

June 10, 2003

COMBUSTIBLE SENSOR PERFORMANCE

By Robert E. Henderson

IGNITABLE GASES AND VAPORS

The ignitable gases and vapors encountered in confined spaces arise from a number of sources. These can include microbial decomposition, displacement of the atmosphere originally contained in the space by ignitable gases and vapors, residuals from previous uses of the space or emissions from work activity. Sources from previous uses of the space include:

- Vaporization of residual contents (liquids and sludges)
- Products from chemical processes
- Desorption from structural materials

Desorption from vessel walls or other structural elements is a special concern. Desorbed vapors create a number of potential hazards ranging from oxygen displacement to toxic contamination far in excess of exposure limits. Desorption of substances that form ignitable mixtures from the inner walls of vessels is a particular concern. During storage, liquid propane is absorbed into the porous walls of the tank in which it is being held. Following drainage, propane continues to desorb into the atmosphere of the tank.

Many work activities involve the use of organic solvents in a manner that creates highly concentrated mixtures in air. A prime example is spray-painting. Spray-painting creates a suspension of droplets of volatile

liquid, as well as large wetted surfaces on structures. Both are sources of vapor.

A wide variety of ignitable gases and vapors may be encountered during initial evaluation of conditions in a confined space and work activity following initial entry. When present in sufficient concentration, gases and vapors of many substances become ignitable. Following contact with energy provided by suitable ignition sources ignition can occur. Ignition sources present in confined spaces can include hot work activity, sparking tools, lighting, power tools, electrical equipment, or even static electricity.

In order for an atmosphere to be ignitable (i.e. capable of the propagation of flame away from the source of ignition when ignited), 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 or incomplete or insubstantial, combustion will not occur.

Any gas or vapor capable of forming an ignitable mixture when mixed with air or oxygen will ignite at some inherent minimum concentration, provided that the other conditions in the fire tetrahedron are met. An ignitable mixture contains a flammable or combustible substance. The temperature at which there is sufficient

vapor from a flammable substance is less than 38 °C (100 °F). The temperature at which there is sufficient vapor from a combustible substance is between 38 °C (100 °F) and 93 °C (200 °F). The minimum concentration at which a mixture ignitable is the Lower Flammable Limit or LFL. A mixture that will burn also can be made to explode. The term, Lower Explosive Limit or LEL, often is used interchangeably with LFL. While these terms are not equivalent in strictest terms, both will be used interchangeably here to avoid confusion. Below the LFL/LEL the ratio of gas/vapor to oxygen is too low for combustion to occur. Stated in other words, the mixture is "too lean" to burn.

Most (but not all) ignitable gases/vapors also have an upper limit of concentration beyond which ignition will not occur. The Upper Flammable Limit or UFL is the maximum concentration of gas/vapor in air that will support combustion. The term, Upper Explosive Limit or UEL, is often used synonymously with LFL. This convention will be used here. Above the UFL/UEL the ratio of gas/vapor to oxygen is too high for the fire reaction to propagate. Stated in other words, the mixture is "too rich" to burn. The difference in concentration between the LFL/LEL and UFL/UEL is the Flammable Range. Gas/vapor concentrations within the flammable range will burn or explode provided that the other conditions required in the fire tetrahedron are met.

The flammable range varies widely between individual gases and vapors. This partly results from the convention of expressing LFL/LEL and UFL/UEL in percent units rather than in g/m³ (grams per cubic meter). When expressed in the latter units, the LFL/LEL for many substances are similar, averaging around 45 to 50 g/m³. Table 10.3 provides flammability limits for some commonly encountered substances.

Table 4		
Examples of Flammability Limits (NFPA Flammable Liquids, Gases, and Volatile Solids, 1977)		
Substance	LFL/LEL (% Vol.)	UFL/UEL (% Vol.)
acetone	2.6	12.8
acetylene	2.5	100
ammonia	16	25
carbon monoxide	12.5	74
ethylene oxide	3	100
hydrogen	4	75
hydrogen sulfide	4.3	46
methane	5	15
propane	2.2	9.5
From National Fire Protection Association, <i>Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids</i> , NFPA, Boston, 1977		

Flammability limits commonly listed in tables are determined at ambient temperatures and pressures, and at standard atmospheric concentrations of oxygen. Moderate oxygen enrichment exerts a profound effect on the flammability range by dramatically promoting and accelerating combustion.

Flammable/combustible gas and vapor detecting instruments usually read in "percent LEL" rather than "percent by volume". This distinction is extremely important! To illustrate, consider an environment in which an instrument produces a reading of 3 % by volume. If the exact composition of the gas/vapor or mixture producing the reading is known, ignitability of the atmosphere can be determined. On the other hand, if the exact composition of the gas/vapor or mixture producing the reading is not known, ignitability of the atmosphere cannot be determined. If the reading is due to methane,

(since the LEL for methane is 5 % by volume), the concentration is less than the LFL/LEL. If the reading is due to propane, (since the LEL for propane is 2.2 % by volume), the concentration is above the LEL, and a source of ignition could cause a fire or explosion.

Most instruments read from 0 to 100 % LEL. The reason for this is that consensus and regulatory standards use a percent value of the LFL/LEL to impose a margin of safety in hazard management. The most common limits are 5 or 10 % LFL/LEL. Ten percent of LFL/LEL is the default alarm setpoint on many instruments. Figure 3 illustrates the relationship between the "Percent LFL/LEL" scale for a flammable gas or vapor, and the flammability range for the same substance.

A fire hazard should always be deemed to exist whenever readings exceed 10 % LFL/LEL. This is the least conservative (or highest acceptable) alarm setpoint for instruments used for monitoring flammable/combustible gases and mixtures in confined spaces. An important consideration about the setpoint of 10% LFL/LEL is that many circumstances warrant a more conservative, lower alarm setpoint. 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% LFL/LEL.

Most evaluation for ignitable gases and vapors occurs with instruments designed to detect the widest possible variety of mixtures. Evaluations should consider the size of the source, release or emission rate, the distance of the source to the point where ignition could occur and work activity.

