In spite of the millions of combustible sensor equipped atmospheric monitors in service around the world, there is still a lot of misinformation and misunderstanding when it comes to the performance characteristics and limitations of this very important type of sensor. Understanding how combustible sensors detect gas is critical to correctly interpreting readings, and avoiding misuse of instruments that include this type of sensor.

The potential presence of combustible gases and vapors is one of the most common of all categories of atmospheric hazards. It stands to reason that the sensors used to measure combustible gases are the most widely used type of sensor included in portable atmospheric monitors; especially those used in confined space atmospheric monitoring procedures. In spite of the millions of combustible sensor equipped atmospheric monitors in service in the United States, there is still a lot of misinformation and misunderstanding when it comes to the performance characteristics and limitations of this very important type of sensor. Understanding how combustible sensors detect gas is critical to correctly interpreting readings, and avoiding misuse of instruments that include this type of sensor.

What do percent LEL combustible gas sensors measure?

In order for an atmosphere to be capable of burning explosively, four conditions must be met. The atmosphere must contain adequate oxygen, adequate fuel, a source of ignition, and sufficient molecular energy to sustain the fire chain reaction.

These four conditions are frequently diagrammed as the "Fire Tetrahedron". If any side of the tetrahedron is missing, incomplete or insubstantial; combustion will not occur.

The minimum concentration of gas or vapor in air that will ignite and explosively burn if a source of ignition is present is the Lower Explosive Limit. Different gases and vapors have different LEL concentrations. Below the LEL, the ratio of combustible gas molecules to oxygen is too low for combustion to occur. In other words, the mixture is "too lean" to burn.

Most (but not all) combustible gases and vapors also have an upper limit of concentration beyond which ignition will not occur. The Upper Explosion Limit or UEL is the maximum concentration of combustible gas or vapor in air that will support combustion. Above the UEL, the ratio of gas to oxygen is too high for the fire reaction to propagate. In other words, the mixture is "too rich" to burn. The difference in concentration between the LEL and UEL is commonly referred to as the Flammability Range. Combustible gas concentrations within the flammability range will burn or explode provided that the other conditions required in the fire tetrahedron are met.

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Figure 3: The G460 is able to use wide range of sensors and detection technologies including O₂, standard pellistor LEL, NDIR combustible gas and CO₂, PID and over 23 different substance-specific electrochemical sensors for toxic gas measurement.

Because the flammability range varies widely between individual gases and vapors, most regulatory standards express hazardous condition thresholds for combustible gas in air in percent LEL concentrations.

Most combustible gas instruments read from 0 to 100 % LEL. For this reason, most combustible gas reading instruments also display readings in percent LEL increments, with a full range of 0 – 100% LEL. Typically, these sensors are used to provide a hazardous condition threshold alarm set to 5% or 10% of the LEL concentration of the gases or vapors being measured. Readings are usually displayed in increments of + 1% LEL. Ten percent LEL is the default alarm set point on many instruments.

A fire hazard should always be deemed to exist whenever readings exceed 10 % LEL. This is the least conservative (or highest acceptable) alarm set point for instruments used for monitoring combustible gases and vapors in confined spaces. An important consideration is that many circumstances warrant a more conservative, lower alarm set point. The presence of any detectable concentration of flammable/combustible gas...
in the confined space indicates the existence of an abnormal condition.

The only completely safe concentration of combustible gas in a confined space is 0% LEL. In addition, specific procedures or activities may require taking action at a lower concentration. For instance, the preamble to OSHA 29 CFR 1910.146, “Permit-required confined spaces,” suggests that a maximum “safe for entry” threshold of only 5% LEL should be used for entries conducted according to the “Alternate Entry Procedures” in paragraph (c)(5) of the standard.

**How combustible sensors detect gas**

Most commonly used combustible gas sensors detect gas by catalytically oxidizing or “burning” the gas on an active bead or “pellistor” located within the sensor.

While there are numerous variations, the underlying detection principle has not changed for the better part of a century. The catalytic-bead sensor contains two coils of fine platinum wire which are coated with a ceramic or porous alumina material to form beads.

