Capabilities, Limitations and Proper Use of Multi-sensor and Photoionization Detector (PID) Equipped Atmospheric Monitors

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- [www.goodforgas.com](http://www.goodforgas.com)
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  - Software and software updates
  - Data sheets
  - Training materials and presentations
- Application Notes, Technical Notes and Presentations:
  [http://goodforgas.com/support/#appnotes](http://goodforgas.com/support/#appnotes)
- Complete AIHA PDC: Methods and Applications for Chemical Detection Real-Time
Real-Time Detection Equipment Classification

Level 1
Small, Handheld Simple Detectors

Level 2
Small, Handheld Instrumental Detectors

Level 3
Man-portable Detection Systems

Level 4
Transportable Detection Systems

Complexity, Cost, Training Level
Chapter:

1. Introduction
2. The Importance of Real-Time and Near Real-Time Detection Instrumentation for Human Exposure Assessment
3. Colorimetric Detection methods and Devices
4. Photoionization
5. Surface Acoustic Wave (SAW)-Based Instrumentation for Field Detection of Gases and Vapors
6. Ion Mobility Spectrometry
7. Specialized Detectors
8. Field-Portable Fourier Transform (FTIR) Spectroscopy for Gas and Vapor Analysis
9. Field-Portable Gas Chromatography
10. Mass Spectrometry
11. Solid Phase Microextraction
12. The Development and Application of Thermal Desorption - Gas Chromatography for Personal Exposure Assessment and Field Analysis
Analytical Sensitivity

- Controlled by the signal-to-noise ratio of the Analytical Method being used
- Expressed as an MDL -- Minimum Detection Limit
- Analytical requirement determined by the severity of the toxic hazard of the analyte of interest
Selectivity

- The ability of an analytical method to quantify an analyte of interest, even in the presence of interfering, or potentially interfering materials in the atmosphere and its principal components
Repeatability

- *The most difficult parameter to quantify*

- **Affected by:**
  - Analyses by different analysts
  - Analyses using older vs. newer analyzers
  - Analyses using different analytical methods
  - Analyses in different matrices
Accuracy, Precision, & Bias

- **Accuracy:** Agreement between the instrument reading and the true concentration
- **Precision:** Agreement among repeated independent measurements
- **Bias:** A consistent or systematic difference between the true concentration and the measured value
Common Terms

• **Linearity**: Measure of how well an instrument’s concentration-response curve fits the equation for a straight line

• **Linear Range**: The concentration range over which the instrument’s concentration-response curve matches a straight line

• **Dynamic Range**: Concentration range over which the instrument reading changes with a change in concentration of the target analyze
LOD and LOQ

- **LOD:** Limit of detection is the lowest concentration of the target compound that the instrument can reliably detect as different from zero.

- **LOQ:** Limit of quantification is the lowest concentration of the target compound that the instrument can reliably measure.
- **Noise**: Rapid random fluctuations in the instrument signal that are not caused by changes in the concentrations of the target compound.

- **Drift**: Slow long-term changes in the instrument reading that are not caused by changes in the concentrations of the target compound.
Performance Parameters

- **Response Time:** The time between when the sensor is exposed to a step change in concentration and the time when the instrument shows 95% of the final reading

- **Rise Time:** The time between when the sensor reads 10% and 90% of the final reading following a step increase in concentration

- **Recovery Time:** The time between when the sensor is exposed to a step decrease in concentration and the instrument displays 5% of the initial (high) concentration
Performance Parameters

Response of H2S Sensor When Exposed to 25 PPM Gas

- Time to alarm at 10 PPM (2:03) = approximately 7 seconds
- Time to T-90 of 22.5 PPM (2:24) = approximately 28 seconds
- Time to T-100 of 25 PPM (3:42) = approximately 106 seconds
Specificity & Interference

- **Specificity:** The ability to measure one specific compound in the presence of other similar materials.

- **Interference:** Inaccuracy caused by changes in operating conditions or concentrations of compounds other than the target compound.
Specificity & Interference

City Technology 4COSH CO / H₂S and two 4S Rev 2 SO₂ sensors exposed to "Quad Mix" calibration gas with 23 ppm H₂S

Both 4S Rev 2 SO₂ sensors showed same relative response to H₂S of about 5%.
Specificity & Interference

4CM CO, 2CF CO and 4HYT H₂ sensors exposed to 20% LEL (5,000 ppm) acetylene (C₂H₂)

Readings (ppm)

1600
1400
1200
1000
800
600
400
200
0

Time (hh:mm:ss)

15:48:29
15:49:14
15:50:42
15:51:32
15:53:41
15:54:32
15:55:42
15:56:03
15:57:34
15:58:24
15:59:30
16:00:39
16:01:18
16:02:30
16:03:24
16:04:39
16:05:04
16:06:34
16:07:39
16:08:35
16:09:30
16:10:19
16:11:09
16:12:35
16:14:05
16:15:39
16:16:20
16:18:50

Linear range of 2CF CO sensor is 0 - 1,000 ppm. Dynamic range is 0 - 1,500 ppm. Over-limit concentration is about 1,500 ppm.

Linear range of 4CM CO sensor is 0 - 300 ppm. Dynamic range is 0 - 450 ppm. Over-limit concentration is about 450 ppm.

Both the 4CM CO and the 2CF CO sensor went into over-range condition when exposed to 5,000 ppm acetylene. Values at or above the over-range limit of the sensor are logged at this maximum value.

