AP 1001:
Choosing the best detection technologies for measuring combustible gas and VOC vapors

No one single sensor (or type of sensor) is capable of detecting all types of dangerous gases and vapors. This is why workers who may be exposed to multiple hazards use instruments with multiple sensors installed.

The most commonly used sensors are for the measurement of combustible gas, oxygen, carbon monoxide and hydrogen sulfide. The majority of multi-sensor instruments are equipped with at least these four sensors. However, in many cases, these basic sensors are not capable of measuring all of the atmospheric hazards that are potentially present.

The sensors utilized in portable gas detectors are extremely good at detecting what they are designed to measure. The problem is that users are frequently unaware of the limitations, and use the sensors in ways that result in inaccurate readings. It is critically important for instrument users to understand what the sensors in their instrument cannot properly measure as well as what they can.

The good news is that there is an extremely wide range of technologies and types of sensors available for use in portable multi-sensor instruments. Just because one type of sensor does not work for a particular gas does not mean there are no alternatives. The only limitation is that the instrument must be sufficiently flexible to make use of the most appropriate detection technologies (Figures 1 and 2).

Oxygen, carbon monoxide and hydrogen sulfide sensors are designed to measure a single type of gas. There is very little ambiguity in the readings these sensors provide. The only

gas an oxygen sensor responds to is oxygen. Electrochemical sensors designed to measure a particular gas may not be quite so specific. Although sensor manufacturers design their products to minimize responsiveness to gases other than the one they are supposed to measure, no design is perfect. For instance, carbon monoxide (CO) sensors may also respond to hydrogen as well as to the vapors produced by alcohols, solvents and other volatile organic chemicals (VOCs). Since most interfering effects are positive, the possibility that the sensor may occasionally provide higher than actual readings for CO is generally not regarded as a safety concern. It just means that workers leave the affected area a little sooner. Similarly, hydrogen sulfide (H_2S) sensor readings can be affected by exposure to degreasers and solvents such as methanol and citrus oil cleaners.

The sensor with the most important limitations is the traditional "catalytic" or "pellistor" type percent lower explosive limit (% LEL) combustible gas sensor. 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.

Figure 1: Flexibility to support the needed sensors is critical! The G460 Multi-sensor Atmospheric Monitor from GfG Instrumentation is capable of measuring up to six different atmospheric hazards at the same time.

How combustible sensors detect gas

Understanding how combustible sensors detect gas is critical to correctly interpreting readings, and avoiding misuse of instruments that include this type of sensor. 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. The "active" bead is treated with a platinum or palladium-based catalyst that facilitates the oxidation of combustible gas on the bead. A "reference" bead in the circuit that has not been treated with catalyst provides a comparison value.

As oxidation occurs the active bead is heated to a higher temperature. Since heating due to oxidation of the combustible gas only occurs on the active bead, the difference in temperature between the two beads is proportional to the concentration of gas in the area where the sensor is located. 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.

Catalytic-bead sensors respond to a wide range of ignitable gases and vapors, but 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. The heating effect or "relative response" of the sensor varies from gas to gas. Generally speaking, the larger the molecule, the lower the relative response. For instance, when a pellistor type LEL sensor that has been calibrated for the measurement of methane (CH_4) is exposed to 50% LEL CH_4, the instrument shows a reading of 50% LEL. However, if that same instrument is exposed to 50% LEL pentane, (C_5H_{12}) it will show a reading of only about 25% LEL.

Pellistor type sensors generally include a flame arrestor that can slow, reduce or prevent larger sticky hydrocarbon molecules from entering the sensor. Small combustible gas molecules like hydrogen (H_2), methane and propane (C_3H_8) diffuse through the flame arrestor very rapidly. (Figure 3)

The larger the molecule, the slower it diffuses through the flame arrestor into the active bead in sensor where it is oxidized. Figures 4 and 5 show the difference in the time it takes for the same pellistor LEL sensor to respond to methane (CH_4) compared to hexane (C_6H_{14}). Saturated hydrocarbons larger than nonane (C_9H_{20}) are unable to penetrate the flame arrestor and bead in appreciable quantities. Traditional pellistor type LEL sensors should not be used to measure hydrocarbon gases larger than nonane in size. To put this in perspective, less than 4% of the molecules in a bucket of diesel fuel are small enough to be detected by the sensor. This is one of the reasons that LEL sensors show such a low response when exposed to the vapors of "heavy" fuels such as diesel, kerosene, jet fuel and heating oil.