The beads are wired into opposing arms of a balanced Wheatstone Bridge electrical circuit. One bead is additionally treated with a platinum or palladium-based material that allows catalyzed combustion to occur on the "active" (or detector) bead. The catalyst is not consumed during combustion. Combustion occurs at concentrations far below the LEL concentration. Even trace amounts of gas or vapor in the air surrounding the sensor can oxidize catalytically on the active bead. The "reference" bead in the circuit lacks the catalyst material, but in other respects exactly resembles the active bead.

A voltage applied across the active and reference beads causes them to heat. In fresh air the Wheatstone Bridge circuit is balanced; that is, the voltage output is zero.

The temperature of the active bead must be high enough for the gas to be oxidized. While other gases can be oxidized at lower temperatures, in order to detect detect methane the temperature of the active bead must be 500°C or higher.

If combustible gas is present, oxidation heats the active bead to an even higher temperature. The temperature of the untreated reference bead is unaffected by the presence of gas. Because the two beads are strung on opposite arms of the Wheatstone Bridge circuit, the difference in temperature between the beads is registered by the instrument as a change in electrical resistance.

Heating the beads to normal operating temperature requires power from the instrument battery. The amount of power required is a serious constraint on the battery life of the instrument. Recent sensor designs have attempted to reduce the amount of power required by reducing the size of the beads, sometimes operating the beads at a lower temperature, and...
using discontinuous or pulsed power patterns during periods when the beads are not actually responding to gas. While this approach may result in longer battery life, it may also result in the sensor being easier to poison or inhibit. Since smaller beads contain less catalyst, it takes less exposure to poisons or inhibitors to affect the sensor. It is particularly important to verify the calibration of low power combustible sensors by exposure to known concentration test gas on a regular basis. The combustible sensor elements are usually enclosed in a robust stainless-steel housing.

Gas enters the sensor by first passing through a sintered, stainless steel flame arrestor. The sensor may additionally include external moisture barrier and/or other filters designed to remove specific contaminants (such as silicones or hydrogen sulfide).

The sintered flame arrestor acts as a physical barrier that slows or inhibits the free diffusion of gas molecules into the sensor. The smaller the molecule, the more readily it is able to diffuse.

**Figure 6:** Most catalytic-bead LEL sensors are flame-proof devices housed in a robust, stainless steel housing. A flame arrestor (sinter) prevents energy that could potentially ignite combustible gases from being released by the sensor.

![Graph showing response of catalytic type LEL sensor to various combustible gases](image)

**Figure 7:** Catalytic type LEL sensors used in portable instruments generally show lower relative responses to larger molecules than to smaller. In the example above the response to methane (CH₄) is about two times higher than the response to pentane (C₅H₁₂), and about four times higher than the response to heptane (C₇H₁₆). The response to larger molecules is also much slower. It takes 10 seconds for the methane reading to reach t₉₀ (90% of its final stable response), while it takes a full minute for heptane.
Relative response of a flammable / combustible gas sensor

<table>
<thead>
<tr>
<th>Combustible gas / vapor</th>
<th>Relative response when sensor calibrated to pentane</th>
<th>Relative response when sensor calibrated to propane</th>
<th>Relative response when sensor calibrated to 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>0.65</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>0.75</td>
<td>0.5</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.9</td>
<td>0.7</td>
<td>0.45</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>1.75</td>
<td>1.15</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>1.05</td>
<td>0.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.4</td>
<td>1.05</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>0.35</td>
</tr>
<tr>
<td>Gasoline (unleaded)</td>
<td>1.2</td>
<td>0.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 1: Catalytic pellistor LEL combustible gas sensor response curves. The smallest molecules (CH\(_4\) and H\(_2\)) have the highest relative responses. The largest detectable hydrocarbon molecules (octane and nonane) have the lowest relative responses.

through the flame arrestor, penetrate the sintered surface of the bead, and interact with the catalyst in the oxidation reaction.

