical sensors for the measurement of specific toxic gases and oxygen deficiency. Technologies discussed include standard LEL, infrared (IR) combustible gas, photoionization (PID) and electrochemical sensors; and provide guidance on using multiple types of sensors to achieve the best monitoring results.

Outline:

Confined space regulations
- OSHA 29 CFR 1910.146 “Permit-Required Confined Spaces”
- NFPA 306 “Standard for the Control of Gas Hazards on Vessels”
- Confined space definitions
- Frequency and types of confined space accidents

Electrochemical sensors for oxygen and toxic gas measurement
- Detection principle
- Relative response to interfering gases
- Electrochemical sensor limitations
- Failure mechanisms
- Setting alarms
- Advice for using electrochemical sensors

Catalytic “Hot Bead” combustible gas (LEL) sensors
- Detection principle
- Response curves and correction factors
- Setting alarms
- Combustible sensor limitations
- Combustible sensor poisons
- Advice for using standard combustible sensors

Non-dispersive infrared (IR) combustible gas sensors
- Detection principle
- Capabilities
- Combustible gas response curves
- Correction factors
- Response to smaller (C1 – C4) hydrocarbon gases such as methane, propane, natural gas and butane
- Response to larger detectable gases (C5 – C9) such as pentane, hexane and octane
- Response to gases too large to be measured with standard LEL sensor like diesel, jet fuel, turpentine and kerosene
- IR combustible sensor limitations
- Advice for using IR combustible gas sensors
Photoionization Detectors
- PID - Operating Principle
- LEL vs. PID Sensors
- Operation of PID lamp, sensing and counter electrodes
- How does a PID work?
- Ionization Energy
- Ionization Energy values
- Technical Advances in PIDs
- Characteristics of PID Lamps Effects of Humidity and Contamination
- Use of PID as “Broad-Range” sensor
- Using correction factors

Integrated gas detection approach to Confined Space, Fire Service and HAZMAT applications
- Choosing the best sensor configuration
- Available sensors for combustible gas and VOC measurement
- Actual downloaded measurement results of sensors exposed to various gases and VOC vapors
- What about benzene?
- Examples of sensor configurations for specific scenarios

Instructor information:

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OK to print this information: Yes

Biography: Robert is the President of GfG Instrumentation, Inc., a leading supplier of portable and fixed gas detection, and indoor air quality monitoring products. GfG’s instruments are used in Fire Service, HAZMAT, confined space, oil production and refining, industrial hygiene and other atmospheric monitoring applications all over the world. Robert has over 30 years of experience in the design, marketing and manufacture of gas detection instruments. Over his career he has held senior management positions at GfG Instrumentation, RAE Systems, BW Technologies and Biosystems. He has been a member of the American Industrial Hygiene Association since 1992. Robert is a past Chairman of both the AIHA Real Time Detection Systems Technical Committee, and the AIHA Confined Spaces Committee. He is also past Chairman of the Instrument Products Group of the International Safety Equipment Association. Robert has a BS in biological science and an MBA from Rensselaer University.
Capabilities, Limitations and Use of Multi-sensor Atmospheric Monitors in Confined Space Entry Procedures

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Technical support and downloads

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- Complete AIHA PDC: Methods and Applications for Chemical Detection Real-Time

Confined Space Entry
Confined Space Entry Requirements for General Industry in USA

- OSHA 29 CFR 1910.146 “Permit-Required Confined Spaces”

Characteristics of Confined Spaces

- Large enough for worker to enter
- Are not designed for continuous worker occupancy
- Limited openings for entry and exit

Meeting basic CS criteria

- Limited means of entry and exit
- Not designed for continuous occupancy
Permit Required Confined Spaces

- One or more of the following:
  - Hazardous atmosphere (known or potential)
  - Material with the potential for engulfment
  - Inwardly sloping walls or dangerously sloping floors
  - Contains any other serious safety hazard

Typical Confined Spaces

- Fully enclosed confined spaces:
  - Storage tanks
  - Ship compartments
  - Process vessels
  - Boilers
  - Sewers
  - Tunnels
  - Underground utility vaults
  - Pipelines
  - Storm drains

- Open topped confined spaces:
  - Pits
  - Degreasers
  - Open-topped water tanks
  - Ship holds
  - Excavations

Permit Program

- If hazards cannot be eliminated or controlled, only remaining option is implementation of comprehensive permit space program
- Permit specifies means, procedures, and practices for safe entry
- Establishes all protective measures have been taken
Rescue

- Self rescue: Entry procedures should aim at getting workers out under their own power BEFORE conditions become life threatening.
- Non-entry rescue: Second best approach is to use procedures that allow rescue without having to enter the space.
- Rescuer entry: Least desirable, highest risk, most equipment and personnel intensive approach.

Work in confined spaces can produce dangerous atmospheric conditions

- Welding
- Painting
- De-greasing
- Scraping
- Sandblasting
- Mucking
- Inerting

Monitor and ventilate continuously

- Many accidents result from changes in the CS atmosphere which occur after the entry is initiated.
- Monitoring determines the air is safe, ventilation keeps it that way.
- The only way to pick up changes before they become life threatening is to monitor continuously!
USA Shipyard and Maritime
Confined Space Entry
Requirements

- OSHA 29 CFR Part 1915, Subpart B,
  “Confined and Enclosed Spaces and
other Dangerous Atmospheres in
Shipyard Employment”

NFPA 306 Standard for the Control
of Gas Hazards on Vessels

- NFPA 306 impacts all shipyards who use
Marine Chemists and their competent
persons
- Standard is a mandatory requirement for
Marine Chemist inspections and for the
follow up competent person inspections
- NFPA 306 originally developed to cover
repair to vessels carrying bulk flammable,
combustible and toxic products
- Over the years the standard has been
changing to cover repair and alterations
to all types of vessels
- In most recent revision there is a shift in
306 to enable it to provide direction for
spaces which are not cargo tanks and are
not adjacent to cargo tanks.

Toxicity testing questions

- If a PEL and a TLV exist for a
substance does 306 require the CMC to use the lower of
the two?
- If there is no PEL listed does but there is a TLV, does 306
require the CMC to use the
TLV?
- If there is no PEL does 306
require the CMC to make any
measurement at all?
- What is the definition of
“permissible concentrations?”
NIOSH Report December 1979

- Most confined space accidents are caused by failure to recognize the hazards!

<table>
<thead>
<tr>
<th>Ref. #</th>
<th>Accident Type</th>
<th>Events</th>
<th>Injuries</th>
<th>Deaths</th>
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<tr>
<td>1</td>
<td>Atmospheric condition in CS</td>
<td>80</td>
<td>72</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>Explosion or fire in CS</td>
<td>15</td>
<td>49</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Explosion or fire at point of entry</td>
<td>23</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>Electrical shock or electrocution</td>
<td>11</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>Caught in / crushed by machinery</td>
<td>10</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Struck by falling objects</td>
<td>16</td>
<td>0</td>
<td>16</td>
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<td>7</td>
<td>Ingress / egress</td>
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<td>15</td>
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<td>8</td>
<td>Falls inside Confined Space</td>
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<td>26</td>
<td>1</td>
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<td>30</td>
<td>3</td>
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<td>Other</td>
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<td>11</td>
<td>Eye injury</td>
<td>10</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>12</td>
<td>Other</td>
<td>21</td>
<td>6</td>
<td>15</td>
</tr>
</tbody>
</table>

Total 276 234 193

65% of fatalities due to atmospheric hazards

Capabilities and Limitations of Multi-sensor Instruments

- First line screening tool for CS, HAZMAT and WMD response
- Many brands available (BW, MSA, ISC, GfG, RAE, etc.)
- Typically 1 – 6 sensors: O2 / LEL / PID / NDIR and / or 1 to 3 substance-specific toxic gas sensors
- Many new types of sensors available for use in these instruments
Requirements for use of portable real-time gas detectors

- Common uses for real-time portable gas detectors:
  - Hazard assessment
  - Exposure assessment
  - Indoor-air quality
  - General atmospheric monitoring
  - Non-permit spaces
  - Permit spaces which have been reclassified as non-permit spaces
  - Permit-required confined spaces (per 29CFR 1910.146)

Common atmospheric hazards

- Oxygen deficiency
- Oxygen enrichment
- Presence of toxic gases
- Presence of combustible gases

Many technologies are available for use in portable real-time instruments

- Oxygen deficiency and enrichment:
  - Fuel cell oxygen sensors
  - Solid polymer ("oxygen pump") sensors