Although most VOC vapors are combustible, the toxic exposure limits are much lower than the flammability limits. For example, for diesel fuel 10% LEL is equal to about 600 ppm vapor. However, the TLV® (Threshold Limit Value®) for diesel vapor is only 15 ppm (as an 8 hour TWA). If you wait for the combustible gas alarm to go off at 10% LEL you could potentially exceed the toxic exposure limit by 40 times! Clearly,

Figure 2: Multi-sensor instruments are able to use a wide range of sensors and detection technologies including O₂, standard pellistor LEL, NDIR combustible gas and CO₂, PID and over 20 different substance-specific electrochemical sensors for toxic gas measurement.

from a toxic exposure limit standpoint a different detection technique is required.

Another limitation of pellistor type sensors is that they require the presence of oxygen in order to oxidize the gas being measured. Most manufacturers stipulate that the atmosphere must contain at least 10% O_2 in order for the LEL sensor to detect gas accurately. Readings are increasingly affected as the concentration drops below this level. In zero percent O_2 pellistor type combustible sensors cannot detect gas at all. For this reason confined space instruments that contain catalytic pellistor type LEL sensors should also include a sensor for measuring oxygen.

Another concern is loss of sensitivity due to the age and usage of the sensor. Catalytic bead sensors are easily damaged or destroyed by exposure to sensor "poisons" such as silicones, phosphine (PH_3) and high concentrations of H_2S.

Fortunately, there are alternative detection techniques that are not affected by these constraints. It is important to note that these alternative types of sensors should not be seen as replacements for the pellistor sensor. Pellistor sensors are still the best and most cost effective solution for many applications. It is also true, however, that in many cases the best approach is to include one or more additional types of sensor in the instrument.

GfG Application Note 1018, *"Combustible sensor performance"* discusses the technology, limitations and use of catalytic LEL sensors in greater detail. The note is posted on www.goodforgas.com at the following link: http://goodforgas.com/wp-content/uploads/2013/12/AP1018_Combustible-sensor-performance_6_30_13.pdf
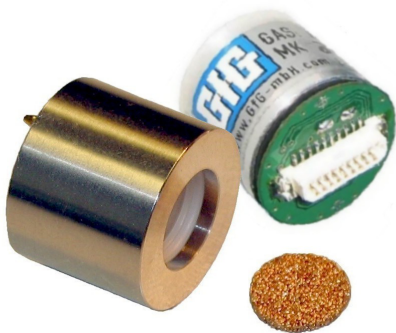

Figure 3: Pellistor type LEL sensor with flame arrestor (sinter) removed from stainless steel housing
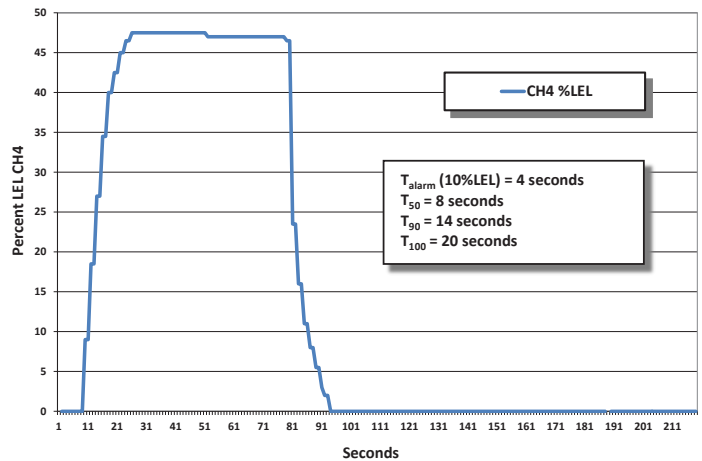

Figure 4: Pellistor type LEL sensor response to 50% LEL methane (2.5% Volume). Note that the "time to alarm" (10% LEL) is about 4 seconds.

What other types of sensors are available for combustible gas and VOC measurement?

The major alternatives for combustible gas and VOC measurement are thermal conductivity detectors (TCDs), photoionization detectors (PIDs) and non-dispersive infrared (NDIR) sensors.

• **Thermal conductivity (TCD) sensors**

Thermal conductivity sensors are a specialized type of sensor most frequently used to detect high range concentrations of combustible gas.