The 4HYT hydrogen sensor showed no response at all to the 5,000 ppm acetylene.
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)
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
Partial Pressure $O_2$ vs. % Vol at Varying Altitudes

<table>
<thead>
<tr>
<th>Height</th>
<th>Atm. Pressure</th>
<th>$PO_2$</th>
<th>Con.</th>
</tr>
</thead>
<tbody>
<tr>
<td>feet</td>
<td>meters</td>
<td>mmHg</td>
<td>mmHg</td>
</tr>
<tr>
<td>16,000</td>
<td>4,810</td>
<td>421.8</td>
<td>88.4</td>
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<td>10,000</td>
<td>3,050</td>
<td>529.7</td>
<td>111.0</td>
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<tr>
<td>5,000</td>
<td>1,525</td>
<td>636.1</td>
<td>133.3</td>
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<tr>
<td>3,000</td>
<td>915</td>
<td>683.3</td>
<td>143.3</td>
</tr>
<tr>
<td>1,000</td>
<td>305</td>
<td>733.6</td>
<td>153.7</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>760.0</td>
<td>159.2</td>
</tr>
</tbody>
</table>

19.5% $O_2$ at sea level = 18 kPa
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 O₂ 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

1. External Moisture Barrier
2. Diffusion Barrier
3. Diffusion Capillary
4. $O_2$ Sensing Electrode
5. Current Collector
6. Separator
7. Current Collector
8. Lead Anode (within electrolyte)
9. Electrolyte
10. Outer casing
11. Connector pins
12. Placement pin
Most $O_2$ sensors have a “capillary pore” used to allow sensor to self-stabilize at new pressure

- $O_2$ sensors with capillary pore are true percent by volume measurement devices
- Are able to self stabilize to changes in pressure due to:
  - Barometric pressure
  - Pressurized buildings
  - Altitude
- Stabilization at new pressure is not instantaneous, may take 30 seconds or longer
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 23.0% is dangerously enriched
Actual readings of oxygen sensor cycled from +20°C to –20°C then back to +20°C

- While temperature dropping O₂ readings slightly high
- Once stabilized at –20°, readings return to 20.9%
- As chamber returned to room temperature O₂ readings slightly depressed
- Once stabilized at room temperature, O₂ readings return to 20.9%
- Most other common sensors (LEL, CO, H₂S) much less affected by temperature
Effects of changes in pressure on $O_2$ sensor readings

- Readings from instrument taken through negative pressure airlock at a nuclear generating station.
- Readings recovered to above 19.5% $O_2$ within 55 seconds.
- $O_2$ sensor took 3.3 minutes to stabilize at 20.5% $O_2$.
- Readings eventually reached 20.9% after about 10.5 minutes.
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%.

![Graph showing O₂ concentration over time](attachment:image.png)
Deliberate displacement of oxygen (inertion) in a fully enclosed vessel

- For every 5% total volume displaced, $O_2$ concentration drops by about 1%

- If 5% of the fresh air in a closed vessel is displaced by methane, the $O_2$ concentration would be about 19.9%

- The atmosphere would be fully explosive while the $O_2$ concentration would still be above the normal alarm setting!
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%

**Effects of CO₂ introduced into a confined space on the concentration of oxygen in the space**

It takes about 67,000 ppm CO₂ (6.7% volume) to displace enough oxygen to cause the concentration to drop below the 19.5% oxygen deficiency alarm threshold.
O$_2$ sensor response to 25% CO$_2$ and 75% N$_2$

Oxygen and carbon dioxide sensors exposed to 25% Vol CO2 in N2

Maximum range of CO2 sensor is 7.5% volume. Values above this concentration logged as 7.5%.

O2 reading rapidly stabilized at zero. Readings rapidly stabilized at 20.9% when sensor returned to fresh air. No overshoot.
Fuel cell type $O_2$ sensor failure mechanisms

- **Lower current output:**
  - All available surface of Pb anode converted to PbO$_2$
  - 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 $O_2$ 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!
• 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: \[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]
  
  Counter: \[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]

- Oxygen generated on counter electrode

- Amount electricity required to remove reaction product and return sensor to ground state (by generating \( O_2 \) 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 $O_2$ reading lower than 20.9% indicates there is too much of some other gas present in the atmosphere.
In this example as O$_2$ reading drops CO concentration rises.
Although $O_2$ 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.
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 interferents 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**
H₂S Sensor:

Hydrogen sulfide is oxidized at the sensing electrode:

\[ H₂S + 4H₂O \rightarrow H₂SO₄ + 8H^+ + 8e^- \]

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

\[ 2O₂ + 8H^+ + 8e^- \rightarrow 4H₂O \]

And the overall reaction is:

\[ H₂S + 2O₂ \rightarrow H₂SO₄ \]

4HS Signal Output: 0.7 μA / ppm H₂S
**H₂S Gas Reaction:**

H₂S Sensing Electrode Reaction: \( H₂S + 4H₂O \rightarrow H₂SO₄ + 8H^+ + 8e^- \)

H₂S Counter Electrode Reaction: \( 2O₂ + 8H^+ + 8e^- \rightarrow 4H₂O \)

**Overall reaction:** \( H₂S + 2O₂ \rightarrow H₂SO₄ \)

**CO Gas Reaction:**

CO Sensing Electrode Reaction: \( CO + H₂O \rightarrow CO₂ + 2H^+ + 2e^- \)

CO Counter Electrode Reaction: \( \frac{1}{2} O₂ + 2H^+ + 2e^- \rightarrow H₂O \)

**Overall reaction:** \( CO + \frac{1}{2}O₂ \rightarrow CO₂ \)

**H₂S signal output:** 775 nA / ppm

**CO signal output:** 80 nA / ppm
Response of H₂S Sensor When Exposed to 25 PPM Gas

- Time to alarm at 10 PPM (2:03) = approximately 7 seconds
- Time to T-90 of 22.5 PPM (2:24) = approximately 28 seconds
- Time to T-100 of 25 PPM (3:42) = approximately 106 seconds