Some types of instruments do read concentration in percent by volume flammable/combustible. The most notable example is the methanometer approved for use in MSHA-regulated mines. (MSHA is the Mine Safety and Health Administration.) Readings are always stated in units of percent by volume of methane. Monitoring activities related to "gassy" mines fall under the scope of MSHA regulations. These indicate explicitly the amount of methane that may be permissible. A reading of 5 % methane unambiguously indicates to the instrument operator that the atmosphere is 100 % explosive!

Instruments designed to measure high range flammable/combustible concentrations also read concentration in percent by volume. While the primary purpose of these instruments is to read concentrations higher than the LFL/LEL, when used in lower concentration ranges, concentrations are frequently still provided in percent by volume concentrations. For example, a typical flammable/combustible gas detector used to measure natural gas provides readings on a scale of 0 - 100 % by volume regardless of whether the concentration exceeds the LFL/LEL. At the other extreme, some instruments have a low range scale that reads in parts per million (ppm) of combustible gas. It should be noted that some designs include an auto-ranging feature which displays readings in increments which are appropriate to the concentration encountered. In the case of these designs the same instrument may display readings in ppm, percent LFL/LEL, or percent by volume.

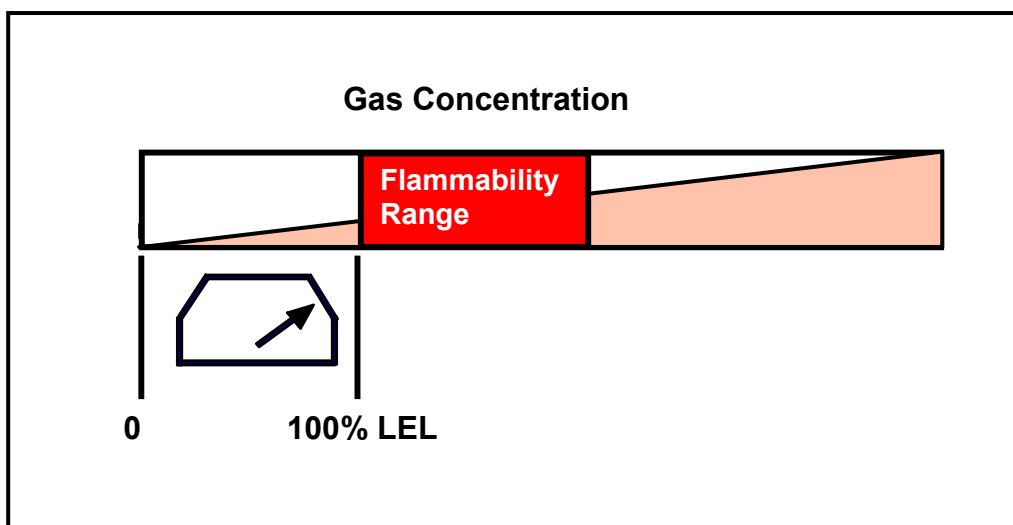


Figure 3 Flammable/combustible gas sensors read in percent LEL.
 (Reprinted courtesy Ergonomics Inc, “Corporate Health and Safety”, 1996)

Role of flash point in monitoring of ignitable gases and vapors

Vapors are the gaseous state of substances that are either liquids or solids at room temperature. Vaporization or evaporation rate, the rate at which the change from liquid or solid to vapor occurs, is a key property in consideration of formation of ignitable mixtures. Vaporization is a function of temperature. Increasing the temperature of the liquid increases the rate and amount of vapor that is produced. Conversely, cooling the atmosphere decreases the amount of vapor produced and may condense vapors back to liquid.

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. The temperature at which sufficient vapor is present for combustion is a key concept in fire protection. This applies especially to confined spaces where boundary surfaces reduce or eliminate the

influence of air currents and the wind in vapor dispersion. Flash point is the minimum temperature at which a liquid gives off enough vapor to form an ignitable concentration. The flash point is the temperature at which the LFL/LEL first occurs. The flash point is an inherent property of the substance. Table 4 lists the flash point for a few common substances.

Table 5		
Examples of Flash Points		
Substance	Flash Point	
	°C	°F
Gasoline (aviation grade) ^a	- 46	- 50
Acetone	- 20	- 4
Methyl ethyl ketone	- 9	16
Ethanol (96%)	17	62
Diesel Oil (#1-D) ^a	38	100
^a Approximate minimum temperatures		
From National Fire Protection Association, <i>Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids</i> , NFPA, Boston, 1977		

The practitioner must consider the flash point of liquids which may be present in the workplace as part of the monitoring strategy.

Diesel oil or turpentine and other substances that have higher flash points may not be detectable at normal room temperature with a flammable/combustible gas indicator that reads in percent LEL. The detector cannot detect until the substance is present in the atmosphere as a vapor at some minimum level.

An extremely important caveat regarding the assessment process is temperature of the substance. Increasing the temperature of the liquid after the initial test can dramatically alter the amount of vapor in the atmosphere. This could occur in various ways:

- Solar heating on surfaces of the structure
- General work activity
- Spot heating during hot work, such as cutting, grinding, welding, gouging, drilling, and so on.

Increasing the temperature sufficiently could provide sufficient vapor for the composition of the atmosphere to enter the flammable range. Lack of attention to this situation has caused many fires and explosions during work activity in confined spaces and during work on the exterior of "empty" containers. Testing must occur under the conditions of work. Testing before work begins in the morning when a structure is cool may not predict the hazard that can arise later in the work shift. At 10 °C (50 °F), ethanol does not produce a sufficient amount of vapor for ignition. At 21 °C (70 °F), vapor generation is sufficient to produce an ignitable mixture. A common concern of individuals attempting to monitor vapor from high flash liquids, such as diesel fuel, is detection by nose but not by the

instrument. The person knows the substance is present because it is clearly nose detectable; yet the combustible gas monitor shows no response in the percent LEL range. Several factors might contribute to this situation. First, the instrument should be directly calibrated to the substance being measured. An instrument calibrated with methane may not be sensitive to vapor from diesel fuel. The fittings, hoses, or tubing used to convey the sample from the environment to the instrument may absorb the vapor. In this case, the vapor may never reach the sensor. Readings would be strongly depressed. There may also be a temperature-related effect. In winter, atmosphere in the space is often warmer than the external environment where the instrument and operator are located. While the atmosphere inside the space may be warm enough for the diesel fuel to exist as a vapor, the vapor may cool sufficiently while being ducted through the sample tubing to recondense into a liquid. The sensor detects only vapors. Another important issue is the resolution of the instrument. An instrument that reads in percent LEL, with readings incremented in 1 % steps, cannot resolve changes in concentration smaller than ± 1 % of LFL/LEL. To illustrate, consider a combustible vapor which has an LFL/LEL of 0.7 % (7,000 ppm). (One percent is 10,000 ppm.) A properly calibrated instrument will only be able to resolve changes that are greater than 70 ppm. Although an individual might be able to smell the substance at 20 ppm, this would be below the detection minimum for the instrument. The instrument reading in this circumstance would probably be zero! It is very important to understand the resolution limits of the equipment being used when monitoring vapor from high flash liquids, such as turpentines, diesel fuel or jet fuel. In many cases percent LEL range instruments are simply not appropriate. Increasingly, many monitoring programs are turning to