Thermal conductivity sensors are capable of measuring combustible gas in concentrations up to 100% by volume. 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 is treated with a catalyst. Instead, the reference bead is isolated from the air being monitored in a sealed or semi-sealed chamber. The active bead is exposed to the atmosphere being monitored for gas. 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 lighter than air combustible gas is present (such as hydrogen or methane), the active bead will dissipate heat in the attenuated atmosphere more efficiently than the reference

bead. If a heavier than air gas is present (such as propane) the bead is insulated by the denser atmosphere. Once again, the difference in temperature between the two beads is proportional to the amount of combustible gas present in the atmosphere being monitored.

Some pellistor type sensors 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 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 it is the "air-conditioning" effect of the combustible gas on the compensating bead that is used to provide a reading.

TCD type sensors are often paired with a pellistor type sensor in the same instrument. The pellistor sensor (or mode) is used for 0 – 100% LEL range measurement, while the TCD is used for high range 0 – 100% volume measurement. In fact, a common approach is to put both types of sensor into a single housing that shares the same flame arrestor and certification as a flame proof device.

The chief limitation of TCD sensors is the effect that changes in the makeup of the air being tested can have on readings. TCD sensors are not recommended for use in confined spaces where there is the potential for oxygen deficiency. The "air conditioning" effect of combustible gas on the active bead in the sensor is significantly different when the gas is present in fresh air than when the gas is present in oxygen deficient air, or air that contains elevated concentrations of nitrogen or carbon dioxide. It is also difficult to use TCD sensors to measure the concentrations of mixtures of combustibles gases. Changes in the relative concentrations of the gases in the mixture can change the heating or cooling effect on the sensor, affecting the accuracy of readings.

Another issue is the damaging effect sensor poisons and / or high concentrations of gas can have on the pellistor sensor, or on the TCD sensor if it includes a catalytic pellistor bead or is operable in a catalytic LEL detection mode.

Pellistor type LEL and TCD sensors are usually constructed and certified as "flame proof" devices. Flame proof sensor designs depend on physical barriers such as robust stainless steel housings and flame arrestors to limit the amount of
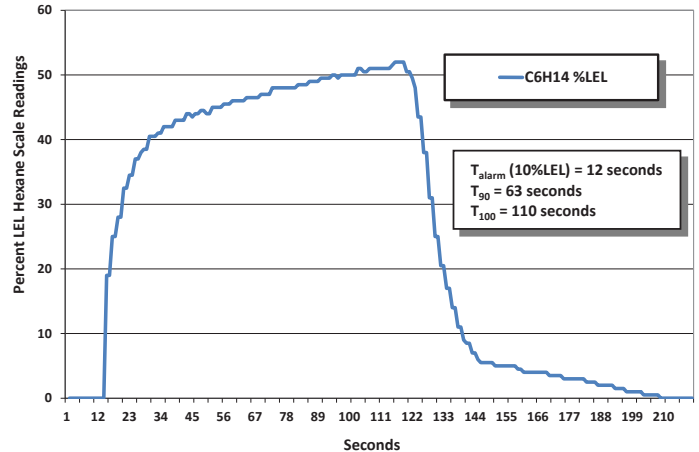

Figure 5: Pellistor type LEL sensor response to 50% LEL hexane (0.6 % Volume). Note that the "time to alarm" (10% LEL) is about 12 seconds.

energy that can ever be released by the sensor. Even under catastrophic failure conditions (i.e. a "flame" on the inside of the sensor) the sensor is incapable of releasing enough energy to be the source of ignition when located in a fully combustible atmosphere. Flame proof sensors can be certified as safe for use in different categories or "gas groups" of combustible gases. Most flame proof sensors installed in instruments sold in North America are Certified for use in Class I, Division 1, Gas Groups A, B, C and D Hazardous Locations. The indicator gas for the most highly explosive "Group A" category is acetylene.

Even though TCD sensors are not dependent on the ability of the gas to penetrate the bead in order to be oxidized and detected, the gas still has to diffuse through the flame arrestor in order to be detected. TCD sensors (as well as other types of sensors that include or share a flame arrestor) are subject to the same limitations as catalytic LEL sensors regarding the diffusion of molecules through the sinter into the sensor. The larger the molecule, the slower it diffuses through the flame arrestor into the sensor. Heavy and sticky hydrocarbon molecules larger than nonane (C_9H_{20}) may be held out entirely.