- Combustible gases and vapors:
  - Catalytic % LEL ("Wheatstone bridge") sensors
  - Non-dispersive infrared (NDIR) % LEL and % volume sensors
  - Thermal conductivity (TC) sensors

- Toxic gases and vapors:
  - Electrochemical sensors
  - Photoionization detectors
  - Non-dispersive infrared (NDIR)
  - Flame ionization (FID)
  - Ion Mobility Spectroscopy (IMS)

The most commonly used technologies are highlighted in red

Each type of detection has capabilities and limitations which must be understood for safe use
Measuring Oxygen (Deficiency and Enrichment)

Composition of fresh air

- 78.1% Nitrogen
- 20.9% Oxygen
- 0.9% Argon
- 0.1% All other gases
  - Water vapor
  - CO₂
  - Other trace gases

Effects of oxygen at various concentrations

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 23%</td>
<td>Oxygen enrichment</td>
</tr>
<tr>
<td>20.9%</td>
<td>Normal air concentration</td>
</tr>
<tr>
<td>19.5%</td>
<td>Minimum “safe level”</td>
</tr>
<tr>
<td>16%</td>
<td>First sign of anoxia appears</td>
</tr>
<tr>
<td>16 – 12%</td>
<td>Breathing and pulse rate increase, muscular co-ordination is slightly impaired</td>
</tr>
<tr>
<td>14 – 10%</td>
<td>Consciousness continuous, emotional upsets, abnormal fatigue upon exertion, disturbed respiration</td>
</tr>
<tr>
<td>10 – 6%</td>
<td>Nausea and vomiting, inability to move freely and loss of consciousness may occur</td>
</tr>
<tr>
<td>&lt; 6%</td>
<td>Convulsive movements and gasping occurs, respiration stops</td>
</tr>
</tbody>
</table>
Causes of Oxygen Deficiency

- Combustion
  - Welding and cutting torches
  - Internal combustion engines
- Decomposing of organic matter
  - Rotting foods, plant life and fermentation
- Oxidation of metals
- Rusting
- Inerting
- Displacement
- Absorption

Oxygen displacement in an open topped confined space

Argon

Oxygen Deficiency

- Any area that has an oxygen level of less than 19.5% by volume is considered to be oxygen deficient
Fuel Cell Oxygen Sensors

- Sensor generates electrical current proportional to the $O_2$ concentration
- Sensor used up over time (one to three years)
- Oxygen reduced to hydroxyl ions at cathode:
  $$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
- Hydroxyl ions oxidize lead (anode):
  $$2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$$
- Overall cell reaction:
  $$2Pb + O_2 \rightarrow 2PbO$$

Major components of a “fuel cell” type oxygen sensor

Oxygen Enrichment

- Proportionally increases rate of many chemical reactions
- Can cause ordinary combustible materials to become flammable or explosive
- Any area with an $O_2$ level of more than 23.5% is dangerously enriched

23.0%
Deliberate displacement of oxygen (inertion) in a fully enclosed vessel

- For every 5% total volume displaced, O₂ concentration drops by about 1%
- If 5% of the fresh air in a closed vessel is displaced by methane, the O₂ concentration would be about 19.9%
- The atmosphere would be fully explosive while the O₂ concentration would still be above the normal alarm setting!

O₂ sensor response to 100% N₂

- When exposed to 100% N₂, oxygen readings should drop to zero within 1.5 minutes
- O₂ instruments used to measure near zero should be calibrated at zero as well as 20.9%

Presence of displacing gas on oxygen concentration

- Be very cautious when using O₂ concentration to estimate concentration of some other displacing gas
- Every 5% of displacing gas introduced into a confined space reduces O₂ concentration by only about 1%
O₂ sensor response to 25% CO₂ and 75% N₂

- Oxygen and carbon dioxide sensors exposed to 25% vol CO₂ in N₂
- Maximum range of O₂ sensor is 10% - 21% O₂. Exposed to 25% vol CO₂ in N₂.
- Sensor reaction time is noted at 1%.

O₂ sensor response to 6% O₂ in CO₂

- Response of fuel cell O₂ and infrared CO₂ sensors exposed to 6% O₂ in CO₂
- CO₂ reacts more slowly due to slow release.
- O₂ sensor reaches steady state near 6% O₂.
- CO₂ reaches 6% O₂ by 20 minutes.

Fuel cell type O₂ sensor failure mechanisms

- Lower current output:
  - All available surface of Pb anode converted to PbO₂
  - Electrolyte leakage
  - Loss of structural integrity of housing
  - Desiccation
  - Blockage of capillary pore
  - Electrolyte poisoned by exposure to contaminants
- Higher current output:
  - Short-term upward "ramping" readings due to cracks, tears or leaks allowing O₂ direct access to anode
  - Contraction of "bubbles" in electrolyte due to rapid temp change
- Readings do not change:
  - Loss (reduction) in platinum content in current collector and / or sensing electrode
  - Partial occlusion of capillary pore
- Test sensor before each day's use!
Oxygen Pump (Lead Free) O₂ Sensors

- European Union (EU) “Reduction of Hazardous Substances” (ROHS) directive restricts use of certain substances in new electronic equipment
  - Pb, Cd, Hg, hexavalent chromium, polybrominated biphenyls (PBB’s), and polybrominated diphenyl ethers (PBDE’s)
- Lead containing “fuel cell” sensors specifically excluded (for the time being)
- “Oxygen pump” sensors are lead-free alternative to fuel cell sensors

Oxygen Pump Detection Principle

- Oxygen passively diffuses into polymer (catalyst) substrate
- Power from instrument battery used to “pump” the oxygen back out
- Reactions: Oxidation / Reduction of target gas by catalyst
  - Sensing: O₂ + 4H⁺ + 4e⁻ → 2 H₂O
  - Counter: 2 H₂O → O₂ + 4H⁺ + 4e⁻
- Oxygen generated on counter electrode
- Amount electricity required to remove reaction product and return sensor to ground state (by generating O₂ at counter electrode) proportional to concentration of oxygen present

Oxygen Pump Sensor Advantages and disadvantages

- Advantages:
  - Non-consuming detection technique (sensor does not lose sensitivity or consume itself over time)
- Disadvantages / concerns:
  - Detection reaction may be influenced by shifts in humidity
  - Sensor is net consumer of electricity (drain on power supply)
  - Important to ensure that reaction product (H₂O) is removed from sensor
An O₂ reading lower than 20.9% indicates there is too much of some other gas present in the atmosphere.

In this example as O₂ reading drops CO concentration rises.

Although O₂ never dropped below 19.5%, CO concentration reached alarm level more than once.
CO₂ (not CO) actually the primary contaminant replacing the O₂ in the monitored atmosphere

Important to directly measure all the contaminants that can materially affect the atmosphere

**Toxic Gases and Vapors**

- The two most common CS related toxic gases:
  - Hydrogen sulfide (H₂S)
  - Carbon monoxide (CO)

- Many other toxic gases related to specific activities and industries including:
  - Sulfur dioxide (SO₂)
  - Nitrogen dioxide (NO₂)
  - Chlorine (Cl₂)
  - Chlorine dioxide (ClO₂)
  - Ammonia (NH₃)
  - Cyanide (HCN)
  - Carbon dioxide (CO₂)
  - Volatile organic chemicals (VOCs)
Common causes of toxic gases during CS work

- Contents that were stored in the space
- Compounds absorbed into walls of the space
- Contents being disturbed upon entry
- Work being done in the space
- Decomposing materials in the space
- Adjacent areas

USA Permissible Exposure Limit (PEL)

- Determined by the United States Occupational Safety and Health Administration (OSHA)
- Sets limits for legal unprotected worker exposure to a listed toxic substance
- Force of law in USA!
- Individual states free to enact stricter, but never less conservative limits
- Given in “Parts-per-Million” (ppm) concentrations
  - 1 % = 10,000 ppm

NIOSH Recommended Exposure Limit (REL)

- Determined by USA National Institute of Occupational Safety and Health (NIOSH)
- Guidelines for control of potential health hazards
- Usually more conservative than Federal OSHA exposure limits
- Intended as recommendation but incorporated by adoption in many states with OSHA approved safety and health plans
- Force of law in these states
### Threshold Limit Value (TLV®)

- Threshold Limit Values® are published by American Conference of Governmental Industrial Hygienists (ACGIH®)
- Usually more conservative than USA Federal OSHA PEL, frequently more conservative than NIOSH REL
- Guidelines for control of potential health hazards
- Intended as recommendations based on best available science
- Feasibility, availability and expense of monitoring equipment, as well as costs to industry for conforming not considered