Catalytic combustible gas sensors are unable to differentiate between different combustible gases. They provide one signal based on the total heating effects of all the gases capable of being oxidized that are present in the vicinity of the sensor.

Catalytic-bead sensors respond to a wide range of ignitable gases and vapors. The heating effect on the active bead varies between gases. For this reason readings may vary between equivalent concentrations of different combustible gases. As an example, a 50% LEL concentration of pentane provides only about one-half of the heating effect on the active bead of the sensor as a 50% LEL concentration of methane on the same sensor. Another way of expressing this relationship is as a “relative response” of the sensor to pentane. When the instrument is calibrated to methane, the relative response of the sensor to pentane is only 50%. This means that the readings for pentane will be only 50% of the true concentration.

As a general rule, with regards to the catalytic type LEL sensors used in portable instruments, the larger the molecule, the lower the relative response, and the longer it takes for the sensor to reach a final stable reading.

Role of flash point in monitoring of ignitable gases and vapors

In order for combustion to occur, the vapor of the substance must be present in the atmosphere. As a general rule, it’s the vapor, not the liquid that burns. Vaporization is a function of temperature. Increasing the temperature of the liquid increases the rate and amount of vapor that is produced. The flashpoint temperature is the minimum temperature at which a liquid gives off enough vapor to form an ignitable concentration.

Catalytic-bead sensors, at least when operated in the percent LEL range, may not adequately detect “heavy” or long-chain hydrocarbons, or the vapors from high flashpoint temperature liquids such as turpentines, diesel fuel or jet fuel. Use of alternative types of gas detectors, such as a photoionization detector (PID) may be a better approach if you need to monitor for the presence of these types of hydrocarbon vapors. Some manufacturers suggest that their percent LEL sensors should not be used measure volatile aromatic compounds (VOCs) or combustible liquids with flashpoint temperatures higher than 100°F (38°C). Consult the Operator’s Manual, or contact the manufacturer directly to verify the capabilities of the instrument design when using a catalytic-bead LEL sensor to monitor for the presence of these types of contaminants.
Sensor optimization for specific gases

Fixed pellistor sensors are quite a bit different from the low power LEL sensors used in portable instruments. They have much larger beads, (hence they are a lot harder to poison), take a lot more power to operate, and are built in a way that optimizes performance for certain types of detectable gas.

Ways to modify the sensor to optimize it for a specific category of hydrocarbon vapor (like gasoline) include changing the characteristics of the flame arresting sinter to allow larger molecules to penetrate it more easily, leaving out or changing the characteristics of other internal or external filters, making changes to the catalyst used to oxidize gas, changing the porosity of the bead to allow larger molecules to penetrate more readily, and allowing the molecules created by the oxidation of the flammable gas to escape from the sensor more easily.

Large molecules, when they are oxidized, produce a lot more water vapor molecules than smaller hydrocarbon molecules. The catalyzed oxidation reaction proceeds stoichiometrically, is very clean, and in most cases does not produce soot or other by-products of incomplete oxidation. The oxidation of a typical hydrocarbon consumes the molecule of gas, the necessary molecules of oxygen; and produces CO$_2$ and H$_2$O as reaction by-products.

For instance:

Oxidation of methane:  \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

Oxidation of pentane:  \[ \text{C}_5\text{H}_{12} + 8\text{O}_2 \rightarrow 5\text{CO}_2 + 6\text{H}_2\text{O} \]

Oxidation of nonane:  \[ \text{C}_9\text{H}_{20} + 14\text{O}_2 \rightarrow 9\text{CO}_2 + 10\text{H}_2\text{O} \]

Most of the oxidation occurs within the volume of the active bead rather than on the surface. Although oxidation occurs only when the molecules are in physical contact with the catalyst coated surfaces within the bead, the by-products of the reaction, once produced, rapidly diffuse away from the catalyst surface. The very hot CO$_2$ and H$_2$O gas molecules produced by the oxidation reaction regionally attenuate the density of the air within the volume of the bead, allowing the bead to shed heat a little more efficiently, thus reducing the heating effect of the oxidation of the gas on the bead. This translates into a lower signal output, since the temperature of the compensator bead is unaffected (or little effected) by these local changes in atmospheric density.

