Detecting and measuring atmospheric hazards in underground mines

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Technical support and downloads

- www.goodforgas.com
- Application Notes, Technical Notes and Presentations:  
  http://goodforgas.com/support/appnotes
- Complete AIHA PDC: Methods and Applications for Chemical Detection Real-Time  
Common atmospheric hazards

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

Oxygen (deficiency and enrichment)

- Any area that has an oxygen level of less than 19.5% by volume is considered to be oxygen deficient
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. percent volume 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>
</tr>
<tr>
<td>10,000</td>
<td>3,050</td>
<td>529.7</td>
<td>111.0</td>
</tr>
<tr>
<td>5,000</td>
<td>1,525</td>
<td>636.1</td>
<td>133.3</td>
</tr>
<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
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>20.90%</td>
<td>Normal air concentration</td>
</tr>
<tr>
<td>19.50%</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>

Most O₂ sensors have a “capillary pore” used to allow sensor to self-stabilize at new pressure

- O₂ 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
**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.

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**O\(_2\) concentration in fresh air as function of temperature and humidity**

- O\(_2\) in dry air = 20.95%
- O\(_2\) at 20°C and 25% RH = 20.8%
- O\(_2\) at 40°C and 85% RH = 19.7%
- O\(_2\) at 40°C and 90% RH = 19.5%
- O\(_2\) at 40°C and 100% RH = 19.4%
- What should you do if the instrument is used in high temp, high RH conditions?
- Use cylinder of “Zero Air “ to fresh air adjust the O\(_2\) 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 23.0% is dangerously enriched

Heavy vehicle exhaust hazards

- Exhaust gas from diesel and gasoline engines primarily consists of nitrogen ($N_2$), water vapor ($H_2O$), and carbon dioxide ($CO_2$)
- A relatively small part of the exhaust consists of toxic materials such as:
  - Particulate contaminants (soot)
  - Carbon monoxide (CO) from incomplete combustion
  - Hydrocarbons from unburnt fuel
  - VOCs from incomplete combustion
  - Nitrogen oxides (NOx)
  - Sulfur oxides (SOx) from fuel impurities
Diesel engine exhaust

- By nature, diesel engines run “lean” rather than rich
  - Fuel must be injected, vaporized and heated in order for combustion to occur
  - Diesel engines consume oxygen!
  - When warm, produce very little CO
- Diesel engines produce:
  - Carbon particulates (soot)
  - Hydrocarbons (from unburned fuel)
  - VOCs and other combustion by-products
    - Often adsorbed on particles of soot, increasing danger of respirable particles carrying toxic VOCs deep into lungs
  - Carbon dioxide (CO₂)
  - Oxides of nitrogen (NOx)
    - Especially when the engine is running hot, or in reduced levels of O₂
  - Oxides of sulfur (SOx)
    - Especially when the fuel contains high concentrations of sulfur

An O₂ reading lower than 20.9% indicates there is too much of some other gas present in the atmosphere

July 17, 2013

[Graph showing O₂ and CO readings over time]
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
Effect of displacing gas on oxygen concentration

- Be very cautious when using $O_2$ concentration to estimate concentration of some other displacing gas.
- Every 5% of displacing gas introduced into a confined space reduces $O_2$ concentration by only about 1%.

Measuring specific toxic exhaust gases

- Carbon dioxide ($CO_2$)
  - $CO_2$ is not only an asphyxiant; it is a toxic gas!
- Carbon monoxide (CO)
- Sulfur oxides (SOx)
  - Primary gas of interest is sulfur dioxide ($SO_2$)
- Nitrogen oxides (NOx)
  - Primary gases of interest are nitric oxide (NO) and nitrogen dioxide ($NO_2$)
- Volatile organic chemical (VOC) vapors
**CO₂ Properties**

- Present as a natural component in fresh air (approximately 350 ppm)
- Colorless
- Odorless
- Tasteless
- Heavier than air (density of 1.5 times that of fresh air)
- When released into enclosed space it tends to settle to the bottom
- Because of its tendency to settle, as CO₂ is produced it can reach higher and higher concentrations

**CO₂ exposure symptoms**

- Besides displacing oxygen in fresh air, high concentrations may worsen symptoms related to oxygen deficiency, and interfere with successful resuscitation
- Exposure Symptoms include
  - Headaches
  - Dizziness
  - Shortness of breath
  - Nausea
  - Rapid or irregular pulse
  - Depression of central nervous system
Even moderate concentrations of \( \text{CO}_2 \) can produce symptoms

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Symptom</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 – 400 ppm</td>
<td>Normal background concentration in outdoor ambient air</td>
</tr>
<tr>
<td>350 – 1,000 ppm</td>
<td>Concentrations typical of occupied indoor spaces with good air exchange</td>
</tr>
<tr>
<td>1,000 – 2,000 ppm</td>
<td>Complaints of drowsiness and poor air</td>
</tr>
<tr>
<td>2,000 – 5,000 ppm</td>
<td>Headaches, sleepiness, and stagnant, stale, stuffy air. Poor concentration, loss of attention, increased heart rate and slight nausea may also be present</td>
</tr>
<tr>
<td>&gt;5,000 ppm</td>
<td>Exposure may lead to serious oxygen deprivation resulting in permanent brain damage, coma and even death</td>
</tr>
</tbody>
</table>

\( \text{CO}_2 \) is toxic contaminant with strictly defined exposure limits

- 8-hour TWA limit is 5,000 ppm
- 15-minute STEL limit is 30,000 ppm.
- IDLH concentration is 40,000 ppm
- Concentration of 100,000 ppm leads to loss of consciousness within 15 minutes or less
- High altitude makes symptoms worse!