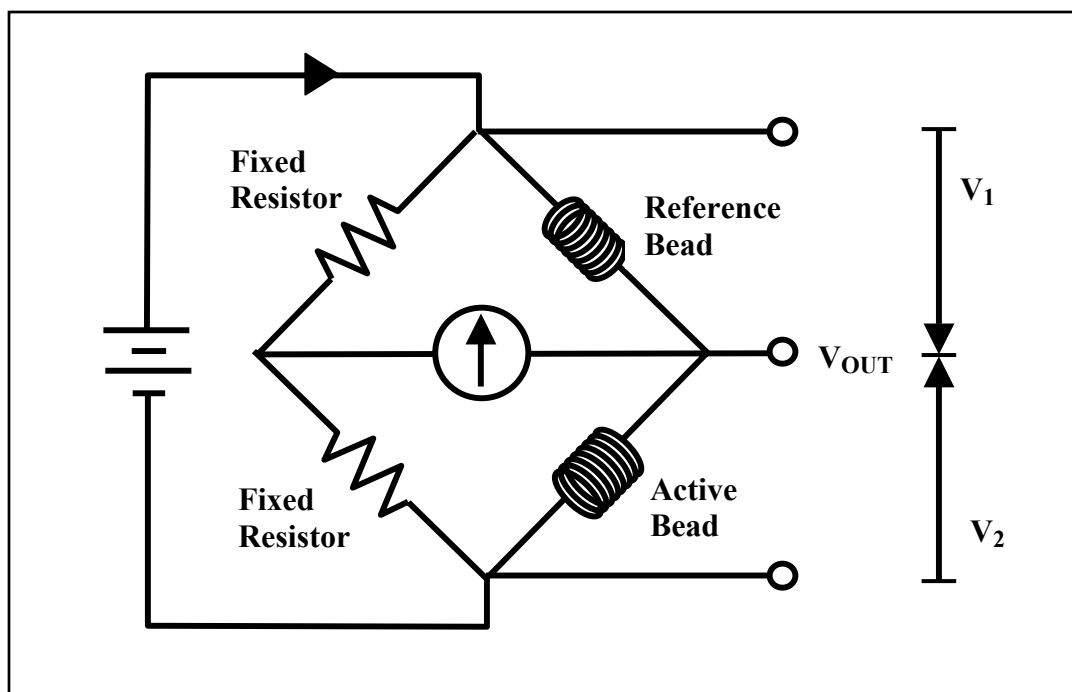


Figure 4 Wheatstone bridge electrical circuit. (Reprinted courtesy Ergonomics Inc, "Corporate Health and Safety", 1996)

photoionization detectors, or use of combustibles sensors operable in the low parts-per-million range when monitoring for high flashpoint combustibles liquid vapors.

An important point to stress in circumstances where the vapor cannot be detected with an instrument that reads in percent LEL is that this is not an indicator of lack of hazard. An instrument that is capable of resolving vapors into the ppm range may be more appropriate. On the other hand, if what is needed is a determination of ignitability, a properly configured and calibrated instrument that reads in percent LEL will provide that information.

Testing at all levels in a confined space during hazard assessment is critical. Gases and vapors that are less dense than air

tend to rise to the top of a structure, while denser than air gases and vapors tend to sink. In confining environments this can lead to stratification of the gases into density dependent layers. Typical low density gases that can form flammable mixtures include hydrogen, methane and ammonia. Typical denser-than-air contaminants that can form ignitable mixtures include propane, hydrogen sulfide and gasoline, and many commonly used organic solvents.

CATALYTIC (HOT BEAD) SENSORS

General discussion

Instruments for monitoring ignitable mixtures most frequently use catalytic (hot bead) sensors. Sensors of this type are

frequently referred to as pellistors. While there are numerous variations, the underlying detection principle has not changed for the better part of a century. The hot bead sensor is a miniature calorimeter that contains two coils of fine platinum wire which are coated with a ceramic or porous alumina material to form refractory 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 treated surface of the "active" (or detector) bead. (Moseley, Solid State Gas Sensors, 1987) It should be noted that the porous or sintered nature of the bead means that the available surface is large compared to the diameter of the bead. The catalyst is not consumed during combustion. Combustion occurs at concentrations far below the LFL/LEL. Trace amounts of gas/vapor in the air surrounding the sensor will oxidize catalytically on the surface of the bead. The "reference" (or compensator) bead in the circuit lacks the catalytic outer coating, but in other respects exactly resembles the active bead. Figure 4 illustrates a simplified version of the Wheatstone Bridge electrical circuit utilized in most catalytic bead type combustible gas sensors. Figure 5 illustrates the structure of the pellistor bead, and Figure 6 illustrates the placement of the beads within the sensor housing and flame-proof stainless steel sinter (or fret).

A voltage applied across the active and reference beads causes them to heat. Heating is necessary for catalytic oxidation to occur. The temperature required may be as high as 500(C, or in some cases, even higher. (City Technology Product Data Handbook, 1997) In normal air the Wheatstone Bridge circuit is balanced; that is, $V_1 = V_2$ and the voltage output (V_{out}) is zero. If ignitable gas/vapor is present, oxidation will heat the active bead to a 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 circuit, the difference in temperature between the beads is registered by the instrument as a change in electrical resistance. Under these conditions, $V_2 > V_1$ and V_{out} is proportional to the amount of oxidation that occurred.