T-zero (1:56)
- **Reducing gas sensor:**
  - $H_2S + 2O_2 \rightarrow H_2SO_4$
  - $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- **Oxidizing gas sensor reaction:**
  - $Cl_2 + H_2 \rightarrow 2HCl$
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
Reducing gases:
- $H_2S$
- CO
- $SO_2$
- $PH_3$

Oxidizing gases:
- $Cl_2$
- $NO_2$
- $O_3$
- $HCl$
- HF
- $ClO_2$
## 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; 30</td>
</tr>
<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

Response of 4HYT hydrogen, and 4COSH and 2CF carbon monoxide sensors exposed to 1,000 ppm hydrogen calibration gas

- Highest reading 4COSH sensor: 330 ppm (= 33% relative response)
- Highest reading 2CF sensor: 56 ppm (= 5.6% relative response)
Notable recent gas and vapor TLV® updates

- Hydrogen sulfide (2010)
- Sulfur dioxide (2009)
- Nitrogen dioxide (2012)
## Exposure limits for H$_2$S

<table>
<thead>
<tr>
<th>OSHA PEL</th>
<th></th>
<th></th>
<th>Acceptable Maximum Peak above Ceiling for an 8-hour shift</th>
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</thead>
<tbody>
<tr>
<td>TWA</td>
<td>STEL</td>
<td>Acceptable Ceiling (C) Concentration</td>
<td>Concentration</td>
</tr>
<tr>
<td>NA</td>
<td>NA</td>
<td>20 ppm</td>
<td>50 ppm</td>
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<table>
<thead>
<tr>
<th>NIOSH REL</th>
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<th>Ceiling</th>
</tr>
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<tbody>
<tr>
<td>TWA</td>
<td>STEL</td>
<td>10.0 ppm</td>
<td>15.0 ppm</td>
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<tr>
<td>10.0 ppm</td>
<td>NA</td>
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<tr>
<th>2009 ACGIH TLV</th>
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<tr>
<td>TWA</td>
<td>STEL</td>
<td>10.0 ppm</td>
<td>15.0 ppm</td>
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<tr>
<td>10.0 ppm</td>
<td>NA</td>
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<th>2010 ACGIH TLV</th>
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<th></th>
<th>Ceiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWA</td>
<td>STEL</td>
<td>1.0 ppm</td>
<td>5.0 ppm</td>
</tr>
<tr>
<td>1.0 ppm</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Are $\text{H}_2\text{S}$ sensors capable of measuring at the new TLV limits?

- The answer is “Yes” BUT with qualifications…..
  
  - Some $\text{H}_2\text{S}$ sensors easily capable of providing readings with 0.1 or 0.2 ppm resolution
  
  - Instrument programming (firmware) must permit setting the alarms at the desired concentration
  
  - May be necessary to update firmware or replace older instrument with a newer model
  
  - Dual channel COSH sensors used to measure both CO and $\text{H}_2\text{S}$ have a smaller measurement signal
  
  - Depends on the manufacturer whether or not the instrument can be used with alarms set to the new TLV
Not all electrochemical $H_2S$ sensors are created equal!

- Different $H_2S$ sensors are optimized for different performance requirements (e.g. cost, life, size, response to interfering contaminants, sensitivity, AND ACCURACY!)

- No single sensor design is equally optimized along all performance dimensions

- The electrical output per ppm of gas varies widely between sensor models:
  
  - City Technology MICROceL™ HS version $H_2S$ sensor has an output signal of $0.105 \pm 0.025 \mu A/ppm$
  
  - City Technology 4HS/LM CiTiceL® version $H_2S$ sensor is optimized for higher sensitivity, and has an output signal of $0.7 \pm 0.25 \mu A/ppm$
So how accurate are the readings?

- **Instrument manufacturers frequently state accuracy of +/- 5% of readings**

- **If the instrument is set to display readings in ± 0.2 ppm increments:**
  
  - From 0 – 4.0 ppm the accuracy is +/- 0.2 ppm; from 4.0 to 100 ppm the accuracy is +/- 5% of reading.

- **If the instrument is set to display readings in ± 0.1 ppm increments:**
  
  - From 0 – 2.0 ppm the accuracy is +/- 0.1 ppm, from 2.0 to 100 ppm the accuracy is +/- 5% of reading
How does the accuracy of the cal gas affect the accuracy of the readings?

- Standard “Quad Mix” cal gas with 20 ppm H₂S is available with ± 3% accuracy, 6-months shelf life dating.

- Using ± 3% accuracy gas means that new accuracy statement for the combined instrument and cal gas system becomes (with standard setup) 0.2 ppm or ± 8% of reading, whichever is greater.

- So from 0 – 2.0 ppm the accuracy is ± 0.2 ppm.
Combined effects of sensor and calibration gas accuracy

Consider the accuracy of an H₂S monitor when:
1. Readings displayed in 0.2 ppm H₂S
2. Linear range of sensor is 0 – 100 ppm H₂S
3. Accuracy of sensor is ± 5% of reading
4. Reading of sensor in fresh air is 0 ppm
5. Gas used to calibrate sensor is 20.0 ppm H₂S
6. Accuracy of the calibration gas is ± 3%

At 10 ppm the accuracy is ± 8% of the reading; = ± 0.8 ppm

At 1.0 ppm, ± 8% of the reading (± 0.08 ppm) is less than the minimum 0.2 ppm resolution of the sensor. Thus, the accuracy at 1.0 ppm = ± 0.2 ppm
Where should practitioners who care about the TLV® set the alarms?