<table>
<thead>
<tr>
<th>Standard / Country</th>
<th>8-hour Time Weighted Average</th>
<th>15-minute Short Term Exposure Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA NIOSH REL</td>
<td>5,000 ppm</td>
<td>30,000 ppm</td>
</tr>
<tr>
<td>USA OSHA PEL</td>
<td>5,000 ppm</td>
<td>None Listed</td>
</tr>
<tr>
<td>ACGIH® TLV®</td>
<td>5,000 ppm</td>
<td>30,000 ppm</td>
</tr>
</tbody>
</table>
Non-dispersive infrared (NDIR) sensors

- Infrared sensors shine a beam of IR light through a sensing chamber
- Molecules present in the chamber absorb some of the IR
- The rest of the light is transmitted through the chamber without hindrance
- The presence of a chemical group within the molecule determines the wavelengths where IR light is absorbed
- Non-dispersive IR sensors measure at a specific range of wavelengths associated with a particular gas or class of gases

Infrared transmittance spectra for methane, water (vapor) and carbon dioxide (2.63 μm to 5.0 μm wavelength range)
Carbon monoxide

- Colorless
- Odorless
- Slightly lighter than air
- By-product of combustion
- Flammable (LEL is 12.5%)
- Toxic!

Carbon monoxide

- Bonds to hemoglobin in red blood cells
- Contaminated cells can’t transport O₂
- Chronic exposure at even low levels harmful, especially if there are underlying medical conditions, or when there are additional factors (such as heat stress)
**Toxic effects of CO**

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Toxic Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 ppm</td>
<td>TLV exposure limit for 8 hours (TWA)</td>
</tr>
<tr>
<td>200 ppm</td>
<td>Possible mild frontal headaches in 2-3 hours</td>
</tr>
<tr>
<td>400 ppm</td>
<td>Frontal headaches and nausea after 1-2 hours.</td>
</tr>
<tr>
<td>800 ppm</td>
<td>Headache, dizziness and nausea in 45 min. Collapse and possibly death in 2 hours</td>
</tr>
<tr>
<td>1,600 ppm</td>
<td>Headache and dizziness in 20 min. Unconsciousness and danger of death in 2 hours</td>
</tr>
<tr>
<td>3,200 ppm</td>
<td>Headache and dizziness in 5-10 min. Unconsciousness and danger of death 30 min.</td>
</tr>
<tr>
<td>6,400 ppm</td>
<td>Headache and dizziness in 1-2 min. Unconsciousness and danger of death 10-15 min</td>
</tr>
<tr>
<td>12,800 ppm</td>
<td>Unconsciousness immediately, danger of death in 1-3 min.</td>
</tr>
</tbody>
</table>

**Exposure limits for carbon monoxide**

- **OSHA PEL:**
  - 50 ppm 8-hr. TWA
- **NIOSH REL:**
  - 35 ppm 8-hr. TWA
  - 200 ppm Ceiling
- **TLV:**
  - 25 ppm 8-Hr. TWA
Substance-specific electrochemical sensors

- Electrochemical sensors are used to measure CO, SO₂, NO, NO₂, and many other gases
- 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 sensor detection reaction

**CO Sensor:**

**Carbon monoxide is oxidized at the sensing electrode:**

\[
4\text{CO} + 4\text{H}_2\text{O} \rightarrow 4\text{CO}_2 + 8\text{H}^+ + 8\text{e}^-
\]

**Oxygen (from the air) is reduced at the counter electrode:**

\[
2\text{O}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2\text{O}
\]

**Thus the overall reaction is:**

\[
4\text{CO} + 2\text{O}_2 \rightarrow 4\text{CO}_2
\]

**2CF CO sensor signal output:** 50 ± 20 nA / ppm CO
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
Exposure limits for sulfur dioxide $\text{SO}_2$

- **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 $\text{SO}_2$

- **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
Explosive or Flammable Atmospheres

Measuring combustible gases and vapors

April, 2016       Detecting and measuring atmospheric hazards in underground mines        Slide 38
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!
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.

<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 (51.7ºC)</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 (-45.6ºC)</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 (11.7ºC)</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 – 72.3ºC)</td>
<td>None Listed</td>
<td>None Listed</td>
<td>100 mg/M³ TWA; (approx. 14.4 PPM)</td>
<td>200 mg/M³ TWA (approx. 29 PPM)</td>
</tr>
<tr>
<td>MEK</td>
<td>1.4%</td>
<td>16°F (-8.9 ºC)</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 (35ºC)</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 PPM STEL</td>
<td>450 – 550 PPM</td>
</tr>
</tbody>
</table>
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

VOCs are measured with a photoionization detector (PID) sensor
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
Instruments should be tested by exposure to calibration gas on a regular basis!

- Gas detection instruments can only keep miners safe when they are maintained and used properly.
- Mining regulations in the USA, Canada, Europe and South Africa require that gas detectors must be tested at the mine by exposure to known concentration gas before each day’s use.
- No exceptions!

Safest approach is to perform a bump test before each day’s use!

- At this mine, the only way miners can go through the turnstile is with an instrument that has been successfully tested by exposure to gas within the last 24 hours.
- The personally assigned instrument automatically activates the turnstile release, which logs the ID and tracks miners entering and leaving the mine.
Questions?

Thank you for attending!