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 operating the sensor at a lower temperature. While this approach may result in longer battery life, it may also result in the sensor being easier to poison or inhibit, since contaminants which might have been volatilized at a higher temperature can more easily accumulate on the surface of the bead. It is particularly important to verify the calibration of low power combustible sensors by exposure to known concentration test gas on a regular basis.

Sensors used to measure combustible gas in the ppm range are usually operated at a higher temperature. Operation at the higher temperature can improve the ability of the sensor to oxidize volatile organic compounds and certain other classes of difficult to detect substances which may not be measurable by means of a low power sensor. For instance, low power sensors may not be used to measure halogenated hydrocarbons such as methylene chloride. Halogenated hydro-carbons are absorbed or form compounds which are absorbed by the catalyst, thus (at least temporarily) reducing or inhibiting the activity of the sensor. On the other hand, some high power combustible gas sensors are capable of being used to measure halogenated hydrocarbons such as methylene chloride or trichloroethylene. Consult the owner's manual or contact the manufacturer directly

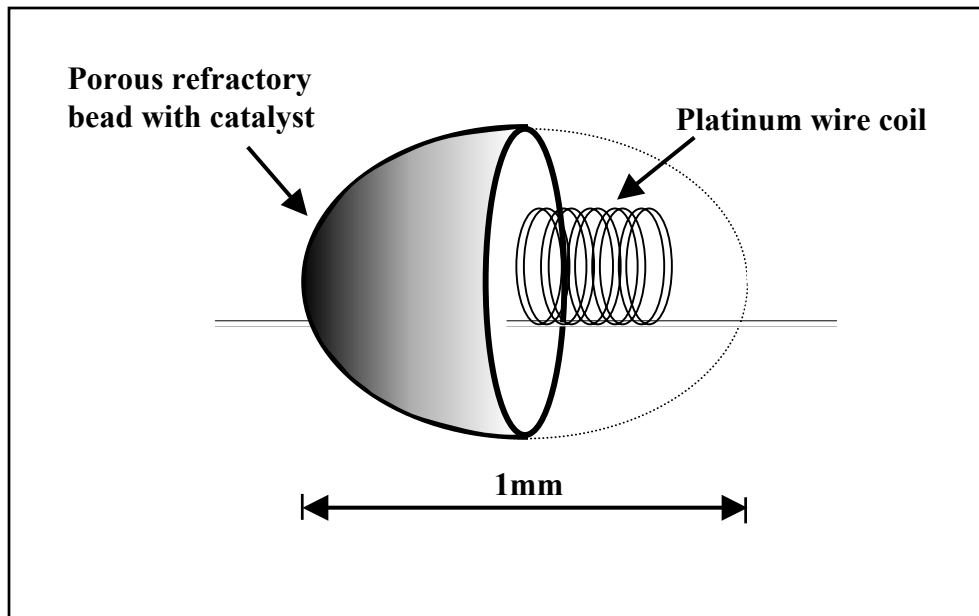


Figure 5 Schematic drawing of a catalytic bead. (Courtesy of City Technology, Ltd. Portsmouth, England)

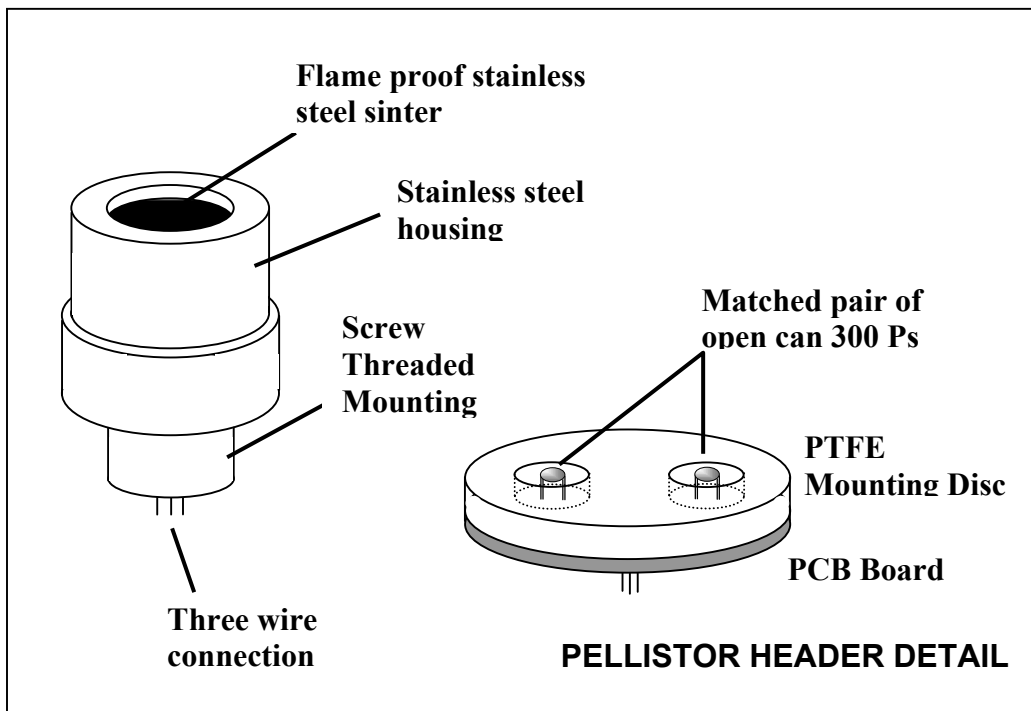


Figure 6 Schematic drawing of combustibile sensor construction. (Courtesy of City Technology, Ltd. Portsmouth, England)

to verify which contaminants may be successfully measured by the sensor prior to use!

A variation on the two bead (active bead / reference bead) theme is the single bead pellistor design. This design utilizes a thermocouple rather than a second bead to provide temperature compensation.

There are numerous other design differences between one brand or model of combustible sensor and another. Each design has been optimized for use in a specific instrument or application. Design differences may be found in the composition of the catalyst, coiling of the filament wire used in the beads, diameter of the filament wire, size and available surface area of the beads, power consumption, resistance to poisoning, and applicability for use in the ppm range. In other words, there may be significant differences in detection capability, power consumption, and general robustness of one design versus another.

An important consideration in use and interpretation of results from instruments equipped with a combustible gas sensor of this type is the concentration of oxygen in the environment being monitored. Catalytic (hot bead) sensors require at least 8 to 10 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 flammable/combustible gas/vapor. For this reason confined space instruments that contain hot 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.