It is alternatively possible to design and certify sensors as "intrinsically safe" devices.   Intrinsically safe devices are incapable of producing or releasing enough energy to be the source of ignition for a flammable concentration of gas. Because they are intrinsically safe it is not necessary to include a flame arrestor in their designs. As long as the combustible gas molecules are present in the form of a vapor, they are capable of entering the sensor and (depending on the type of molecule) being measured by the sensor.

Some catalytic LEL sensors are certified as intrinsically safe rather than (or in addition to) their certification as a flame proof device. Sensors that do not include a flame arrestor are not subject to the same limitations regarding the diffusion of large molecules into the sensor.

• Photoionization Detectors (PIDs) for VOC measurement

Solvent, fuel and other VOC vapors are pervasively common in many workplace environments. Most have surprisingly low toxic exposure limits. For most VOCs the toxic exposure limit is exceeded long before you reach a concentration sufficient to trigger an LEL alarm. PID equipped instruments are generally the best choice for measurement of VOCs at exposure limit concentrations.

Photoionization detectors use high-energy ultraviolet light from a lamp housed within the detector as a source of energy used to remove an electron from neutrally charged VOC molecules, producing a flow of electrical current proportional to the concentration of contaminant. The amount of energy needed to remove an electron from the target molecule is called the ionization energy (IE). In general, larger and / or more reactive molecules have lower ionization energies than smaller less reactive molecules. Thus, as a general rule, the larger the VOC or hydrocarbon molecule, the easier it is to detect! This is exactly the opposite of the performance characteristics of catalytic pellistor type combustible sensor.

Because PID sensors are intrinsically safe devices they do not include flame arrestors that inhibit or prevent the diffusion of large molecules into the sensor. They are particularly well designed for the detection of the large saturated and unsaturated hydrocarbon molecules found in heavy fuel mixtures, combustible liquids and solvents.

GfG Application Note 1021, *"Using PIDs to measure toxic VOCs"* discusses the technology, limitations and general use of PID sensors in greater detail. The note is posted on www.goodforgas.com at the following link: http://goodforgas.com/wp-content/uploads/2013/12/AP1021_Using_PIDs_to_measure_toxic_VOCs_10_10_13.pdf

GfG Application Note 1014, *"Monitoring toxic VOCs in oil industry applications"* discusses using PIDs to measure specific hazards and contaminants (such as benzene) associated with the oil industry. The note is posted at: http://goodforgas.com/wp-content/uploads/2013/12/AP1014_monitoring_toxic_VOCs_in_oil_industry_applications_02_18_13.pdf

Figure 6: Instrument with NDIR sensor. Since the amount of IR light absorbed is proportional to the amount of target gas present, the longer the optical path-length through the IR sensor, the better the resolution.

Pellistor type combustible sensors and photoionization detectors represent complementary, rather than competing detection techniques. Pellistor sensors are excellent for the measurement of methane, propane, and other common combustible gases that are not detectable by means of a PID.

On the other hand, PIDs can detect large VOC and hydrocarbon molecules that are effectively undetectable by pellistor sensors, even when the catalytic sensor is operable in ppm measurement ranges. The best approach for VOC measurement in many cases is to use a multi-sensor instrument equipped with both a pellistor LEL sensor and a PID sensor.

• Non-dispersive infrared (NDIR) sensors for combustible gas measurement

Non-dispersive infrared (NDIR) sensors measure gas as a function of the absorbance of infrared light at a specific wavelength or range of wavelengths. (Figure 6)