### Substance-specific electrochemical (EC) sensors

- Gas diffusing into sensor reacts at surface of the sensing electrode
- Sensing electrode made to catalyze a specific reaction
- Use of selective external filters further limits cross sensitivity

### Available electrochemical sensors, standard ranges and resolution

- More types of EC sensors available every year, both for individual toxic gases as well as sensors designed to detect a range of toxic or combustible gases
Additional gases detectable by means of relative response

- Electrochemical sensors are designed with specific usage requirements in mind
- The same manufacturer may offer multiple models of sensor for the detection of the same gas, but that are optimized for different sets of interferences and operating conditions
- Thus, cross sensitivities may vary widely between different models and brands of sensors!
- In addition, response values may differ at concentrations other than the ones listed in product documentation
- Discuss with manufacturer BEFORE attempting to use relative response values to measure additional gases

Substance-specific electrochemical sensors

- Gas diffusing into sensor reacts at surface of the sensing electrode
- Sensing electrode made to catalyze a specific reaction
- Use of selective external filters further limits cross sensitivity

Typical Electrochemical Detection Mechanism

H₂S Sensor:

Hydrogen sulfide is oxidized at the sensing electrode:

\[ H_2S + 4H_2O \rightarrow H_2SO_4 + 8H^+ + 8e^- \]

The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:

\[ 2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \]

And the overall reaction is:

\[ H_2S + 2O_2 \rightarrow H_2SO_4 \]

4HS Signal Output: 0.7 µA / ppm H₂S
Effects of humidity on EC sensors

- Sudden changes in humidity can cause "transients" in readings
- Sensor generally stabilizes rapidly
- Avoid breathing into sensor or touching with sweaty hand

Cross sensitivities of City Technology 4S – Rev. 2 sensor at 20°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration used (ppm)</th>
<th>Reading (ppm SO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide (CO)</td>
<td>300</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Nitric oxide (NO)</td>
<td>50</td>
<td>0 to 5.0</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO₂)</td>
<td>6</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Hydrogen sulfide (H₂S)</td>
<td>25</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Chlorine (Cl₂)</td>
<td>5</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>400</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Hydrogen cyanide (HCN)</td>
<td>10</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Acetylene (C₂H₂)</td>
<td>10</td>
<td>&lt; 0.1</td>
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<tr>
<td>Ethene (C₂H₄)</td>
<td>50</td>
<td>&lt; 45</td>
</tr>
</tbody>
</table>
CO and LEL sensor response to 500 ppm (2.0% LEL) acetylene in air

Important notes:
1. 500 ppm acetylene = 2.0% LEL
2. Sensitivity of LEL sensor set to hexane scale

Effects of hydrogen on CO sensor readings

Notable recent gas and vapor TLV updates

- Hydrogen sulfide (2010)
- Sulfur dioxide (2009)
- Nitrogen dioxide (2012)
Exposure limits for H₂S

<table>
<thead>
<tr>
<th>Exposure limits</th>
<th>OSHA PEL</th>
<th>NIOSH REL</th>
<th>ACGIH TLV</th>
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<tbody>
<tr>
<td>TWA</td>
<td>15 ppm</td>
<td>5 ppm</td>
<td>NA</td>
</tr>
<tr>
<td>STEL</td>
<td>15 ppm</td>
<td>5 ppm</td>
<td>NA</td>
</tr>
<tr>
<td>Ceiling</td>
<td>5 ppm</td>
<td>5 ppm</td>
<td>NA</td>
</tr>
</tbody>
</table>

Where should you set the H₂S alarms?

- H₂S TLV® only includes STEL and TWA limits; does not include a Ceiling or “Peak” limit
- Instruments typically have four user settable alarms for each toxic sensor (Low, High, STEL and TWA)
- Suggested alarms:
  - NIOSH:
    - Low: 10 ppm
    - High: 15 ppm
    - STEL: 15 ppm
    - TWA: 10 ppm
  - TLV®:
    - Low: 3 ppm
    - High: 5 ppm
    - STEL: 5 ppm
    - TWA: 1.0 ppm

Exposure limits for SO₂

- OSHA REL:
  - TWA = 5 ppm
- NIOSH REL:
  - TWA = 2.0 ppm
  - STEL = 5 ppm
- Old TLV:
  - TWA = 2 ppm
  - STEL = 5 ppm
- New (2009) TLV:
  - STEL = 0.25 ppm
Suggested alarm settings for SO₂

- Suggested alarms:
  - NIOSH:
    - Low: 2.0 ppm
    - High: 5.0 ppm
    - STEL: 5.0 ppm
    - TWA: 2.0 ppm
  - TLV®:
    - Low: 0.75 ppm
    - High: 1.25 ppm
    - STEL: 0.25 ppm
    - TWA: 0.25 ppm

Exposure limits for NO₂

- US OSHA PEL:
  Ceiling = 5 ppm
- US NIOSH REL:
  15 min. STEL = 1 ppm
- Old TLV:
  8 hr. TWA = 3 ppm
  5 min. STEL = 5 ppm
- New 2012 TLV
  8 hr. TWA = 0.2 ppm

Suggested alarm settings for NO₂

- Suggested alarms:
  - NIOSH:
    - Low: 3.0 ppm
    - High: 5.0 ppm
    - STEL: 1.0 ppm
    - TWA: 1.0 ppm
  - TLV®:
    - Low: 0.6 ppm
    - High: 1.0 ppm
    - STEL: 0.2 ppm
    - TWA: 0.2 ppm
Explosive or Flammable Atmospheres

Fire Tetrahedron

Explosive limits

- **Lower Explosive Limit (LEL):**
  - Minimum concentration of a combustible gas or vapor in air which will ignite if a source of ignition is present

- **Upper Explosive Limit (UEL):**
  - Most but not all combustible gases have an upper explosive limit
  - Maximum concentration in air which will support combustion
  - Concentrations which are above the UEL are too "rich" to burn

Above UEL mixture too rich to burn

Flammable range

Below LEL mixture too lean to burn
Different gases have different flammability ranges

<table>
<thead>
<tr>
<th>Gas Concentration</th>
<th>LEL (%VOL)</th>
<th>UEL (%VOL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>2.2</td>
<td>85</td>
</tr>
<tr>
<td>Ammonia</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.0</td>
<td>7.1</td>
</tr>
<tr>
<td>Butane</td>
<td>1.6</td>
<td>6.4</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>12</td>
<td>72</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2.7</td>
<td>38</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>3.0</td>
<td>15</td>
</tr>
<tr>
<td>Fuel Oil #1 (Diesel)</td>
<td>0.7</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>1.8</td>
<td>9</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>LPG</td>
<td>1.4</td>
<td>7.6</td>
</tr>
<tr>
<td>Methane</td>
<td>1.0</td>
<td>8</td>
</tr>
<tr>
<td>Methanol</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.1</td>
<td>7.2</td>
</tr>
<tr>
<td>Pentane</td>
<td>1.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Propane</td>
<td>3.1</td>
<td>10.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.2</td>
<td>7.1</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>1.1</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Flammable range

Methane

Flammable range 5.0 – 15.0%

Propane

Flammable range 2.2 – 9.0%
Explosive Limits

- Acetylene ($\text{C}_2\text{H}_2$) has no Upper Explosion Limit!

Vapor density

- Measure of a vapor’s weight compared to air
- Gases lighter than air tend to rise; gases heavier than air tend to sink

Stratification

- Atmospheric hazards in confined spaces form layers
- Check all levels!
Vaporization is a function of temperature

- Vapors are the gaseous state of substances that are either liquids or solids at room temperatures
  - Gasoline evaporates
  - Dry ice (solid carbon dioxide) sublimes
- Increasing the temperature of the combustible liquid increases the amount of vapor produced

Flashpoint Temperature

- Temperature at which a combustible liquid gives off enough vapor to form an ignitable mixture

<table>
<thead>
<tr>
<th></th>
<th>Degrees F</th>
<th>Degrees C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline (aviation grade)</td>
<td>-50 °F (approx.)</td>
<td>-45 °C (approx.)</td>
</tr>
<tr>
<td>Acetone</td>
<td>0 °F</td>
<td>-18 °C</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>24 °F</td>
<td>-4 °C</td>
</tr>
<tr>
<td>Ethanol (96 %)</td>
<td>62 °F</td>
<td>17 °C</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>100 - 190 °F</td>
<td>38 - 88 °C</td>
</tr>
</tbody>
</table>

Catalytic “Hot Bead” Combustible Sensor

- Detects combustible gas by catalytic oxidation
- When exposed to gas oxidation reaction causes the active (detector) bead to heat
- Requires oxygen to detect gas
Traditional LEL sensors are “Flame proof” devices

- Flame proof sensors depend on physical barriers such as stainless steel housings and flame arrestors to limit the amount of energy that can ever be released by the sensor.
- The flame arrestor can slow, reduce, or even prevent larger molecules from entering the sensor.
- The larger the molecule, the slower it diffuses through the flame arrestor into the sensor.
- The response of the sensor is so slow to molecules larger than nonane (C9) in size that they are effectively undetectable.