- Concentrations above the TLV® TWA limit permitted as long as balanced by equal amount of time spent below the limit.

- Exposure above the TWA up to the STEL should be less than 15-minutes, should not occur more than four times per day; and any 15-minute interval which exceeds the TWA limit should be separated by at least one hour from the next.

- ACGIH® “Excursion Limit” applies to TLVs® that do not have a STEL.

- Excursions may exceed 3X the TLV® TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5X the TLV® TWA.
Where should you set the $H_2S$ alarms?

- $H_2S$ 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: 10.0 ppm
    - High: 15.0 ppm
    - STEL: 15.0 ppm
    - TWA: 10.0 ppm
  - TLV®:
    - Low: 3.0 ppm
    - High: 5.0 ppm
    - STEL: 5.0 ppm
    - TWA: 1.0 ppm
Exposure limits for SO$_2$

- **OSHA PEL:**
  - TWA = 5.0 ppm

- **NIOSH REL:**
  - TWA = 2.0 ppm
  - STEL = 5.0 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 NO$_2$

- **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
What should you do for extended work shifts?

• Most industrial hygienists use Brief and Scala model
  • Corrects for increased exposure time and decreased recovery time
  • Simple to use
  • Very conservative

• Adjusted TLV =

\[
= \text{TLV} \times \left( \frac{8}{h} \right) \times \left( \frac{24 - h}{16} \right)
\]

Where \( h = \# \) of hours worked per day

• Model used for chemicals where the TLV\(^\circledR\) is based on acute or chronic toxicity and not for chemicals that have a TLV\(^\circledR\) based on irritation (i.e. Ammonia)

• For 12 hour shift according to this model the TWA TLV\(^\circledR\) limit should be reduced to one-half the 8-hour value
Explosive or Flammable Atmospheres
Fire Tetrahedron

- Oxygen
- Fuel
- Chain reaction
- Source of ignition
Different gases have different flammability ranges

<table>
<thead>
<tr>
<th>Fuel Gas</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>1.3</td>
<td>7.1</td>
</tr>
<tr>
<td>Butane</td>
<td>1.8</td>
<td>8.4</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>12</td>
<td>75</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2.7</td>
<td>36</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>3.3</td>
<td>19</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>Gasoline</td>
<td>1.4</td>
<td>7.6</td>
</tr>
<tr>
<td>Kerosine</td>
<td>0.7</td>
<td>5</td>
</tr>
<tr>
<td>Methane</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>MEK</td>
<td>1.8</td>
<td>10</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.1</td>
<td>7.5</td>
</tr>
<tr>
<td>Pentane</td>
<td>1.5</td>
<td>7.8</td>
</tr>
<tr>
<td>Propane</td>
<td>2.1</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>7.0</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.

Diagram:
- Porous refractory bead with catalyst
- Platinum wire coil
- 0.1 mm
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) sublimes
  - Increasing the temperature of the combustible liquid increases the amount of vapor produced
<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 140 °F</td>
<td>Below 200 °F</td>
<td>Aniline, Carbolic acid, Phenol, Naphthalenes</td>
</tr>
<tr>
<td>IIIB combustible liquid</td>
<td>At or above 200 °F</td>
<td></td>
<td>Pine oil</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-Hexane</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>2.3</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>Gasoline (unleaded)</td>
<td>1.2</td>
<td>0.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Catalytic pellistor combustible gas response curves

- Methane
- Hydrogen
- Propane
- Ether
- Acetone
- Butane
- Ethane
- Pentane
- Hexane
- Heptane
- Nonane
- Methanol
- Benzene
- Ethene
- Acetylene
- Ethanol

Reading % LEL vs True LEL Concentration
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:

  \[
  40 \% \text{ LEL} \times 1.25 = 50 \% \text{ LEL}
  \]

<table>
<thead>
<tr>
<th>Instrument Reading</th>
<th>Correction Factor</th>
<th>True Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 % LEL</td>
<td>1.25</td>
<td>50 % LEL</td>
</tr>
</tbody>
</table>
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-Hexane</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.

- **CH4 response**
- **Propane response**

<table>
<thead>
<tr>
<th>True LEL Concentration</th>
<th>Instrument Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% LEL</td>
<td>50% LEL</td>
</tr>
<tr>
<td>20% LEL</td>
<td>20% LEL</td>
</tr>
<tr>
<td>10% LEL</td>
<td>10% LEL</td>
</tr>
<tr>
<td>5% LEL</td>
<td>5% LEL</td>
</tr>
</tbody>
</table>

Response to nonane
Typical catalytic percent LEL sensor response to 50% LEL methane (2.5% vol. CH₄)

$\text{t}_{90} = 14 \text{ seconds}$

$\text{Time to alarm (10% LEL)} = 5 \text{ seconds}$

$\text{t}_0 = 11 \text{ seconds}$
Typical catalytic percent LEL sensor response to 50% LEL pentane (0.7% vol. C$_5$H$_{12}$)

- **t$_{90}$ = 38 seconds**
- **Time to alarm (10% LEL) = 5 seconds**
- **t$_0$ = 11 seconds**

Readings (percent LEL) vs. Time (seconds)
Catalytic combustible sensor exposed to various gases

- **CC 50% LEL hydrogen** (t90 = 8 sec.)
- **CC 50% LEL methane** (t90 = 10 sec.)
- **CC 50% LEL ethylene** (t90 = 16 sec.)
- **CC 50% acetylene** (t90 = 17 sec.)
- **CC 50% LEL ethane** (t90 = 18 sec.)
- **50% LEL propane** (t90 = 22 sec.)
- **CC 50% LEL propylene** (t90 = 24 sec.)
- **CC 50% LEL isobutylene** (t90 = 31 sec.)
- **CC 50% LEL pentane** (t90 = 37 sec.)
- **CC 50% LEL hexane** (t90 = 47 sec.)
- **CC 50% LEL heptane** (t90 = 60 sec.)