The water vapor produced by the oxidation of larger molecules creates a significant net outward flux of molecules from the active bead. To oxidize one molecule of methane, three molecules enter the sensor, and three molecules are produced as by-products of the reaction. To oxidize one molecule of pentane, nine molecules enter the sensor, and 11 molecules are produced as by-products. With nonane, 15 molecules enter, but 19 need to leave the sensor.

One way to optimize a sensor for the detection of a large hydrocarbon molecule (like nonane) is to etch the bead a little more deeply, creating larger channels (or “chimneys”) through which the gas diffuses to reach the active sites within the bead. The larger channels facilitate both entry and exit of molecules from the bead. Because the heated molecules produced in the oxidation reaction escape more easily, there is less attenuation of the atmosphere within the volume of the bead, and you see a higher relative response of the sensor to the larger molecules of gas being oxidized.
Changing the characteristics of the active bead has a profound effect on the sensor. The relative response curves for a GfG fixed LEL sensor optimized for “hexane” are very different than the response curves for the “methane” optimized version of the sensor. For instance, the relative response of the methane sensor to pentane is about 50% (just like it is for most portable LEL sensors). However, the relative response of the fixed “hexane” LEL sensor to methane is very close to one to one.

**Catalytic-bead combustible sensors need oxygen to detect gas**

Catalytic-bead sensors require at least eight to ten percent oxygen by volume to detect accurately. A combustible sensor in a 100 percent gas or vapor environment will produce a reading of zero percent LEL. This is the reason that testing protocols for evaluating confined spaces specify measuring oxygen first and then combustible gases and vapors. For this reason confined space instruments that contain catalytic-bead sensors should also include a sensor for measuring oxygen. If the instrument being used does not include an oxygen sensor, be especially cautious when interpreting results. A rapid up-scale reading followed by a declining or erratic reading may indicate that the environment contains insufficient oxygen for the sensor to read accurately. (It may also indicate a gas concentration beyond the upper scale limit for the sensor, the presence of a contaminant which has caused a sudden inhibition or loss of sensitivity in the sensor, or other condition which prevents the sensor or instrument from obtaining proper readings.) The minimum amount of oxygen that must be present for the sensor to detect accurately is a function of design. Capabilities vary from one manufacturer to another. Users who anticipate using their instruments in potentially oxygen deficient environments should contact the manufacturer for assistance.
Calibration and relative response of combustible sensors

A combustible gas sensor may be calibrated to any number of different gases or vapors. Where possible, the user should calibrate the instrument to achieve the level of sensitivity required for the substances to be measured.

Calibration is a two-step procedure. In the first step the instrument is exposed to contaminant free "fresh" air (that is, air which contains 20.9 % oxygen and no combustible gas), turned on, and allowed to warm-up fully. The combustible sensor should read zero. If necessary, the combustible sensor is adjusted to read zero. Instrument manuals and other support materials usually refer to this step as the "fresh air zero."

The second step is to expose the sensor to known concentration calibration gas, and (if necessary) adjust the readings to match the concentration. This is called making a "span adjustment". A "span adjustment" sets the sensitivity of the sensor to a specific gas. Always follow the manufacturer's instructions when calibrating or adjusting the instrument.

Instruments used only for a monitoring a single gas should be calibrated with that particular gas. Calibration choices are more difficult when the instrument may be exposed to a variety of different combustible gases because, as noted previously, equivalent concentrations of different combustible gases may produce different readings.

Gases that produce lower relative readings than the gas used to calibrate the instrument can create a potentially dangerous error.