Combustible Gas Sensor

- The catalyst in the LEL sensor bead can be harmed if it is exposed to certain substances.
- The larger the molecule, the slower it diffuses into the bead, the longer it takes to be oxidized, and the lower the relative response.

Catalytic Sensor Structure
Typical carbon number distribution in No. 2 Diesel Fuel (liquid)

Less than 2% of molecules in diesel vapor are small enough to be measured by means of standard LEL sensor.

Vaporization is a function of temperature
- Vapors are the gaseous state of substances that are either liquids or solids at room temperatures
  - Gasoline evaporates
  - Dry ice (solid carbon dioxide) sublimates
- Increasing the temperature of the combustible liquid increases the amount of vapor produced

Flammable and combustible liquid classifications (OSHA 29 CFR 1910.106)

<table>
<thead>
<tr>
<th>Class</th>
<th>Flash Point Temp °F</th>
<th>Boiling Point °F</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA flammable liquid</td>
<td>Below 73 °F</td>
<td>Below 100 °F</td>
<td>Methyl ethyl ether, Pentane, Petroleum ether</td>
</tr>
<tr>
<td>IB flammable liquid</td>
<td>Below 73 °F</td>
<td>Above 100 °F</td>
<td>Acetone, Ethanol, Gasoline, Methanol</td>
</tr>
<tr>
<td>IC flammable liquid</td>
<td>At or above 73 °F</td>
<td>Below 100 °F</td>
<td>Styrene, Turpentine, Xylene</td>
</tr>
<tr>
<td>II combustible liquid</td>
<td>At or above 100 °F</td>
<td>Below 140 °F</td>
<td>Fuel oil no. 44 (Diesel), Mineral spirits, Kerosene</td>
</tr>
<tr>
<td>IIIA combustible liquid</td>
<td>At or above 100 °F</td>
<td>Below 200 °F</td>
<td>Aniline, Carbolic acid, Phenol, Naphthalene, Pine oil</td>
</tr>
<tr>
<td>IIIB combustible liquid</td>
<td>At or above 200 °F</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Typical catalytic LEL sensor relative responses

<table>
<thead>
<tr>
<th>Combustible gas / vapor</th>
<th>Relative response when sensor calibrated on pentane</th>
<th>Relative response when sensor calibrated on propane</th>
<th>Relative response when sensor calibrated on methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>2.2</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Methane</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Propane</td>
<td>1.3</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1.2</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1.0</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.5</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.6</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>1.4</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.4</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Ammonia</td>
<td>2.6</td>
<td>2.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.7</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Gasoline (unleaded)</td>
<td>1.2</td>
<td>0.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Catalytic pellistor combustible gas response curves

Correction Factors

- Correction factor is the reciprocal of the relative response
- The relative response of 4P-75 LEL sensor (methane scale) to ethanol is 0.8
- Multiplying the instrument reading by the correction factor for ethanol provides the true concentration
- Given a correction factor for ethanol of 1.25, and an instrument reading of 40 per cent LEL, the true concentration would be calculated as:

\[
\text{Instrument Reading} \times 1.25 = \text{True LEL Concentration}
\]
Catalytic combustible LEL sensor correction factors

<table>
<thead>
<tr>
<th>Combustible gas / vapor</th>
<th>Relative response when sensor calibrated on pentane</th>
<th>Relative response when sensor calibrated on propane</th>
<th>Relative response when sensor calibrated on methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.45</td>
<td>0.59</td>
<td>0.91</td>
</tr>
<tr>
<td>Methane</td>
<td>0.50</td>
<td>0.67</td>
<td>1.00</td>
</tr>
<tr>
<td>Propane</td>
<td>0.77</td>
<td>1.00</td>
<td>1.54</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.83</td>
<td>1.11</td>
<td>1.67</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1.00</td>
<td>1.33</td>
<td>2.00</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.11</td>
<td>1.43</td>
<td>2.22</td>
</tr>
<tr>
<td>n-Octane</td>
<td>1.25</td>
<td>1.67</td>
<td>2.50</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.43</td>
<td>0.57</td>
<td>0.87</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.63</td>
<td>0.83</td>
<td>1.25</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.71</td>
<td>0.95</td>
<td>1.43</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.71</td>
<td>0.95</td>
<td>1.43</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.38</td>
<td>0.50</td>
<td>0.77</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.43</td>
<td>2.00</td>
<td>2.86</td>
</tr>
<tr>
<td>Gasoline (unleaded)</td>
<td>0.83</td>
<td>1.11</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Using a lower alarm setting minimizes effect of relative response on readings

Typical catalytic percent LEL sensor response to 50% LEL methane (2.5% vol. CH₄)
Typical catalytic percent LEL sensor response to 50% LEL pentane (0.7% vol. C5H12)

Catalytic combustible sensor exposed to various gases

Response to methane over life of sensor

- Relative response to methane may change substantially over life of sensor
Response of new LEL sensor to methane

Response of new LEL sensor to 50% LEL (2.0% vol.) H₂ and 50% LEL (2.5% vol.) CH₄ in air

Response of partially inhibited LEL sensor to methane

CC LEL sensor with reduced sensitivity to CH₄ response to 50% LEL (2.0% vol.) H₂ and 50% LEL (2.5% vol.) CH₄ in air

Methane based equivalent calibration gas mixtures

<table>
<thead>
<tr>
<th>Combustible Gas / Vapor</th>
<th>Relative response when sensor is calibrated to 2.5% (50% LEL) methane</th>
<th>Concentration of methane used for equivalent 50% LEL response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.1</td>
<td>2.75% CH₄</td>
</tr>
<tr>
<td>Methane</td>
<td>1.0</td>
<td>2.5% Vol CH₄</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.8</td>
<td>2.0% Vol CH₄</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.7</td>
<td>1.75% Vol CH₄</td>
</tr>
<tr>
<td>Propane</td>
<td>0.65</td>
<td>1.62% Vol CH₄</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.5</td>
<td>1.25% Vol CH₄</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.45</td>
<td>1.12% Vol CH₄</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.4</td>
<td>1.0% Vol CH₄</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.35</td>
<td>0.88% Vol CH₄</td>
</tr>
</tbody>
</table>
### Combustible sensor limitations

<table>
<thead>
<tr>
<th>Component</th>
<th>LEL (Vol %)</th>
<th>Flashpoint (ºF)</th>
<th>OSHA PEL</th>
<th>NIOSH REL</th>
<th>TLV</th>
<th>EN PEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.5%</td>
<td>-6ºF (-26 ºC)</td>
<td>1,500 PPM TWA</td>
<td>500 PPM TWA</td>
<td>500 PPM TWA</td>
<td>1,500 PPM</td>
</tr>
<tr>
<td>Diesel (No.2) vapor</td>
<td>0.6%</td>
<td>125ºF (201 ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>15 PPM</td>
<td>200 PPM</td>
</tr>
<tr>
<td>Ether</td>
<td>3.3%</td>
<td>55ºF (13.9 ºC)</td>
<td>1,000 PPM TWA</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>1,500 PPM</td>
</tr>
<tr>
<td>Gasoline</td>
<td>1.5%</td>
<td>-60ºF (-46ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>500 PPM TWA</td>
<td>620 PPM</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.1%</td>
<td>-7ºF (-24.9 ºC)</td>
<td>300 PPM TWA</td>
<td>30 PPM TWA</td>
<td>30 PPM TWA</td>
<td>500 PPM</td>
</tr>
<tr>
<td>Inorganics</td>
<td>5%</td>
<td>-5ºF (-45.9 ºC)</td>
<td>430 PPM TWA</td>
<td>45 PPM TWA</td>
<td>45 PPM TWA</td>
<td>500 PPM</td>
</tr>
<tr>
<td>Kerosene/ jet fuels</td>
<td>0.7%</td>
<td>100–112ºF (37.8 – 44.4 ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>200 mg/M3 TWA (approx. 14.4 PPM)</td>
<td>250 mg/M3 TWA (approx. 17.9 PPM)</td>
</tr>
<tr>
<td>MEA</td>
<td>1.4%</td>
<td>-14ºF (-25.6 ºC)</td>
<td>250 PPM TWA</td>
<td>25 PPM TWA</td>
<td>25 PPM TWA</td>
<td>700 PPM</td>
</tr>
<tr>
<td>Turpentine</td>
<td>8.6%</td>
<td>85ºF (29.4 ºC)</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>400 PPM</td>
</tr>
<tr>
<td>Xylenes (o, m &amp; p isomers)</td>
<td>0.8–1.1%</td>
<td>61–88ºF (27.8–31.1 ºC)</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>400–500 PPM</td>
</tr>
</tbody>
</table>