**t0 = 23 seconds**
Response to methane over life of sensor

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

CH4 response new sensor

Propane response

CH4 response partially poisoned sensor
Response of new LEL sensor to methane

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

NOTE: Response of new LEL sensor with no known loss of sensitivity to methane. Note that after calibration sensor was properly responsive to hydrogen. The relative response to methane compared to hydrogen was as expected for a new sensor, about 81.6%.
Response of partially inhibited LEL sensor to methane

NOTE: LEL sensor installed was deliberately selected "old" sensor with known partial loss of sensitivity to methane. Note that after calibration sensor was properly responsive to hydrogen, but the relative response to methane compared to hydrogen was only about 39.7%.
### 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>
CC LEL sensor response to 50% LEL methane (2.5% vol. CH\(_4\)), 50% LEL pentane (7.0% vol. C\(_5\)H\(_{12}\)) and 50% LEL "pentane equivalent" (1.25% vol. CH\(_4\))
**Combustible sensor limitations**

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>LEL (Vol %)</th>
<th>Flashpoint Temp (°F)</th>
<th>OSHA PEL</th>
<th>NIOSH REL</th>
<th>TLV</th>
<th>5% LEL in PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.5%</td>
<td>-4°F (-20 ºC)</td>
<td>1,000 PPM TWA</td>
<td>250 PPM TWA</td>
<td>500 PPM TWA; 750 PPM STEL</td>
<td>1250 PPM</td>
</tr>
<tr>
<td>Diesel (No.2) vapor</td>
<td>0.6%</td>
<td>125°F (51.7°C)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>15 PPM</td>
<td>300 PPM</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.3%</td>
<td>55°F (12.8 ºC)</td>
<td>1,000 PPM TWA</td>
<td>1000 PPM TWA</td>
<td>1000 PPM TWA</td>
<td>1,650 PPM</td>
</tr>
<tr>
<td>Gasoline</td>
<td>1.3%</td>
<td>-50°F (-45.6°C)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>300 PPM TWA; 500 PPM STEL</td>
<td>650 PPM</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1.1%</td>
<td>-7°F (-21.7 ºC)</td>
<td>500 PPM TWA</td>
<td>50 PPM TWA</td>
<td>50 PPM TWA</td>
<td>550 PPM</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>2.0%</td>
<td>53°F (11.7°C)</td>
<td>400 PPM TWA</td>
<td>400 PPM TWA; 500 PPM STEL</td>
<td>200 PPM TWA; 400 PPM STEL</td>
<td>1000 PPM</td>
</tr>
<tr>
<td>Kerosene/Jet Fuels</td>
<td>0.7%</td>
<td>100 – 162°F (37.8 – 72.3°C)</td>
<td>None Listed</td>
<td>100 mg/M3 TWA (approx. 14.4 PPM)</td>
<td>200 mg/M3 TWA (approx. 29 PPM)</td>
<td>350 PPM</td>
</tr>
<tr>
<td>MEK</td>
<td>1.4%</td>
<td>16°F (-8.9°C)</td>
<td>200 PPM TWA</td>
<td>200 PPM TWA; 300 PPM STEL</td>
<td>200 PPM TWA; 300 PPM STEL</td>
<td>700 PPM</td>
</tr>
<tr>
<td>Turpentine</td>
<td>0.8</td>
<td>95°F (35°C)</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>20 PPM TWA</td>
<td>400 PPM</td>
</tr>
<tr>
<td>Xylenes (o, m &amp; p isomers)</td>
<td>0.9 – 1.1%</td>
<td>81 – 90°F (27.3 – 32.3 ºC)</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA; 150 PPM STEL</td>
<td>100 PPM TWA; 150 STEL</td>
<td>450 – 550 PPM</td>
</tr>
</tbody>
</table>
Response of electrochemical and LEL sensor to 20,000 ppm hydrogen in nitrogen

EC Hydrogen and CC LEL Sensors Exposed to 20,000 ppm (50% LEL) Hydrogen in Nitrogen

- EC Hydrogen Sensor
- CC LEL Sensor

CC LEL sensor initially responds to gas, but as soon as O₂ trapped within sensor is used up reading rapidly falls to zero.

Once calibration cup remove (interval 100) and O₂ in fresh air begins to reach sensor, remaining H₂ trapped within sensor is oxidized.
Combustible sensor poisons:

- Silicones (by far the most virulent poison)
- Hydrogen sulfide

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.

- 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.)
Effects of hexamethyldisiloxane (HMDS) on pellistor sensor

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

Signal in 20ppm HMDS/2.5% Methane

Time of Exposure (mins)
Effects of silicone filter on LEL sensor performance

Response of IR LEL, CC LEL (with silicone filter) and PID sensors to 5% LEL (2,150 ppm) ethanol in air

Notes:
1. PID was calibrated to isobutylene. The CF<sub>iso</sub> for ethanol is 10.0. PPM readings were converted to ethanol scale %LEL.
2. IR LEL sensor was directly calibrated to 50% LEL hexane (0.6% volume C6H14).
3. CC LEL sensor was directly calibrated to 76% LEL propane (1.6% volume C3H8). The sensor was equipped with silicone and moisture barrier filters.
Effects of silicone filter on LEL sensor performance

Response of IR LEL, CC LEL (no silicone filter) and PID sensors to 5% LEL (1,650 ppm) ethanol in air