Molecules can be conceptualized as balls (atoms) held together by flexible springs (bonds) that can vibrate (stretch, bend or rotate) in three dimensions. Each molecule has certain fixed modes in which this vibratory motion can occur. Each mode represents vibrational motion at a specific frequency.
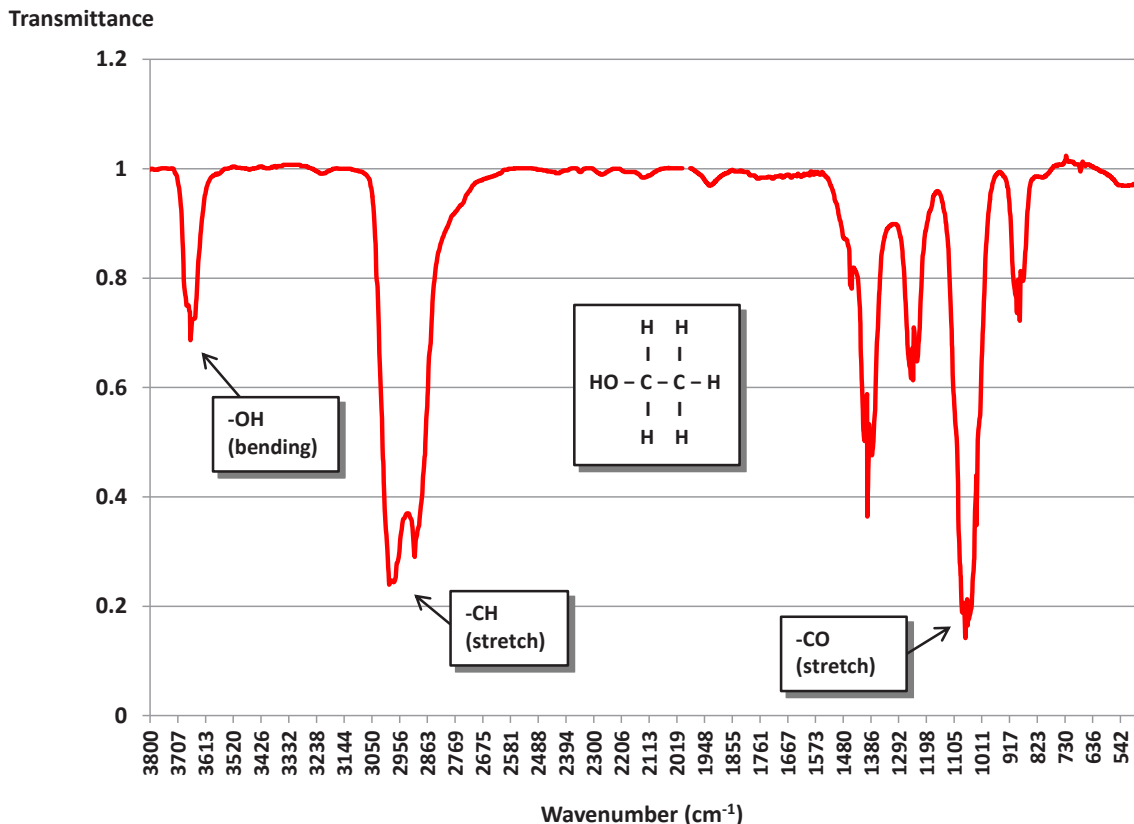
Transmittance

Figure 7: Infrared transmittance spectrum for ethyl alcohol measured over a full (dispersive) measurement range. Spectrograms like this one are frequently presented in wavenumber (cm^{-1}) rather than micrometer (µm) wavelength measurement units. To convert wavenumbers (cm^{-1}) to wavelength (µm), simply divide 10,000 by the wavenumber. In micrometers the above range is equal to 2.6 µm to 20.0 µm.

When a chemical bond absorbs infrared radiation the bond continues to vibrate at the same frequency but with greater amplitude after the transfer of energy. For infrared energy to be absorbed (that is, for vibrational energy to be transferred to the molecule), the frequency must match the frequency of the mode of vibration.

When infrared radiation passes through a sensing chamber that contains a measurable gas, only those wavelengths that match the vibration modes of the chemical bonds in the molecules of gas are absorbed. The rest of the light is transmitted through the chamber without hindrance. The instrument measures the amount of light that is absorbed by the molecules in the sensing chamber. The greater the concentration of gas, the greater the reduction in the amount of light that reaches the active detector when compared to the reference signal.

Most chemical compounds absorb at a number of different IR wavelenghts. The chemical groups and bonds within the molecule give rise to these characteristic absorption bands. The spectrogram produced by the absorbance of infrared light over a wide or "dispersive" range of wavelengths is highly specific, and can provide a "fingerprint" for use in identification of unknown contaminants. (Figure 7)

Alternatively, for some types of molecules it may be possible to find an absorbance peak at a specific wavelength that is not shared by other types of molecules likely to be present. When this is the case absorbance at a particular wavelength can be used to provide measurement for a specific molecule or category of molecule (like combustible gases).