### Response of electrochemical and LEL sensor to 20,000 ppm hydrogen in nitrogen

![Graph showing the response of electrochemical and LEL sensor to 20,000 ppm hydrogen in nitrogen.](image)

- **Combustible sensor poisons:**
  - Silicones (by far the most virulent poison)
  - Hydrogen sulfide
  - Other sulfur containing compounds
  - Phosphates and phosphorus containing substances
  - Lead containing compounds (especially tetraethyl lead)
  - High concentrations of flammable gas!
  - Combustible sensor inhibitors:
    - Halogenated hydrocarbons (Freons®, trichloroethylene, methylene chloride, etc.)

*Note: The LEL sensor includes an internal filter that is more than sufficient to remove the H₂S in calibration gas. It takes very high levels of H₂S to overcome the filter and harm the LEL sensor.*
Effects of hexamethyldisiloxane (HMDS) on pellistor sensor

- Accelerated Life Tests
- 4P-75 vs 4P-73C - HMDS Poison Resistance

Low-power pellistor advice

- Allow enough time for full stabilization prior to performing fresh air zero
  - DO NOT PERFORM AUTO ZERO AS PART OF AUTOMATIC START-UP SEQUENCE
- Perform functional test before each day’s use!
- Use methane based test gas mixture OR if you use a different gas (e.g. propane or pentane) challenge the sensor with methane periodically to verify whether the sensor has disproportionately lost sensitivity to methane

Non-dispersive infrared (NDIR) sensors

- Many gases absorb infrared light at a unique wavelength
- In NDIR sensors the amount of IR light absorbed is proportional to the amount of target gas present
- IR absorption has advantages of high sensitivity, low cross-sensitivity, long life, and resistance to contamination
- IR absorption employed in both very high-performance laboratory analyzers and in very low-performance systems (e.g. inexpensive, non-intrinsically safe hand-held CO₂ detectors)
Non-dispersive infrared (NDIR) sensors

- When infra-red radiation passes through a sensing chamber containing a specific contaminant, only those frequencies that match one of the vibration modes are absorbed.
- The rest of the light is transmitted through the chamber without hindrance.
- The presence of a particular chemical group within a molecule thus gives rise to characteristic absorption bands.
- Non-dispersive IR sensors measure at a specific range of wavelengths associated with a particular gas or class of gases.

Beer-Lambert Law

\[ I_1 = I_0 e^{-\alpha L c} \]

Size (length) matters...

Infrared Detectors

- Chemical bonds absorb infrared radiation.
- For infrared energy to be absorbed (that is, for vibrational energy to be transferred to the molecule), the frequency must match the frequency of the mode of vibration.
- Thus, specific molecules absorb infrared radiation at precise frequencies.
Energy Absorbed by “Bond Stretching” and “Bending” Vibration

- Must have a COVALENT CHEMICAL BOND

Nonlinear Molecules

Geometry and specific bonds in molecule give rise to IR spectrum

Requirements for IR Absorption

- Lower quantum levels must be “populated”
- Dipole moment (degree of charge imbalance) must change with the vibrational “motion”
- CO$_2$ and CH$_4$ absorb IR
- Homonuclear diatomics such as hydrogen DO NOT absorb IR
- IR-transparent gases:
  - H$_2$
  - N$_2$
  - O$_2$
  - F$_2$
  - Cl$_2$
  - HBr
  - Ar
Combustible gas NDIR sensor advantages and limitations

- **Limitations:**
  - Molecule must include chemical bonds that absorb at the wavelength(s) used for measurement
  - Not all combustible gases can be detected!
    - "Diatomic" molecules like hydrogen ($H_2$) cannot be detected at all
    - Gases with double and triple bonds (like acetylene) detect poorly or not at all at some measurement wavelengths
    - NDIR sensors with short optical path-lengths may have limited ability to measure gases with lower relative responses

- **Advantages:**
  - Sensor cannot be poisoned
  - Does not require oxygen to detect gas
  - Can be used for high-range combustible gas measurement
  - Responds well to large hydrocarbon molecules that cannot be measured by means of standard LEL sensor

---

IR LEL sensor performance unaffected by the absence of oxygen

IR and CC LEL sensors exposed to 44% LEL hexane (0.48% vol. C$_6$H$_{14}$)

- Response of IR LEL sensor unaffected by absence of $O_2$
- Response of CC LEL sensor nearly linear to sensor $O_2$ content compared to the sensor’s content

---

IR combustible sensors can be used for high range measurement up to 100% volume gas

Response of G460 infrared (IR) combustible gas and oxygen sensors exposed to 100% volume methane

- G460 NDIR
- G440 NDIR
- $O_2$ NDIR

- The IR combustible gas sensor was set to the present oxygen "HI range" where the IR combustible gas reading increased significantly from 0% to 100% volume methane. The oxygen sensor rapidly increased and stabilized at a reading of 8% volume oxygen when exposed to the 4.1% LEL gas.
Linearized 3.33 μm NDIR combustible gas response curves

Relative response of pellistor and infrared sensors to n-Pentane

Response of calibrated pellistor and IR sensors to 50% LEL n-Hexane

- Both sensors were calibrated to 50% LEL n-Hexane
- Readings for both sensors are now very close to the true 50% LEL concentration
- Initial response of IR sensor is slightly quicker than the pellistor sensor
- However, the time to the final stable response (T100) is virtually identical for both sensors, (about 150 seconds)
Photoionization Detectors

Photoionization Detectors

September, 2014                Capabilities, limitations and use of CSE gas detectors
Slide 118

What are VOCs?

• Volatile organic chemicals (VOCs) are organic chemicals or mixtures characterized by tendency to evaporate easily at room temperature
• VOCs present multiple potential threats in the workplace environment: Heavier than air, flammable and toxic
• Increased awareness of toxicity is leading to lowered exposure limits
• Increased awareness of toxicity has led to lowered exposure limits, and increased requirements for direct measurement

Volatile organic compounds (VOCs)

• VOCs are organic chemicals or mixtures characterized by tendency to evaporate easily at room temperature
• Familiar VOCs include:
  • Solvents
  • Paint thinner
  • Nail polish remover
  • Gasoline
  • Diesel
  • Heating oil
  • Kerosene
  • Jet fuel
  • Benzene
  • Butadiene
  • Hexane
  • Toluene
  • Xylene
  • Many others
VOC Toxicity

- Toxic substances produce symptoms in two time frames: acute and chronic
- While some VOCs acutely toxic at low concentrations, most VOCs chronically toxic
- Because of long-term nature of the physiological effects, tendency has been to overlook presence in workplace at PEL concentrations
- Exposure via skin or eye contact with liquid or aerosol droplets, or inhalation of vapors

VOC exposure symptoms

- Symptoms may not become manifest for years
  - Respiratory tract irritation (acute or chronic)
  - Dizziness, headaches (acute or chronic)
  - Long-term neurological: diminished cognition, memory, reaction time, hand-eye and foot-eye coordination
  - Mood disorders: depression, irritability, and fatigue
  - Peripheral neurotoxicity: tremors and diminished fine and gross motor movements
  - Kidney damage and immunological problems, including increased cancer rates
  - Benzene, (toxic VOC found in gasoline, diesel, jet fuel and other chemical products), linked to chemically induced leukemia, aplastic anemia and multiple myeloma (a cancer of the lymphatic system)

Real-time measurement techniques for VOC vapors

- Colorimetric detector tubes
- Passive (diffusion) badge dosimeters
- Sorbent tube sampling systems
- Combustible gas monitors with “Pellistor” percent LEL or ppm sensors
- Photoionization detectors (PIDs)
- Flame ionization detectors (FIDs)
- Infrared spectra-photometers
- Most widely used instrument is compact multi-sensor monitor with O2, LEL, electrochemical toxic and miniaturized photoionization detector (PID)
Why use photoionization detector equipped instruments?