Notes:
1. The CC LEL sensor was directly calibrated to 76% LEL propane (1.6% volume C3H8). The silicone and moisture barrier filters were removed from the CC LEL sensor.
2. IR LEL sensor was directly calibrated to 50% LEL hexane (0.6% volume C6H14).
3. PID was calibrated to isobutylene. The CF10 for ethanol is 10.0. PPM readings were converted to ethanol scale %LEL.
• 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

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

- \( I_0 \) is the intensity of the incident light
- \( I_1 \) is the intensity after passing through the material
- \( L \) is the distance that the light travels through the material (the path length)
- \( c \) is the concentration of absorbing species in the material
- \( \alpha \) is the absorption coefficient or the molar absorptivity of the absorber

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
Must have a COVALENT CHEMICAL BOND

Linear molecules: SO
Infrared Spectroscopy

- Geometry of molecule and absorbance of light by specific bonds gives rise to a characteristic IR absorbance “fingerprint” of molecule
Geometry and specific bonds in molecule give rise to IR spectrum

Infrared transmittance spectrum for ethanol
(3800 to 500 cm$^{-1}$ range)
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$_2$
  - Hg$_2$
  - Ar
Infrared transmittance spectra for methane, propane, water (liquid) and carbon dioxide (2.63 μm to 5.0 μm wavelength range)
Wavelengths typically used for IR LEL measurement

Transmittance

3.33 μm
3.4 μm
4.0 μm (reference)

Wavelength (μm)

Ethanol
Propane
Methane
Acetylene
Water vapor
Benzene
LEL measurement at 3.33\(\mu m\) vs. 3.4\(\mu m\)

- 3.33 \(\mu m\) (used with GfG MK231-5 IR sensor)
- 3.4 \(\mu m\) (used with GfG MK232-5 IR sensor)

- Red: Propane \(C_3H_8\)
- Orange: Ethylacetate \(C_4H_8O_2\)
- Blue: Methane \(CH_4\)
- Purple: Toluene \(C_7H_8\)
- Green: Acetylene \(C_2H_2\)
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. C₆H₁₄)

Response of IR LEL sensor unaffected by absence of O₂

Response of CC LEL sensor rapidly drops to zero as O₂ initially trapped within the sensor is consumed
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.

The IR combustible gas sensor was set to the percent volume "HI Range" choice. The IR combustible gas reading rapidly 100% volume CH4 when exposed to 100% volume methane. The oxygen sensor rapidly dropped and stabilized on a reading of 0.0% volume when exposed to the N2 test gas.
• Shape of raw NDIR CH₄ curve (at 3.33 μm) is less linear than other detectable gases

• CH₄ curve can be mathematically corrected (normalized) against the response curves of other gases of interest
Linearized 3.33 μm NDIR combustible gas response curves

Alarm at 20% LEL

- Methane
- Hydrogen
- Propane
- Ether
- Acetone
- Butane
- Ethane
- Pentane
- Hexane
- Heptane
- Nonane
- Methanol
- Benzene
- Ethene
- Acetylene
- Ethanol
Relative response of pellistor and infrared sensors to n-Pentane

CC and IR sensors calibrated to 50% LEL methane (2.5% vol. CH₄) response to 50% LEL pentane (0.7% vol. C₅H₁₂)

- Initial response of IR LEL sensor faster, but time to 90% for CC LEL sensor to 50% LEL pentane was 20 seconds faster than IR LEL sensor.
- Instrument calibrated to 50% LEL methane (CH₄).
- CC sensor relative response to pentane = 0.58
- IR sensor relative response to pentane = 2.2

Readings (percent LEL)
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)
Relative response of pellistor and infrared sensors to propylene ($C_3H_6$) in air

CC LEL and IR LEL combustible gas sensors calibrated to methane (CH$_4$), exposed to 50% LEL propylene ($C_3H_6$) in air

Notes:
1. Relative response of both sensors to propylene ($C_3H_6$) very similar.
2. Both sensors calibrated to 50% LEL CH$_4$ before exposure to 50% LEL C$_3$H$_6$.
3. Resolution of IR LEL sensor is in increments of 0.2% LEL.
4. Resolution of CC LEL sensor is in increments of 0.5% LEL.
5. IR LEL relative response to propylene (compared to methane) is $46\% \text{ LEL} ÷ 50\% \text{ LEL} = 0.92$
6. CC LEL relative response to propylene (compared to methane) is $44.5\% \text{ LEL} ÷ 50\% \text{ LEL} = 0.89$. 