Unlike "dispersive" IR spectrophotometers that make measurements over a wide range of wavelengths, the "non-
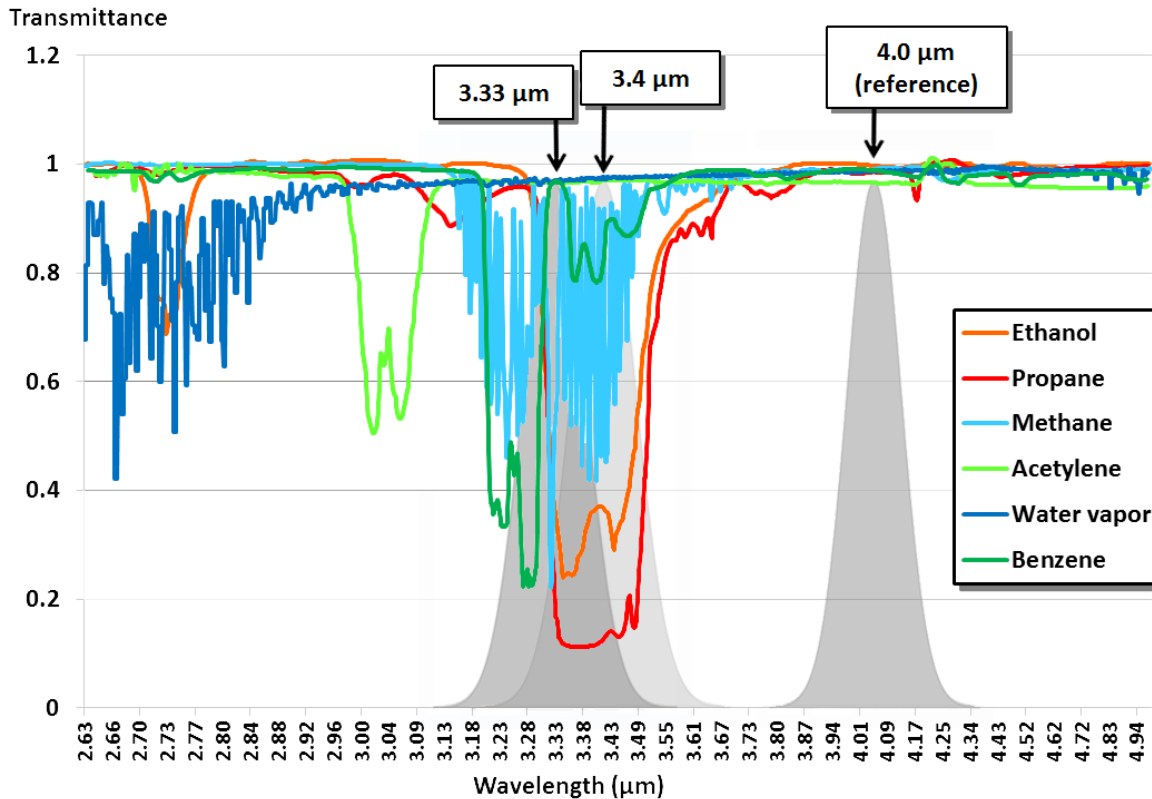
Figure 8: Infrared transmittance spectra for water vapor and several hydrocarbon gases. IR sensors usually measure combustible gas near 3.33 μm or 3.4 μm. Narrow band filters are used to restrict measurement to the desired wavelength ranges (shown in gray). Since water also absorbs some IR light at these wavelengths, the sensor should be zeroed in the ambient atmosphere in which the instrument will be used before each day's use. Note that acetylene does not absorb IR in the 3.33 μm or 3.4 μm measurement range, and cannot be measured by means of standard NDIR LEL sensors. The reference wavelength is usually around 4.0 μm. Water does not absorb appreciable IR light at this wavelength.

dispersive" infrared (NDIR) sensors used in multi-sensor portable instruments (and most fixed systems) measure absorbance over a narrow range, (or ranges) of wavelengths. The wavelengths that are used depend on the types of chemical bonds that are present in the combustible gas molecules to be measured. (Figure 7)

The strength of the NDIR sensor signal is determined by the Beer-Lambert Law, one of the basic laws of physics. Without going too deeply into the math, according to Beer's Law the strength of the signal is proportional to, (1) the intensity of the beam of infrared light, (2) the specific absorbance characteristics of the molecules of gas in the optical sensing chamber, (3) the distance the light travels through the sensing chamber (the optical path length), and of course, (4) the actual concentration of the gas being measured. (Figure 9)