Catalytic hot bead sensors respond to a wide range of ignitable gases and vapors. The amount of heat produced by the combustion of a particular gas/vapor on the active bead will reflect the heat of combustion for that substance. Heat of combustion varies from one substance to another. For this reason readings vary between equivalent concentrations of different combustible gases. Remember that the instrument reads electrical units that depend on change in resistance and not concentration units. The amount of heat provided by oxidation of the molecule on the active bead surface actually is inversely proportional to the heat of combustion for that gas. This occurs because of differences in molecular interaction with the catalytic surface. In general, the larger the size of the molecule the greater the heat of combustion. On the other hand, the smaller the molecule, the more readily it is able to penetrate the sintered surface of the bead, and interact with the catalyst in the oxidation reaction. Catalytic hot 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 flash liquids such as turpentines, diesel fuel or jet fuel. Once again, use of photoionization detectors, or use of combustible sensors operable in the low parts-per-million range

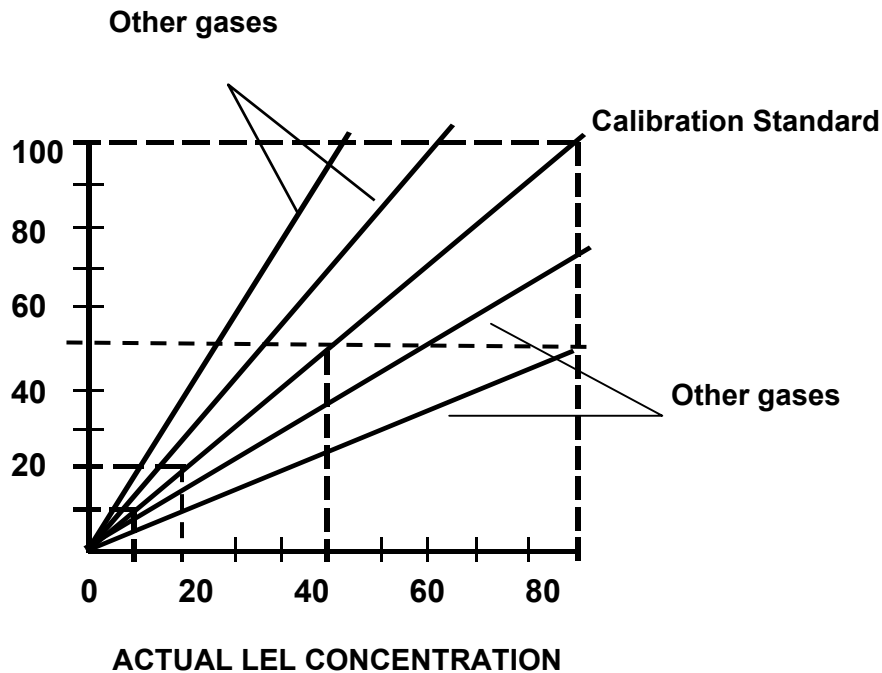


Figure 7 Relative response curves. (Reprinted courtesy Ergonomics Inc, "Corporate Health and Safety", 1996)

may be a better approach. Consult the Operator's Manual, or contact the manufacturer directly to verify the capabilities of the instrument design when using a catalytic hot bead LEL sensor to monitor for the presence of these types of contaminants.

Calibration of these instruments is an important issue. A combustible gas sensor may be calibrated to any number of different gases or vapors. Where possible, the user should calibrate the instrument using the

substance of interest. 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." If the instrument cannot be taken to an area where the air is known to be fresh, "zero air" from a calibration gas cylinder should be used as an alternative source of contaminant-free air.

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. The type and concentration of calibration gas, the flow rate used to introduce gas to the sensors, and the adapters and fittings used during calibration all may affect the accuracy of the calibration procedure.

Never use methods or materials that differ from those described by the manufacturer. Use of incorrect flow rates, fittings, concentration of calibration gas or materials that are incompatible with the gas being used to calibrate the sensor can have a profound affect the accuracy of readings.

The response of a flammable-combustible sensor to an equivalent LEL concentration of gas varies from one substance to another. This is a natural outcome from calibration of these instruments in percent of LFL/LEL, rather than in units of g/m³. Hence, a 50 % LFL/LEL concentration of methane does not produce the same reading as a 50 % LFL/LEL concentration of propane.

Instruments used only for a monitoring a single substance should be calibrated with that substance. An instrument calibrated to a particular substance will be accurate within performance specifications of its design.

Figure 7 shows the response of a typical LEL/LFL reading instrument to several substances. Note that in the case of the gas which was used to calibrate the instrument (the calibration standard), a concentration of 50 percent LFL/LEL produces a meter response (reading) of 50 percent LEL in a properly calibrated instrument. Figure 7 also illustrates what occurs when an instrument is used to monitor substances other than the one to which it was calibrated. The diagram shows the relative response of the instrument to several different substances.

Note that the response to the substance to which the instrument was calibrated is still accurate. For the other substances the responses do not match. In the case of some substances the readings are always too high. The result from this is that the instrument overreacts to conditions and alarms prematurely. This type of error usually is not serious. The most likely result is that workers evacuate the affected area sooner than legally required.

Substances that produce lower relative readings than the calibration standard can create a potentially dangerous error. In Figure 7, the worst case only produces a meter reading of 50 percent LEL when the actual concentration is 100 percent LFL/LEL. If the instrument is set to alarm when the display reads 50 percent LFL/LEL, the alarm would sound simultaneously with a possible fire or explosion. The amount of relative error decreases the lower the alarm point is set. If the instrument is set to alarm when the display reads 20 percent LEL, a 50 percent LFL/LEL concentration of the same gas is enough to cause an alarm. If the alarm point is set to 10 percent LFL/LEL, the

differences due to relative response of the sensor are minimized.