$T_{90}$ IR LEL sensor $= 47$ seconds

$T_{90}$ CC LEL sensor $= 23$ seconds

$T_0$ = 46 seconds
Photoionization Detectors
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 (PID)
- Flame ionization detectors (FID)
- 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>Contaminant</th>
<th>LEL (Vol %)</th>
<th>Flashpoint Temp (°F)</th>
<th>OSHA PEL</th>
<th>NIOSH REL</th>
<th>TLV</th>
<th>5% LEL in PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.5%</td>
<td>-4°F (-20 ºC)</td>
<td>1,000 PPM TWA</td>
<td>250 PPM TWA</td>
<td>500 PPM TWA; 750 PPM STEL</td>
<td>1250 PPM</td>
</tr>
<tr>
<td>Diesel (No.2) vapor</td>
<td>0.6%</td>
<td>125°F (51.7°C)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>15 PPM</td>
<td>300 PPM</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.3%</td>
<td>55°F (12.8 ºC)</td>
<td>1,000 PPM TWA</td>
<td>1000 PPM TWA</td>
<td>1000 PPM TWA</td>
<td>1,650 PPM</td>
</tr>
<tr>
<td>Gasoline</td>
<td>1.3%</td>
<td>-50°F (-45.6°C)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>300 PPM TWA; 500 PPM STEL</td>
<td>650 PPM</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1.1%</td>
<td>-7°F (-21.7 ºC)</td>
<td>500 PPM TWA</td>
<td>50 PPM TWA</td>
<td>50 PPM TWA</td>
<td>550 PPM</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>2.0%</td>
<td>53°F (11.7°C)</td>
<td>400 PPM TWA</td>
<td>400 PPM TWA; 500 PPM STEL</td>
<td>200 PPM TWA; 400 PPM STEL</td>
<td>1000 PPM</td>
</tr>
<tr>
<td>Kerosene/ Jet Fuels</td>
<td>0.7%</td>
<td>100 – 162°F (37.8 – 72.3°C)</td>
<td>None Listed</td>
<td>100 mg/M3 TWA (approx. 14.4 PPM)</td>
<td>200 mg/M3 TWA (approx. 29 PPM)</td>
<td>350 PPM</td>
</tr>
<tr>
<td>MEK</td>
<td>1.4%</td>
<td>16°F (-8.9°C)</td>
<td>200 PPM TWA</td>
<td>200 PPM TWA; 300 PPM STEL</td>
<td>200 PPM TWA; 300 PPM STEL</td>
<td>700 PPM</td>
</tr>
<tr>
<td>Turpentine</td>
<td>0.8</td>
<td>95°F (35°C)</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA</td>
<td>20 PPM TWA</td>
<td>400 PPM</td>
</tr>
<tr>
<td>Xylenes (o, m &amp; p isomers)</td>
<td>0.9 – 1.1%</td>
<td>81 – 90°F (27.3 – 32.3 ºC)</td>
<td>100 PPM TWA</td>
<td>100 PPM TWA; 150 PPM STEL</td>
<td>100 PPM TWA; 150 STEL</td>
<td>450 – 550 PPM</td>
</tr>
</tbody>
</table>
• **PID**s used for measuring solvent, fuel and VOC vapors in the workplace environment

• **PID**s 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 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.
Detection sequence:

1. Neutrally charged molecule diffuses into glow zone

Operation of PID lamp, sensing and counter electrodes

Sensing electrode

Counter electrode

Benzene molecule (neutrally charged)

Reading

---
Detection sequence:

2. Molecule is ionized

Benzene molecule is ionized

Counter electrode

Sensing electrode

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.
Detection sequence:

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

Sensing electrode

Counter electrode

Reading

Neutrally charged molecule diffuses out of detector
Planar "3D" 2-electrode PID design

- **Benefits:**
  - Rapid response and clearing times

- **Limitations:**
  - Gap between window and electrodes increases "quenching" effect of water vapor on signal
  - Potential for drawing particulate contaminants into sensor
  - More ionic fragments left behind to be adsorbed onto electrodes and window

- **Results:**
  - Increased sensitivity to water vapor and humidity
  - Must clean lamp more frequently
3-electrode PID Design

• **Benefits:**
  - Diffusion design includes "fence electrode" to provide mechanical short circuit between sensing and counter electrodes
  - Electrodes housed in replaceable "stack"
  - Diffusion of molecules into and out of glow zone means less ionic fragments or particulates left behind

• **Limitations:**
  - Slightly slower response
  - Operation at higher voltage increases vulnerability to EMI / RFI

• **Results:**
  - Reduced "moisture leakage" response due to humidity
  - Clean lamp less frequently
How does a PID work?
Ionization Energy

- **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**

<table>
<thead>
<tr>
<th>Gas / vapor</th>
<th>Ionization energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon monoxide</strong></td>
<td>14.01</td>
</tr>
<tr>
<td><strong>Carbon dioxide</strong></td>
<td>13.77</td>
</tr>
<tr>
<td><strong>Methane</strong></td>
<td>12.98</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td>12.59</td>
</tr>
<tr>
<td><strong>Oxygen</strong></td>
<td>12.08</td>
</tr>
<tr>
<td><strong>Chlorine</strong></td>
<td>11.48</td>
</tr>
<tr>
<td><strong>Hydrogen sulfide</strong></td>
<td>10.46</td>
</tr>
<tr>
<td><strong>n-Hexane</strong></td>
<td>10.18</td>
</tr>
<tr>
<td><strong>Ammonia</strong></td>
<td>10.16</td>
</tr>
<tr>
<td><strong>hexane (mixed isomers)</strong></td>
<td>10.13</td>
</tr>
<tr>
<td><strong>acetone</strong></td>
<td>9.69</td>
</tr>
<tr>
<td><strong>benzene</strong></td>
<td>9.25</td>
</tr>
<tr>
<td><strong>butadiene</strong></td>
<td>9.07</td>
</tr>
<tr>
<td><strong>toluene</strong></td>
<td>8.82</td>
</tr>
</tbody>
</table>
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>11.83 104.8</td>
<td>1000</td>
<td>Lithium fluoride (LiF)</td>
<td>105 - 5000</td>
</tr>
<tr>
<td>11.62 106.7 500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.6 eV</td>
<td>Krypton</td>
<td>10.64 116.5</td>
<td>200</td>
<td>Magnesium fluoride (MgF₂)</td>
<td>115 - 7000</td>
</tr>
<tr>
<td>10.03 123.6 650</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.8 eV</td>
<td>Krypton</td>
<td>10.03 123.6</td>
<td>650</td>
<td>Calcium fluoride (CaF₂)</td>
<td>125 - 8000</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 $H_2S$)?