For an instrument manufacturer, optimizing performance along one parameter often requires a tradeoff in performance along another parameter. For instance, reducing the optical path length by utilizing a chip based sensor with a micro-miniaturized gap between the emitter and the detector can tremendously reduce the amount of power required by the sensor. However, the shorter the optical path length, the less opportunity there is for the gas being measured to absorb IR light. This can potentially limit the sensor's ability to measure gases with lower relative responses at the measurement wavelength. Using a higher power IR source that produces a brighter beam of light increases signal strength, but takes more power. Lengthening the optical path length provides greater opportunity for the molecules to absorb the light, improving the sensor's ability to measure gases with lower relative responses, (and allows use of a lower power IR source

Beer-Lambert Law

$$I_1 = I_0 * e^{-\alpha Lc}$$

I_0 is the intensity of the incident light

I_1 is the intensity after passing through the material

L is the distance that the light travels through the material (the optical path length)

c is the concentration of absorbing species in the material

α is the absorption coefficient or the molar absorptivity of the absorber
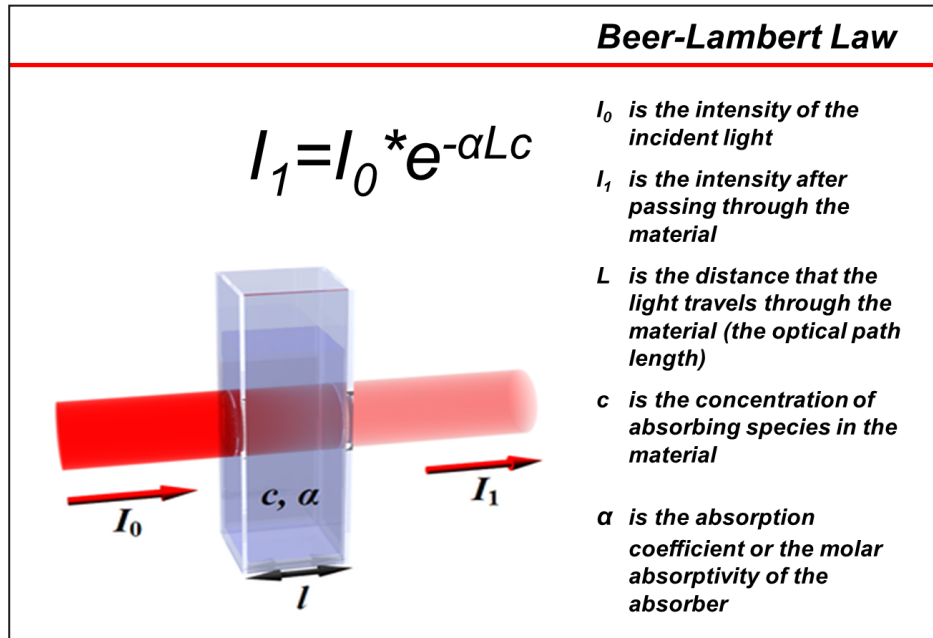