Most regulatory Standards such as OSHA 1910.146, and protocols such as ANSI Z117.1-1995, use 10 percent LFL/LEL as the threshold concentration above which a hazardous condition exists. (OSHA 1993, OSHA 1994, ANSI 1995) Many instruments use 10 percent LEL as the default combustible gas alarm setting. In fact, 10% LEL is the highest or least conservative alarm setpoint which may be used under most regulations and guidelines. This upper limit should not be used as an alarm setting without considerable thought. In its Compliance Directive (CPL 2.100) for Confined Space Entry, OSHA suggests that when entry is made according to the "Alternate entry procedures" specified in paragraph (c)(5)(ii) of 1910.146, a take action threshold of no higher than 5% LEL should be used to terminate entry and initiate evacuation procedures. (OSHA 1995)

Where alarm setpoints and action thresholds are concerned, the primary focus must be to enable work stoppage and safe exit. In some cases where continuous monitoring is occurring, 10% LEL might prove to be a reasonable action level. In other circumstances, the action level is the minimum detection threshold for the instrument being used to monitor for contaminant. Remember that the presence of any measurable ignitable gas/vapor indicates a potential problem.

The curves provided in the Figure 7 are simplified examples. The response of a flammable/combustible sensor is linear over a wide range, but flattens out near the top of its effective range. Standard catalytic (hot bead) sensors are not designed for use in concentrations that exceed the LFL/LEL for the substance being measured. Special techniques must be utilized in order to use catalytic type hot bead sensors in high-range applications.

Table 6

Relative Response of a Flammable/Combustible Sensor

CAUTION: CORRECTION FACTORS LISTED IN THE FOLLOWING TABLE ARE FOR USE ONLY AS EXAMPLES. RELATIVE RESPONSE MAY VARY FROM BRAND TO BRAND, AND OVER THE LIFE OF THE SENSOR. CONSULT MANUFACTURER BEFORE USING ANY RELATIVE RESPONSE FACTOR.

Combustible gas / vapor	Relative response when sensor is calibrated on pentane	Relative response when sensor is calibrated on propane	Relative response when sensor is calibrated on methane
Hydrogen	2.2	1.7	1.1
Methane	2.0	1.5	1.0
Propane	1.3	1.0	0.65
n-Butane	1.2	0.9	0.6
n-Pentane	1.0	0.75	0.5
n-Hexane	0.9	0.7	0.45
n-Octane	0.8	0.6	0.4
Methanol	2.3	1.75	1.15
Ethanol	1.6	1.2	0.8
Isopropyl Alcohol	1.4	1.05	0.7
Acetone	1.4	1.05	0.7
Ammonia	2.6	2.0	1.3
Toluene	0.7	0.5	0.35
Gasoline (Unleaded)	1.2	0.9	0.6

Relative calibration

The accuracy of combustible gas readings will be maximized when the instrument is calibrated using the same gas or vapor that will actually be monitored. When this is not possible or when the substance is an unknown, the user should select an alarm set point of 10 percent LEL or less.

Another approach utilizes the relative response of the sensor when calibrated with one substance and exposed to another. This involves multiplying the actual instrument reading by a correction factor or by using a chart containing the response curve of the sensor to several different substances. Prediction of concentration based on theoretical relative response deserves caution, since the relative response varies from sensor to sensor. In addition, response ratios can change over the life of a sensor. If the substance measured is identified incorrectly, or the wrong correction factor is used, significant inaccuracy in the calculation could occur. This approach is not suitable for mixtures.

Table 6 lists the relative response of a typical flammable/combustible sensor when calibrated to one gas/vapor then exposed to another. Note the difference in the relative responses when the instrument is calibrated to propane or pentane, rather than methane.

It is important to note that the values included in Table 5 are provided as a general example of how this information is typically conveyed, and should not be used as the basis for actual calculations. The sensors used in a particular instrument may or may not have values similar to those shown in Table 5. Even later generations of the same model sensor may exhibit different relative response ratios if the manufacturer has made modifications to the design. Users should consult the owner's manual or contact the manufacturer of the instrument they will be using to verify the correct values to use

when making calculations based on relative response.

As an illustration, consider a detector calibrated on methane that is then used to monitor ethanol. From Table 5 it can be seen that when calibrated on methane, the sensor shows a relative response to ethanol of 0.8. In other words, the readings will be 20% lower than actual.

Some manufacturers provide a table of correction factors rather than relative response ratios for the gas being measured. The correction factor is the reciprocal of the relative response. In the case of our example, the correction factor would be calculated as: $1 / 0.8 = 1.25$. Multiplying the instrument reading by the correction factor for ethanol (as determined above) provides the true concentration. Given a correction factor for ethanol of 1.25, and an instrument reading of 40 percent LEL, the true concentration would be calculated as:

$$40 \% \text{ LFL/LEL} \times 1.25 = 50 \% \text{ LFL/LEL}$$

Instrument Reading	Correction Factor	True Concentration
--------------------	-------------------	--------------------

Note that the correction factor for ethanol is different when the instrument is calibrated on propane. In the case of a propane calibrated instrument, instrument readings for ethanol will be higher than actual. Given that the correction factor for ethanol in this case is $1 / 1.2 = 0.83$, when the instrument reads 40 percent LEL, the true concentration for ethanol is 33 percent LFL/LEL.

$$40 \% \text{ LFL/LEL} \times 0.82 = 33 \% \text{ LFL/LEL}$$

Instrument Reading	Correction Factor	True Concentration
--------------------	-------------------	--------------------

The closer the relative response to 1.0, the more accurate the reading becomes. To illustrate, consider a sensor that is calibrated to propane and then exposed to acetone. The response ratio (1.05) is so close to unity that

for all intents and purposes any error is trivial.

Follow the manufacturer's instructions when selecting the substance to which the instrument will be calibrated. When not sure what substances might be encountered, the best course usually is to use a calibration mixture that provides a broad sensor response. Calibration using other substances should occur in situations where these are predominantly present, or where the relative response closely approximates that of the substance to be measured.

The data in Table 5 indicate that, when an instrument containing this sensor is calibrated with methane, readings for most other substances on the list are dangerously low. On the other hand, when calibrated with pentane, readings for other substances are excessively high. When calibrated with propane, most of the substances on the list produce readings that are close to or slightly higher than actual. For many applications, propane (or a mixture which provides a similar level of sensitivity) is the substance that is most appropriate for calibrating this sensor. Remember that manufacturers that use sensors with different characteristics may offer substantially different advice. Always follow the manufacturer's instructions when deciding which gas to use for calibration.