- 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 $H_2S$) 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 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.
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 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
CF measures sensitivity

- 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 AGCIH, 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)

#### Examples of manufacturer 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>1.10</td>
<td>0.90</td>
<td>0.70</td>
<td>1.20</td>
<td>9.69</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>Benzene</td>
<td>0.50</td>
<td>0.55</td>
<td>0.50</td>
<td>0.53</td>
<td>9.25</td>
</tr>
<tr>
<td>Butadiene</td>
<td>1.00</td>
<td>0.90</td>
<td>0.85</td>
<td>0.69</td>
<td>9.07</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>0.80</td>
<td>0.93</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>8.00</td>
<td>10.10</td>
<td>10.52</td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.90</td>
<td>0.73</td>
<td>1.10</td>
<td>1.10</td>
<td>n/a</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>4.30</td>
<td>4.00</td>
<td>3.30</td>
<td>4.50</td>
<td>10.18</td>
</tr>
<tr>
<td>Jet fuel (JP-8)</td>
<td>0.60</td>
<td>0.51</td>
<td>0.70</td>
<td>0.48</td>
<td>n/a</td>
</tr>
<tr>
<td>Kerosene</td>
<td>n/a</td>
<td>1.11</td>
<td>0.80</td>
<td>n/a</td>
<td>9.53</td>
</tr>
<tr>
<td>Methyl-ethyl-ketone (MEK)</td>
<td>0.90</td>
<td>0.78</td>
<td>0.77</td>
<td>0.90</td>
<td>9.53</td>
</tr>
<tr>
<td>Naptha (iso-octane)</td>
<td>1.20</td>
<td>1.20</td>
<td>1.10</td>
<td>1.30</td>
<td>9.82</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.40</td>
<td>0.45</td>
<td>0.45</td>
<td>0.40</td>
<td>8.47</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.50</td>
<td>0.53</td>
<td>0.51</td>
<td>0.53</td>
<td>8.82</td>
</tr>
<tr>
<td>Turpentine</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>2.00</td>
<td>2.19</td>
<td>2.20</td>
<td>1.80</td>
<td>10.00</td>
</tr>
<tr>
<td>Xylene (mixed isomers)</td>
<td>0.40</td>
<td>0.50</td>
<td>0.43</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
• 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
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

\[ EL_{\text{Isobutylene}} = \frac{EL_{\text{chemical}}}{CF_{\text{chemical}}} \]
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!
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

G460 Infrared (IR) LEL, Catalytic (CC) LEL and Photoionization Detector (PID)
Response to ≈ 7.0 % LEL (560 ppm) Turpentine Vapor

Notes:
1. The CC LEL sensor was directly calibrated to 50% LEL pentane (0.7% volume C5H12). The silicon and moisture barrier filters were removed from the CC LEL sensor.
2. The IR LEL sensor was directly calibrated to 50% LEL hexane (0.6% volume C6H14).
3. The PID was calibrated to 100 ppm isobutylene. The CF₄₉ for turpentine is 0.3. The LEL concentration for turpentine is 8,000 ppm. The readings were converted to turpentine scale %LEL.
4. The dashed line indicates the OSHA PEL of 100 ppm (= 1.25% LEL)
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>Able to detect LEL range C1 – C5 hydro-carbon gases (methane, ethane, propane, butane, pentane and natural gas)</th>
<th>Able to detect LEL range C6 – C9 hydro-carbon gases (hexane, heptane, octane, nonane)</th>
<th>Able to accurately detect LEL range heavy fuel vapors (e.g. diesel, jet fuel, kerosene, etc.)</th>
<th>Able to detect heavy fuel vapors in low ppm range (e.g. diesel, jet fuel, kerosene, etc.)</th>
<th>Able to use in low oxygen atmospheres</th>
<th>Vulnerable to sensor poisons (e.g. silicones, phosphine, tetraethyl lead, H2S, etc.)</th>
<th>Able to use for high range combustible gas measurement (100% LEL and higher)</th>
<th>Able to measure H2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Pellistor type LEL sensor</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>NDIR combustible gas sensor</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes*</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>PID (with standard 10.6 eV lamp)</td>
<td>No</td>
<td>Yes**</td>
<td>Yes**</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Electrochemical H2 sensor</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Thermal Conductivity Sensor</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes**</td>
<td>No***</td>
<td>Yes</td>
<td>Yes</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
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, total BTEX (benzene, toluene, ethylbenzene, and xylenes) and total polycyclic aromatic hydrocarbons (such as naphthalene).
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

**Previous Loadings: Cat Feedstock/Crude Oil/Cat Feedstock**

<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>32.8</td>
<td>0.8</td>
<td>2.44%</td>
</tr>
<tr>
<td>No (2) Port Cargo Tank</td>
<td>0</td>
<td>38.2</td>
<td>0.4</td>
<td>1.05%</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>
</tr>
<tr>
<td>No (4) Port Cargo Tank</td>
<td>0</td>
<td>75.8</td>
<td>0.3</td>
<td>0.4%</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>
</tr>
<tr>
<td>No (1) Stbd Cargo Tank</td>
<td>0</td>
<td>34.8</td>
<td>0.6</td>
<td>1.72%</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>
</tr>
<tr>
<td>No (3) Stbd Cargo Tank</td>
<td>0</td>
<td>39.6</td>
<td>0.2</td>
<td>0.51%</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>
</tr>
<tr>
<td>No (5) StbdCargoTank</td>
<td>0</td>
<td>64.8</td>
<td>0.5</td>
<td>0.77%</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

\[41 \times 0.0244 = 1.0004 \text{ ppm}\]

- 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

### Previous Loadings: Natural Gasoline (3X)

<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:**

<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>172 PPM</td>
<td>86 PPM</td>
<td>17.2 PPM</td>
</tr>
</tbody>
</table>
• Thank you!