- For most VOCs, long before you reach a concentration sufficient to register on a combustible gas indicator, you will have easily exceeded the toxic exposure limits for the contaminant.
- PID equipped instruments are generally the best choice for measurement of VOCs at exposure limit concentrations.
- Whatever type of instrument is used to measure these hazards, it is essential that the equipment is used properly, and the results are correctly interpreted.

Combustible sensor limitations

<table>
<thead>
<tr>
<th>Component</th>
<th>LEL (Vol %)</th>
<th>Flashpoint Temp (ºF)</th>
<th>OSHA PID</th>
<th>NLISH REL</th>
<th>TLV</th>
<th>5% LEL in PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.5%</td>
<td>-20ºF (-29 ºC)</td>
<td>100 PPM TWA</td>
<td>200 PPM TWA</td>
<td>500 PPM TWA</td>
<td>750 PPM TWA</td>
</tr>
<tr>
<td>Diesel (No.2) vapor</td>
<td>0.6%</td>
<td>120ºF (49.ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>50 PPM</td>
<td>100 PPM</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.3%</td>
<td>(12.ºC)</td>
<td>100 PPM TWA</td>
<td>250 PPM TWA</td>
<td>300 PPM TWA</td>
<td>500 PPM TWA</td>
</tr>
<tr>
<td>Gasoline</td>
<td>5.3%</td>
<td>-45ºF (-42.7 ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>100 PPM</td>
<td>200 PPM</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.1%</td>
<td>-7ºF (-20.7 ºC)</td>
<td>150 PPM TWA</td>
<td>200 PPM TWA</td>
<td>500 PPM TWA</td>
<td>1000 PPM TWA</td>
</tr>
<tr>
<td>Isopropanol alcohol</td>
<td>6.5%</td>
<td>53ºF (11.ºC)</td>
<td>200 PPM TWA</td>
<td>400 PPM TWA</td>
<td>1000 PPM TWA</td>
<td>1500 PPM TWA</td>
</tr>
<tr>
<td>Kerosene/Jet Fuels</td>
<td>0.7%</td>
<td>100–162ºF (37.8–72.3 ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>250 mg/m³ (approx. 14.9 PPM)</td>
<td>500 PPM</td>
</tr>
<tr>
<td>NDMA</td>
<td>1.4%</td>
<td>16ºF (6ºC)</td>
<td>150 PPM TWA</td>
<td>200 PPM TWA</td>
<td>300 PPM TWA</td>
<td>500 PPM TWA</td>
</tr>
<tr>
<td>Turpentine</td>
<td>0.8%</td>
<td>65ºF (18ºC)</td>
<td>150 PPM TWA</td>
<td>200 PPM TWA</td>
<td>200 PPM</td>
<td>400 PPM</td>
</tr>
<tr>
<td>Xylenes (o, m, &amp; p isomers)</td>
<td>0.8 – 1.1%</td>
<td>81 – 99ºF (27.3 – 33.3 ºC)</td>
<td>100 PPM TWA</td>
<td>150 PPM TWA</td>
<td>300 PPM TWA</td>
<td>400 – 500 PPM</td>
</tr>
</tbody>
</table>

PID - Operating Principle

- PIDa used for measuring solvent, fuel and VOC vapors in the workplace environment.
- PIDa use ultraviolet light as source of energy to remove an electron from neutrally charged target molecules creating electrically charged fragments (ions).
- This produces a flow of electrical current proportional to the concentration of contaminant.
- The amount of energy needed to remove an electron from a particular molecule is the ionization energy (or IE).
- The energy must be greater than the IE in order for an ionization detector to be able to detect a particular substance.
Catalytic (CC) LEL vs. PID Sensors

- Catalytic LEL and photoionization detectors are complementary detection techniques.
- Catalytic LEL sensors excel for measurement of methane, propane, and other common combustible gases NOT detectable by PID.
- PIDs detect large VOC and hydrocarbon molecules that are undetectable by catalytic sensors.
- Best approach to VOC measurement is to use multi-sensor instrument capable of measuring all atmospheric hazards that may be potentially present.

Detection sequence:
1. Neutrally charged molecule diffuses into glow zone.
   - Sensing electrode
   - Counter electrode
   - Reading
   - Benzene molecule (neutrally charged)

Detection sequence:
2. Molecule is ionized.
   - Sensing electrode
   - Counter electrode
   - Reading
   - Benzene molecule is ionized
Operation of PID lamp, sensing and counter electrodes

Detection sequence:
3. Free electron is electrostatically accelerated to positively charged sensing electrode where it is counted

Operation of PID lamp, sensing and counter electrodes

Detection sequence:
4. Positively charged fragment (ion) is electrostatically accelerated to counter electrode, where it picks up replacement electron and regains neutral charge

How does a PID work?
### Ionization Energy

<table>
<thead>
<tr>
<th>Gas / vapor</th>
<th>Ionization energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>14.01</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>13.77</td>
</tr>
<tr>
<td>Methane</td>
<td>12.38</td>
</tr>
<tr>
<td>Water</td>
<td>12.59</td>
</tr>
<tr>
<td>Oxygen</td>
<td>12.08</td>
</tr>
<tr>
<td>Chlorine</td>
<td>11.48</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>10.46</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>10.18</td>
</tr>
<tr>
<td>Ammonia</td>
<td>10.16</td>
</tr>
<tr>
<td>Hexane (mixed isomers)</td>
<td>10.15</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.69</td>
</tr>
<tr>
<td>Hexane</td>
<td>9.25</td>
</tr>
<tr>
<td>Butadiene</td>
<td>9.07</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.82</td>
</tr>
</tbody>
</table>

IE determines if the PID can detect the gas. If the IE of the gas is less than the eV output of the lamp, the PID can detect the gas. Ionization Energy (IE) measures the bond strength of a gas and does not correlate with the Correction Factor. Ionization Energies are found in the NIOSH Pocket Guide and many chemical texts.

### PID Components

- Detector assembly
- Electrodes: sensing, counter and (in some designs) fence
- Lamp: most commonly 10.6eV, 11.7eV or 9.8 eV

### PID lamp characteristics

- Window material and the filler gas determine output characteristics as well as operational life of lamp.

<table>
<thead>
<tr>
<th>Nominal lamp photon energies</th>
<th>Primary gas in lamp</th>
<th>Major emission lines</th>
<th>Relative intensity</th>
<th>Window crystal</th>
<th>Crystal transmittance λ range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.7 eV</td>
<td>Argon</td>
<td>11.83</td>
<td>104.8</td>
<td>1000</td>
<td>Lithium fluoride (LiF) 105 - 5000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.62</td>
<td>106.7</td>
<td>500</td>
<td>Magnesium fluoride (MgF2) 115 - 7000</td>
</tr>
<tr>
<td>10.6 eV</td>
<td>Krypton</td>
<td>10.64</td>
<td>116.5</td>
<td>200</td>
<td>Calcium fluoride (CaF2) 125 - 8000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.03</td>
<td>123.6</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>9.8 eV</td>
<td>Krypton</td>
<td>10.03</td>
<td>123.6</td>
<td>650</td>
<td></td>
</tr>
</tbody>
</table>
What are broad-range sensors?

- Broad-range sensors (like LEL and PID sensors) are non-specific.
- Broad-range sensors provide aggregate measurements for all detectable molecules within a specified class, for instance:
  - Molecules capable of oxidation by standard LEL sensor
  - Molecules capable of ionization by standard PID with 10.6 eV lamp
- Cannot distinguish between different contaminants they are able to detect
- Provide single total reading for all detectable substances present
- PID and LEL readings always relative to gas used to calibrate detector

Critical PID Performance Issues: Effects of Humidity and Contamination

- Condensation and contamination on lamp window and sensor surfaces can create surface conduction paths between sensing and counter electrodes.
- Buildup of contamination provides nucleation points for condensation, leading to surface currents.
- If present, surface currents cause false readings and/or add significant noise that masks intended measurement (sometimes called “moisture leakage”).
- PID designs MAY require periodic cleaning of the lamp and detector to minimize the effects of contaminants and humidity condensation on PID readings.

Can PIDs be used in high ambient humidity?

- It depends on the design of the PID.
- The greater the gap between the lamp window and the sensing electrode, the greater the effects of humidity and other signal quenching gases (like methane) have on readings.
- Unless a humidity correction factor is used, some PIDs may display readings 30% to 40% below actual when used in humid conditions.
- PID designs where the electrode is positioned flush against the window are the least susceptible to signal quenching.
Does a PID have to include a built-in pump or fan to obtain readings?