Prediction of concentration based on theoretical relative response or correction factors deserves caution, since the relative response varies from sensor to sensor. In addition, response ratios can change over the life of a sensor. If the substance measured is identified incorrectly, or the wrong correction factor is used, significant inaccuracy in the calculation could occur. Also, this approach is not suitable for mixtures. It is also very important to understand the method used by a manufacturer to communicate this information. Some manufacturers

communicate this information in the form of tables or graphs of relative response. Others provide this information in the form of tables of correction factors. A number of manufacturers include a built-in library of correction factors in the instrument's on-board memory. This is by far the most "user friendly" method of conveying this information, since readings are automatically converted into corrected equivalent readings for the substance being measured. Still, all the concerns and limitations discussed in the preceding paragraph remain applicable. It is critical to understand which method is used by the manufacturer before attempting to calculate true concentration based on relative response!

Sensor poisons and inhibitors

The atmosphere in which an instrument is used can have an effect on the sensors. Poisoning or degraded performance can occur when sensors are exposed to certain substances. Some commonly encountered substances which degrade LEL/LFL sensor performance are listed in Table 7.

Table 7 Combustible sensor poisons and inhibitors
Combustible sensor poisons:
<ul style="list-style-type: none">• Lead containing compounds (especially tetraethyl lead)• Sulfur containing compounds• Silicones• Phosphates and phosphorus containing substances
Combustible sensor inhibitors:
<ul style="list-style-type: none">• Hydrogen sulfide• Halogenated hydrocarbons (Freons®, trichloroethylene, methylene chloride, etc.)

In the case of some substances, the compounds decompose on the catalyst and form a solid barrier over the catalyst surface. Exposure to substances of this type leads to irreversible loss of sensitivity. A single exposure to a high concentration of a silicone-containing substance can destroy the sensor almost immediately. Other substances are absorbed or form compounds which are temporarily absorbed by the catalyst, inhibiting normal reaction. In the case of these substances the inhibition is usually temporary, and the sensor may substantially recover after a period of operation in fresh air. (City Technology Product Data Handbook, 1997; Moseley, Solid State Gas Sensors, 1987) Exposure to high concentrations of halogenated hydrocarbons can inhibit sensor performance in this way. Exposure to halogenated solvents causes accumulation of halogen molecules on the surface of the catalyst. Running the instrument while the sensor is located in fresh air tends to "cook off" much of the accumulated contamination. Nevertheless, recovery seldom is complete. Usually some permanent loss of sensitivity is a consequence from any exposure to any sensor poison or inhibitor.

Some substances (such as hydrogen sulfide) may function in both ways to degrade performance. Loss of sensitivity usually is dose dependent. A single very high exposure to hydrogen sulfide may produce an immediate irreversible loss in sensitivity. On the other hand, chronic exposure to low levels of hydrogen sulfide may require years to cause a significant loss of sensitivity.

The accuracy of flammable/combustible sensors can also be affected by exposure to high concentrations of ignitable mixtures. Excessive heating of the active bead can volatilize the catalyst coating. This could cause a partial or total loss of

sensitivity. Excessive heating also can cause a break to develop in the filament or circuit wire of the sensor. Exposure to a very high concentration of ignitable gas or vapor (with concurrently low concentrations of oxygen) can lead to deposition of carbon black within the sintered surface of the active bead. Accumulation of carbon black within the bead can cause splitting to occur. This causes a mechanical break in the circuit or significantly alters the sensitivity and stability of the sensor.

To minimize the potential for damage or loss of sensitivity to the sensor, some instruments "alarm latch" whenever the concentration exceeds 100 percent LEL. (This concentration usually is not high enough to damage the sensor permanently.) Under these conditions the instrument will indicate an over-limit condition, and audible and visual alarms will sound continuously. In addition, power to the sensor is cut to prevent damage. Until the over-limit alarms are cleared by manually resetting the instrument, the combustible sensor remains unpowered.

This logic is utilized by a number of manufacturers that have met requirements for classification for intrinsic safety by the Canadian Standards Association (CSA) under their standard for combustible gas detection instruments. (CSA C-22.2 No. 152-M1984) This testing protocol includes a "methane flood" test which evaluates performance of the instrument when exposed to a high concentration of methane. The instrument is turned on, calibrated, and placed for eight hours in a test chamber containing 80 % by volume of methane. This exposure is followed immediately by a test to verify accuracy when the instrument is exposed to 50% LEL of methane. Without the logic discussed above, most flammable/combustible sensors would be quickly destroyed by exposure to 80% by volume of methane.

Loss of sensitivity to methane

Age and usage affect sensitivity of flammable/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 these instruments.

For most combustible (hot bead) 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 propane while showing a significantly reduced response to methane. This introduces a significant concern when choosing the substance to calibrate a flammable/combustible sensor. While sensitivity to propane or pentane may be all that is needed, use of propane or pentane as the only calibrant may lead the user to overlook a loss of sensitivity to methane. This could potentially be very dangerous, since methane is by far the most commonly encountered of all flammable/combustible gases associated with confined space entry.

Four methods exist for determining a loss of sensitivity to methane. The first is to calibrate the instrument using the calibrant which provides the best level of sensitivity (for instance pentane or propane) 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. As discussed, when the sensor is calibrated with methane, readings for most other substances tend to be dangerously low.

The third approach is to calibrate using methane at a concentration that produces a level of sensitivity equivalent to that provided by another calibrant (for instance, propane, pentane, or hexane). Several manufacturers have begun to make use of these "equivalent" or "simulant" calibration mixtures. For the sensor described in Table 5, consider the methane mixture needed to calibrate to a propane level of sensitivity. The LFL/LEL of propane is 2.2 % by volume. In a properly calibrated instrument, a concentration of 1.1 % propane would produce a reading of 50 % LEL. A concentration of 1.62 % methane produces the same response. This is exactly the reading that should be shown in an instrument which has been calibrated for a propane level of sensitivity. Other concentrations of methane may be used to simulate other calibration gases such as pentane, hexane, or even substances (such as jet fuel vapor) which are not easily packaged in field portable cylinders. Since the calibration is based on methane, any loss of sensitivity to methane will result in over-spanning the sensor. Readings for substances other than methane will be a little higher than actual.

The fourth method is applicable only to instrument designs which include a built-in library of correction factors. In this case the instrument is calibrated by using methane, then the user chooses a correction factor (such as propane or pentane) from the instrument's library to provide a level of sensitivity roughly or exactly equivalent to the substances being measured. 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 ownership.