Catalytic-bead poisons and inhibitors

The atmosphere in which an instrument is used can have an effect on catalytic-bead sensors. Poisoning or degraded performance can occur when combustible sensors are exposed to certain substances. Commonly encountered substances that degrade LEL sensor performance include silicones, lead...
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% Vol. 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>

Table 2: Methane based "equivalent" calibration mixtures can be used to calibrate catalytic LEL sensors to a variety of different gas sensitivity scales

containing compounds (especially tetraethyl lead), sulfur containing compounds, substances containing phosphorus and halogenated hydrocarbons. Combustible sensors can also be affected by exposure to high concentrations of ignitable mixtures.

Any conditions, incidents, experiences, or exposure to contaminants that might adversely affect the combustible sensor should trigger immediate verification of the proper performance of the sensor before continued use. This can be done very simply by flowing known concentration test gas over the sensor, and noting the response. If the readings are accurate, the sensor is safe to use. If the readings are inaccurate or out of calibration, the sensor must be recalibrated before further use.

Potential for loss of sensitivity to methane

Age and usage can affect the sensitivity of combustible sensors. Chronic exposure to low levels of poisons or inhibitors acts cumulatively. This usually means that the sensitivity must be increased when calibration occurs. In the extreme, the sensor may require replacement. This again demonstrates that regular calibration is essential to the safe use of combustible sensors.

For many combustible sensors, if sensitivity is lost due to poisoning, it tends to be lost first with regards to methane. This means that a partially poisoned sensor might still respond accurately to other combustible gases while showing a significantly reduced response to methane. This is a particularly important concern for instruments used to monitor atmospheres associated with confined spaces, where methane is by far the most commonly encountered combustible gas.

There are several calibration strategies used by manufacturers to guard against incorrect readings due loss of sensitivity to methane. The first is to calibrate the instrument using the calibration gas which provides the best level of sensitivity (for instance propane or pentane) and then expose the sensor to a known concentration of methane.

The relative response factor for methane can then be used to verify whether there has been loss of sensitivity. This approach increases the time needed to calibrate the instrument and complicates the logistics. Another problem is what to do if there has been a loss of sensitivity to methane.

The second approach is to calibrate the instrument directly to methane. An instrument "spanned" to methane will continue to detect methane accurately even when loss of sensitivity develops. Spanning the instrument during calibration simply makes up for any loss in sensitivity. However, when the sensor is calibrated with methane, readings for most other substances tend to be lower than actual.
Figure 12: Methane based mixtures can be used to simulate the desired gas sensitivity scale, but remember that the diffusion characteristics of larger gas molecules may change the speed of response of the sensor. Always wait for the readings to stabilize completely before using them as the basis for decisions.

The third approach is to calibrate using methane at a concentration that produces a level of sensitivity equivalent to that provided by the gas of greatest interest. Several manufacturers offer "equivalent" or "simulant" calibration mixtures based on methane, but in concentrations that provide the same span sensitivity as direct calibration using propane, pentane or hexane calibration gas. As previously discussed, 50% LEL pentane produces one-half the heating effect on the active bead in a normally functioning sensor as a 50% LEL concentration of methane.

This also means that if you use a 25% LEL concentration of methane, but "span" adjust the readings to equal 50% LEL while the sensor is exposed to this gas, you wind up with a pentane level of span sensitivity, but since you have used methane to calibrate the instrument, you know that the sensor is still responsive to methane.

The fourth approach now offered by many manufacturers is to include a user selectable library of correction factors in the instrument design. In this case, the user simply calibrates using methane, then selects "pentane" or any other correction factor in the library, and the instrument automatically recalculates readings according to the selected relative response. The benefit of this method, once again, is that since methane is used as the calibration gas, incremental loss of sensitivity to methane simply results in the instrument being "over-
spanned”, or producing higher than actual readings for the gas selected from the library of correction factors.

Calibration verifies that sensors remain accurate. If exposure to test gas indicates a loss of sensitivity, the instrument needs adjustment. If the sensors cannot be properly adjusted, they must be replaced before any further use of the instrument. This is an essential part of instrument ownership.

Figure 13: The catalytic LEL sensors in portable gas detectors should be tested by exposure to known concentration calibration gas before each day's use.