- It depends on the PID design
- Some designs can only be used with a pump, and cannot be used in diffusion mode
- Other designs only use the pump to move the atmosphere being sampled to the face of the sensor
- PID sensors in this second category may be used with a pump for remote sampling, or without a pump for diffusion operation
- In diffusion operation local air currents and Brownian motion are responsible for transporting molecules in and out of the PID sensor

Can a PID be used in place of common substance-specific electrochemical sensors (like those used to measure H₂S)?

- For many common toxic gases, substance-specific electrochemical sensors are available to provide highly accurate readings
- When a quantified reading is necessary for a specific contaminant (like CO or H₂S) it is better if feasible to avoid use of a broad-range sensor, and stick with a detection technology that can provide direct, substance-specific readings

Catalytic (CC) LEL vs. PID Sensors

- Catalytic LEL and photoionization detectors are complementary detection techniques
- Catalytic LEL sensors excellent for measurement of methane, propane, and other common combustible gases NOT detectable by PID
- PIDs detect large VOC and hydrocarbon molecules that are undetectable by catalytic sensors
- Best approach to VOC measurement is to use multi-sensor instrument capable of measuring all atmospheric hazards that may be potentially present
Can I use my PID in place of a traditional LEL sensor?

- Photoionization detectors optimized for use at ppm and sub-ppm toxic exposure limit values
- PID linearity may be affected by high LEL range concentrations of gas
- The PID upper range limit can be exceeded
- Gases such as methane and ethane can have a quenching effect, causing lower than actual PID readings
- PID and catalytic LEL sensors work best when used together as complementary detection techniques

There are strong benefits for including both PID and LEL sensors in the same instrument.

PID, CC LEL, IR LEL and CO sensors exposed to 50% LEL isobutylene (9,000 ppm)

The maximum over-limit reading for the PID is 3,000 ppm (17.5% LEL isobutylene). Readings at or above this concentration are logged at the maximum value.
Correction factors are APPROXIMATE values.

- Correction Factor (CF) is a measure of sensitivity of PID to specific gas.
- CFs do not make PID specific to a chemical, only correct the measurement scale to that chemical.
- CFs allow calibration on inexpensive, non-toxic "surrogate" gas (like isobutylene).
- Most manufacturers furnish tables, or built-in library of CFs to correct or normalize readings when contaminant is known.
- Instrument able to express readings in parts per million equivalent concentrations for the contaminant measured.

Low CF = high PID sensitivity to a gas.

- More toxic the gas, more desirable to have low correction factor:
  - If Exposure limit is < 10 ppm, CF should be < 1
  - If chemical less toxic, higher CF may be acceptable
  - If Exposure limit is > 10 ppm, CF ≤ 10
- When CF > 10 use PIDs as gross leak detectors only.
  - High correction factor magnifies effects of humidity effects, zero drift, and interfering gases and vapors.

Two sensitivities must be understood to make a decision with a PID.

- Human Sensitivity: as defined by AGCIP, NIOSH, OSHA or corporate exposure limits.
- PID Sensitivity: as defined through testing by the manufacturer of your PID.

ONLY USE A CORRECTION FACTOR FROM THE MANUFACTURER OF YOUR PID!
Correction Factors (10.6 eV Lamp)

<table>
<thead>
<tr>
<th>Gas / Vapor</th>
<th>RAE</th>
<th>BW</th>
<th>Ion</th>
<th>GfG</th>
<th>IE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>5.50</td>
<td>4.60</td>
<td>4.90</td>
<td>5.40</td>
<td>10.21</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.20</td>
<td>0.90</td>
<td>0.70</td>
<td>1.20</td>
<td>3.80</td>
</tr>
<tr>
<td>Ammonia</td>
<td>9.70</td>
<td>10.60</td>
<td>8.50</td>
<td>9.40</td>
<td>10.20</td>
</tr>
<tr>
<td>Butane</td>
<td>0.74</td>
<td>0.55</td>
<td>0.39</td>
<td>0.80</td>
<td>1.25</td>
</tr>
<tr>
<td>Butadiene</td>
<td>1.00</td>
<td>0.60</td>
<td>0.20</td>
<td>0.80</td>
<td>2.07</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>0.80</td>
<td>0.94</td>
<td>0.75</td>
<td>0.90</td>
<td>n/a</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.00</td>
<td>13.20</td>
<td>8.70</td>
<td>10.00</td>
<td>10.48</td>
</tr>
<tr>
<td>Ethylene</td>
<td>10.00</td>
<td>11.00</td>
<td>8.80</td>
<td>10.00</td>
<td>10.10</td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.80</td>
<td>0.73</td>
<td>0.60</td>
<td>1.10</td>
<td>n/a</td>
</tr>
<tr>
<td>Hexane</td>
<td>6.90</td>
<td>6.00</td>
<td>3.30</td>
<td>4.50</td>
<td>10.10</td>
</tr>
<tr>
<td>Jet fuel (JP 8)</td>
<td>0.60</td>
<td>0.51</td>
<td>0.20</td>
<td>0.48</td>
<td>n/a</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.52</td>
<td>0.71</td>
<td>0.60</td>
<td>0.73</td>
<td>9.53</td>
</tr>
<tr>
<td>Methyl-ethyl-ketone (MEK)</td>
<td>0.90</td>
<td>0.73</td>
<td>0.47</td>
<td>0.47</td>
<td>8.92</td>
</tr>
<tr>
<td>Naphtha (iso-octane)</td>
<td>1.20</td>
<td>1.20</td>
<td>1.00</td>
<td>1.30</td>
<td>9.82</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>0.40</td>
<td>0.35</td>
<td>0.20</td>
<td>0.40</td>
<td>4.67</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.50</td>
<td>0.71</td>
<td>0.51</td>
<td>0.63</td>
<td>9.92</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.40</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>n/a</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>2.60</td>
<td>2.19</td>
<td>2.00</td>
<td>1.80</td>
<td>10.00</td>
</tr>
<tr>
<td>Vinylidihalon</td>
<td>0.40</td>
<td>0.43</td>
<td>0.10</td>
<td>0.50</td>
<td>8.50</td>
</tr>
</tbody>
</table>

Can I still use a PID even when I need substance-specific readings?

- Broad-range sensors can be calibrated for specific measurable gases, or
- You can choose the correction factor for the desired gas from the on-board library of CF values in the instrument
- Although the sensor will still respond to other measurable gases, readings will be displayed in the correct measurement units and scale
- Alarms should be set at levels which prevent exposure to any of the gases that are potentially present in concentrations that exceed the PEL

PID Alarms: Varying Mixtures

- The Controlling Compound
  - Every mixture of gases and vapors has a compound that is the most toxic and "controls" the setpoint for the whole mixture
  - Determine that chemical and you can determine a conservative mixture setpoint
  - If we are safe for the "worst" chemical we will be safe for all chemicals
Ethanol “appears” to be the safest compound
Turpentine “appears” to be the most toxic
This table only provides half of the decision making equation

### PID Alarms: Varying Mixtures

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>10.6eV CF</th>
<th>NIOSH REL Exposure Limit (8-hr. TWA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>10.0</td>
<td>1000</td>
</tr>
<tr>
<td>Turpentine</td>
<td>0.45</td>
<td>100</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.2</td>
<td>250</td>
</tr>
</tbody>
</table>

- Ethanol “appears” to be the safest compound
- Turpentine “appears” to be the most toxic
- This table only provides half of the decision making equation

Set the PID for the compound with the lowest Exposure Limit (EL) in equivalent units and you are safe for all of the chemicals in the mixture
Divide the EL in chemical units by CF to get the EL in isobutylene

\[
\frac{EL_{ISO}}{EL_{CHM}} = \frac{EL_{CHM}}{CF_{CHM}}
\]

- If you are following the NIOSH REL then ethanol is the “controlling compound” when the exposure limits are expressed in equivalent “Isobutylene Units”
- The equivalent EL_{ISO} is a calculation that involves a manufacturer specific Correction Factor (CF)
- Similar calculations can be done for any PID brand that has a published CF list
- BE CAREFUL: If you are following the TLV the controlling chemical would be turpentine!