Low range hydrocarbon detectors

Although the primary hazard of most flammable/combustible gases and vapors is fire and explosion, they can pose other hazards. Denser than air gases and vapors can displace oxygen in confining environments. In many circumstances, even when the concentration is less than 10% LFL/LEL, a toxic hazard exists. To illustrate, ethanol (or grain alcohol) has an LEL of 3.3 % or 33,000 ppm. At 10% LFL/LEL, the concentration is 3,300 PPM, a significant toxic hazard exists, since the Threshold Limit Value--Time-Weighted Average is only 1 000 ppm. (ACGIH 1997)

Flammable/combustible gas and vapor instruments that read in the percent LEL range are designed to monitor contamination in the flammable range. In some instruments output from the Wheatstone bridge is electronically multiplied and corrected to produce a reading in various ppm ranges. Typical ranges are:

- 0 to 10,000 ppm (closely equivalent for many substances to the flammable range)
- 0 to 1000 ppm
- 0 to 100 ppm

Obtaining a stable signal from a flammable/combustible sensor that is

operated in the ppm range is not a trivial engineering challenge. The combustible sensors used in these designs have large beads that require considerable power. The sensors operate at higher temperatures in the ppm range than in the percent LEL range. These instruments also have integral sample draw pumps to improve stability.

High range flammable/combustible instruments

Standard catalytic (hot bead) sensors require at least 8 to 10 percent by volume of oxygen to detect accurately. In addition, extremely high concentrations of gas can heat the bead so hot that it becomes cracked or damaged, or suffers a loss of sensitivity due to vaporization of the catalyst. Different approaches are required to measure concentrations that exceed the LFL/LEL.

Thermal conductivity sensors

A thermal conductivity sensor measures flammable/combustible mixtures in the 0 to 100 % by volume range. The sensor contains two coils of fine wire that are coated with a ceramic material to form beads. The beads are strung onto the opposite arms of a balanced Wheatstone bridge circuit. Neither bead receives a catalyst coating. Instead, the reference bead is isolated from the air being monitored in a sealed chamber. The active bead is exposed to the air which containing the gas/vapor mixture. Power is provided to the sensor to heat the beads to operating temperature. Detection depends on the "air-conditioning" effect of high concentrations of gas on the active bead. If a flammable/combustible mixture is present, the active bead will dissipate heat more efficiently than the reference bead. Once again, the difference in temperature between the two beads is proportional to the amount of flammable/combustible present. Since the two beads are strung on the opposite arms of a Wheatstone bridge, the difference in

temperature between the beads is perceived by the instrument as a change in electrical resistance.

A recent innovation is the availability of hot bead sensors which are capable of operation in both catalytic oxidation and thermal conductivity modes. In this type of combustible sensor the catalyst coated active bead is constructed and positioned in the normal way within the sensor, but the compensating reference bead is housed in a semi-sealed chamber which is penetrated by a capillary pore to limit diffusion. During percent LEL range detection readings are obtained in the usual way by catalytic oxidation on the active bead. When operated in thermal conductivity mode, power is cut to the active bead is cut to guard against damage to the bead, while the compensating bead continues to be maintained under power. Once again, the "air-conditioning" effect of the combustible gas on the bead is used to provide a reading.

Oxygen displacement

Several brands of flammable/combustible instruments include a high range mode which allows calculation of combustible gas based on the amount of oxygen which has been displaced by the combustible gas. As combustible gas is introduced into an environment being monitored, more and more of the oxygen is displaced by combustible gas. Readings from an oxygen sensor are used to calculate the combustible gas concentration. Readings are generally given in percent-by-volume concentration with a range of 0 to 100 % combustible gas. Again, it is critical to reiterate the difference between readings displayed in percent LEL versus those displayed as percent by volume. Methane has an LFL/LEL of 5 % by volume. A reading of 5 % by volume is equivalent to a reading of 100 % LEL. In either case, the mixture would be fully explosive.

For maximum accuracy the sensor should be calibrated to the specific combustible gas that will be monitored. In fact, the displacement algorithm may be highly specific to a particular flammable/combustible gas/vapor. For instance, some manufacturers explicitly limit use of this type of high range mode to testing for methane or natural gas. Users should check with the manufacturer before using the instrument to monitor for any flammable/combustible gas/vapor other than those explicitly identified by the manufacturer.

Dilution fittings

As discussed, the accuracy of standard hot bead sensors is affected when used in highly oxygen deficient atmospheres. Below 8 to 10 % by volume (depending on the specific design), the sensor does not have sufficient oxygen to function properly.

A dilution fitting is a sample draw adapter that allows use of a standard hot bead sensor to obtain direct readings from oxygen deficient atmospheres. The adapter includes a dilution orifice designed to mix the gas sample with an equal volume of fresh air. Since fresh air contains 20.9 percent oxygen, the sample would contain at least 10 % oxygen. At this level, the sensor will read accurately.

An important consequence of diluting the sample with fresh air is that the amount of flammable/combustible gas/vapor in the sample also is diluted. Since the adapter provides a 50:50 dilution, the combustible and toxic gas readings must be doubled to obtain the true concentrations.

The adapter should be removed as soon as dilution sampling is completed. Leaving the dilution adapter in place during normal operation can lead to potentially dangerous misinterpretation of test results.

Make sure to locate the instrument in fresh air at all times while the dilution orifice is being used. Only fresh air containing 20.9 % oxygen should be used to dilute the sample. If the dilution adapter is located in an oxygen deficient or otherwise contaminated atmosphere, proper sample dilution will not occur, and accurate readings will not be obtained.

The amount of air drawn into the dilution orifice is affected by the length and inner diameter of the sample draw hose. It is also affected by altitude and the flow rate of the mechanical pump contained in the instrument. Each adapter should be

individually calibrated while attached to the monitor and sample probe assembly that will be used during sampling.

Dilution orifices make possible sampling for flammable/combustible gas/vapor from environments which could not be monitored otherwise. Improper use of dilution orifices can lead to inaccurate readings. These have the potential for being the basis of flawed decisions, a major cause of accidents. Manufacturers are very concerned about the potential for misuse of dilution adapters. Users must clearly understand the limitations before making use of this accessory.