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>CF_{10.6eV}</th>
<th>NIOSH REL (8 hr. TWA)</th>
<th>EL_{ISO (PEL)}</th>
<th>TLV® (8 hr. TWA)</th>
<th>EL_{ISO (TLV)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>10.0</td>
<td>1000</td>
<td>100.0</td>
<td>100</td>
<td>100.0</td>
</tr>
<tr>
<td>Turpentine</td>
<td>0.45</td>
<td>100</td>
<td>222.3</td>
<td>20</td>
<td>44.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.2</td>
<td>250</td>
<td>208.4</td>
<td>500</td>
<td>416.7</td>
</tr>
</tbody>
</table>
Choosing the best sensor configuration

- Multi-sensor instruments can include up to seven channels of real-time measurement
- Available sensors for combustible gas and VOC measurement:
  - CC %LEL
  - IR %LEL
  - IR %Vol
  - Thermal Conductivity (TCD) % vol.
  - Electrochemical toxic
  - PID

Response of IR LEL, CC LEL and PID to 7% LEL (560 ppm) turpentine vapor

Response of IR LEL, CC LEL, PID and CO sensors to 15% LEL turpentine vapor
Test run 1: PID, CC LEL, IR LEL and CO sensors exposed to diesel vapor

Selection matrix for Sensors for measurement of combustible gas and VOCs

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>PID</th>
<th>LEL</th>
<th>IR</th>
<th>Mass Spectrometry</th>
<th>Toxicity</th>
<th>Temperature</th>
<th>Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uplift</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Extremely</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes*</td>
<td>Yes**</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Extreme</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Elevated</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes***</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Case Study

- Fuel barge explosion and cleanup
- On February 21, 2003, a fuel barge loaded with gasoline exploded at a fuel loading dock on Staten Island, New York
- Two workers were killed and another critically burned
- The explosion was the result of an accident, not terrorism or sabotage
- The barge had unloaded about half its cargo of 4 million gallons of unleaded gasoline when the explosion occurred
Case Study

- Gasoline was released from the damaged berth area where a section of the aboveground piping ruptured.

USCG photos by PA3 Mike Hvozda

Case Study

- As the blaze was at its height, officials used tugs to push a nearby barge loaded with 8 million gallons of gasoline to the other side of the waterway, where they covered it with water and foam to ensure that it did not explode.

USCG photos by PA3 Mike Hvozda

Case Study

- Once the fire was extinguished and the barges cooled, Marine Chemist and Coast Guard personnel conducted structural inspections.

- Exposure to toxic VOCs was a primary concern.

- Chemicals of concern included the remaining gasoline, benzene, toluene, ethylbenzene, and xylenes) and total polycyclic aromatic hydrocarbons (such as naphthalene).

USCG photos by PA3 Mike Hvozda
What about benzene?

- Benzene is almost never present all by itself
- Benzene is usually minor fraction of total VOC present
- Test for total hydrocarbons (TVOC), especially if the combustible liquid has an established PEL or TLV
  - Diesel 15 ppm
  - Kerosene 30 ppm
  - Jet Fuel (JP-8) 30 ppm
  - Gasoline 300 ppm

Actual toxicity testing results from gasoline fuel barge #1

<table>
<thead>
<tr>
<th>Previous Loadings: Cat Feedstock/Crude Oil/Cat Feedstock</th>
<th>SPACE</th>
<th>% LEL</th>
<th>PPM TVOC (iso)</th>
<th>PPM Benzene</th>
<th>TVOC from benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>No (1) Port Cargo Tank</td>
<td>0</td>
<td>32.8</td>
<td>0.8</td>
<td>2.44%</td>
<td></td>
</tr>
<tr>
<td>No (2) Port Cargo Tank</td>
<td>0</td>
<td>36.2</td>
<td>0.4</td>
<td>1.05%</td>
<td></td>
</tr>
<tr>
<td>No (3) Port Cargo Tank</td>
<td>0</td>
<td>45.5</td>
<td>0.4</td>
<td>0.88%</td>
<td></td>
</tr>
<tr>
<td>No (4) Port Cargo Tank</td>
<td>0</td>
<td>75.8</td>
<td>0.3</td>
<td>0.4%</td>
<td></td>
</tr>
<tr>
<td>No (5) Port Cargo Tank</td>
<td>0</td>
<td>64.3</td>
<td>0.3</td>
<td>0.47%</td>
<td></td>
</tr>
<tr>
<td>No (1) Stbd Cargo Tank</td>
<td>0</td>
<td>34.8</td>
<td>0.6</td>
<td>1.72%</td>
<td></td>
</tr>
<tr>
<td>No (2) Stbd Cargo Tank</td>
<td>0</td>
<td>44.6</td>
<td>0.3</td>
<td>0.67%</td>
<td></td>
</tr>
<tr>
<td>No (3) Stbd Cargo Tank</td>
<td>0</td>
<td>39.6</td>
<td>0.2</td>
<td>0.51%</td>
<td></td>
</tr>
<tr>
<td>No (4) Stbd Cargo Tank</td>
<td>0</td>
<td>58.4</td>
<td>0.4</td>
<td>0.68%</td>
<td></td>
</tr>
<tr>
<td>No (5) Stbd Cargo Tank</td>
<td>0</td>
<td>64.8</td>
<td>0.5</td>
<td>0.77%</td>
<td></td>
</tr>
</tbody>
</table>

TVOC alarm setting based on fractional concentration benzene for Barge #1

- Worst case (No 1 Port Cargo Tank)
  - TVOC hazardous condition threshold alarm of 172 ppm isobutylene would prevent exceeding the PEL for benzene of 1.0 PPM
    \[ 41 \times 0.244 = 1.0004 \text{ ppm} \]
  - TVOC Hazardous Condition Threshold Alarm for compliance with:

<table>
<thead>
<tr>
<th>Benzene Exposure Limit</th>
<th>1.0 PPM</th>
<th>0.5 PPM</th>
<th>0.1 PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVOC alarm setting</td>
<td>41 PPM</td>
<td>20.5 PPM</td>
<td>4.1 PPM</td>
</tr>
</tbody>
</table>
Actual toxicity testing results from gasoline fuel barge #2

<table>
<thead>
<tr>
<th>SPACE</th>
<th>% LEL</th>
<th>PPM TVOC (iso)</th>
<th>PPM Benzene</th>
<th>%TVOC from benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>No (1) Port Cargo Tank</td>
<td>0</td>
<td>37.3</td>
<td>0.0</td>
<td>0 %</td>
</tr>
<tr>
<td>No (2) Port Cargo Tank</td>
<td>0</td>
<td>44.1</td>
<td>0.1</td>
<td>0.23%</td>
</tr>
<tr>
<td>No (3) Port Cargo Tank</td>
<td>0</td>
<td>53.8</td>
<td>0.2</td>
<td>0.37 %</td>
</tr>
<tr>
<td>No (4) Port Cargo Tank</td>
<td>0</td>
<td>48.2</td>
<td>0.1</td>
<td>0.21%</td>
</tr>
<tr>
<td>No (5) Port Cargo Tank</td>
<td>0</td>
<td>68.5</td>
<td>0.4</td>
<td>0.58 %</td>
</tr>
<tr>
<td>No (1) Stbd Cargo Tank</td>
<td>0</td>
<td>13.2</td>
<td>0.0</td>
<td>0 %</td>
</tr>
<tr>
<td>No (2) Stbd Cargo Tank</td>
<td>0</td>
<td>29.0</td>
<td>0.0</td>
<td>0 %</td>
</tr>
<tr>
<td>No (3) Stbd Cargo Tank</td>
<td>0</td>
<td>58.1</td>
<td>0.1</td>
<td>0.17%</td>
</tr>
<tr>
<td>No (4) Stbd Cargo Tank</td>
<td>0</td>
<td>48.7</td>
<td>0.2</td>
<td>0.41 %</td>
</tr>
<tr>
<td>No (5) Stbd Cargo Tank</td>
<td>0</td>
<td>63.3</td>
<td>0.3</td>
<td>0.44%</td>
</tr>
</tbody>
</table>

TVOC alarm setting based on fractional concentration benzene for Barge #2

- Worst case (No 5 Port Cargo Tank)
  - TVOC hazardous condition threshold alarm of 172 ppm isobutylene would prevent exceeding the PEL for benzene of 1.0 PPM
    \[ 172 \times 0.0058 = 0.9976 \text{ ppm} \]
  - TVOC Hazardous Condition Threshold Alarm for compliance with:
    | Benzene Exposure Limit | 1.0 PPM | 0.5 PPM | 0.1 PPM |
    |-----------------------|---------|---------|---------|
    | TVOC alarm setting    | 172 PPM | 86 PPM  | 17.2 PPM|

Questions?

- Thank you!