Figure 9: The Beer-Lambert Law explains the relationship of factors that help determine the strength of the signal of the IR sensor. One of the most important factors is the length of the optical path through the sensor. The longer the pathlength, the greater the opportunity for absorbance to occur. Longer pathlengths are particularly important for the detection of gases with lower relative responses. Longer pathlengths also permit the use of lower power infrared emitters, and providing readings with better resolution.
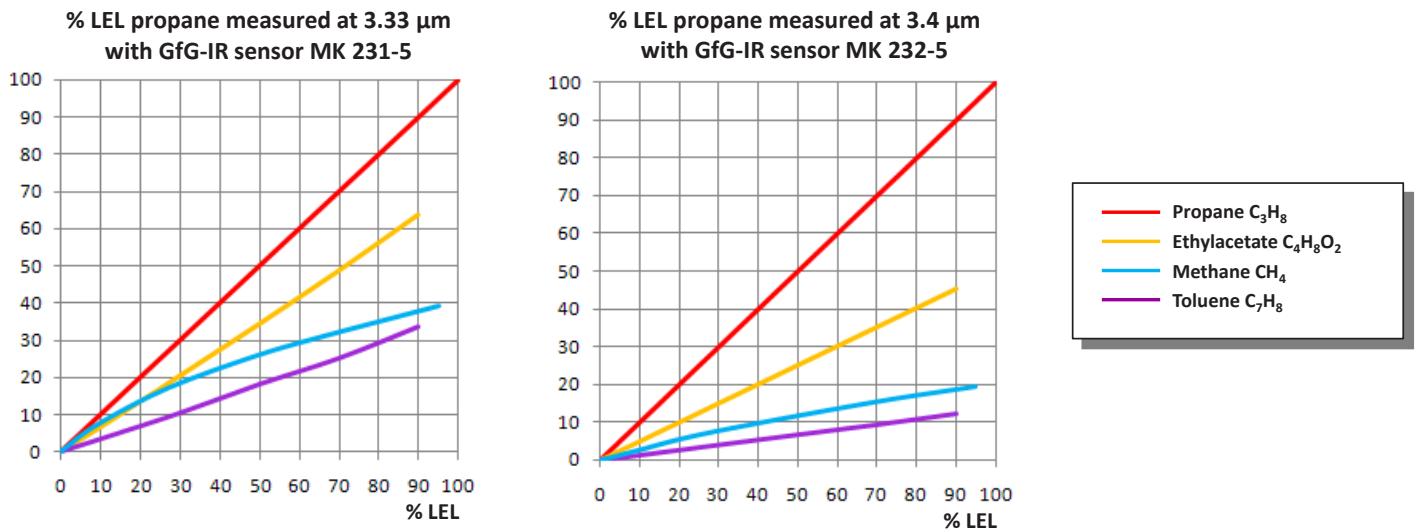
Figure 10: Measurement at 3.33 μm increases the relative response to methane compared to most other detectable gases. Measurement at 3.4 μm decreases relative response to methane and other gases compared to aliphatic hydrocarbon gases such as propane. The best general purpose combustible gas measurement wavelength is usually 3.33 μm, especially if methane is potentially present.
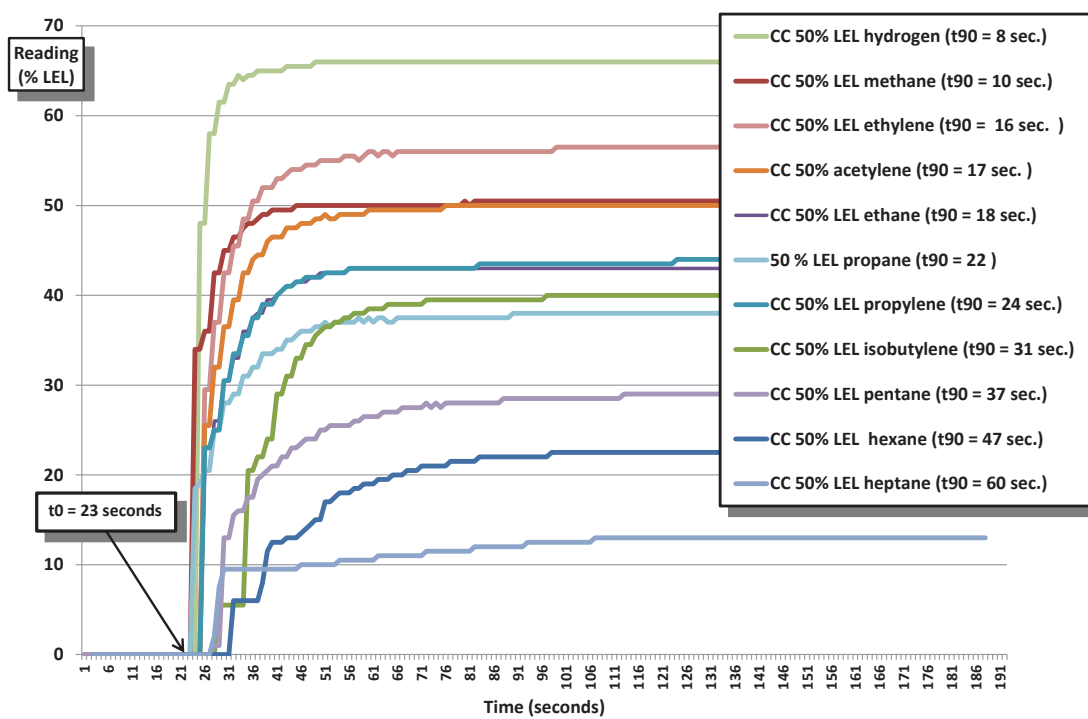
Figure 11: Pellistor type LEL sensors show lower relative responses to larger molecules than to smaller. In the example above the response to methane (CH_4) is about two times higher than the response to pentane (C_5H_{12}), and about four times higher than the response to heptane (C_7H_{16}). The response to larger molecules is also much slower. It takes only 10 seconds for the methane reading to reach t90 (90% of its final stable response), while it takes a full minute for heptane.
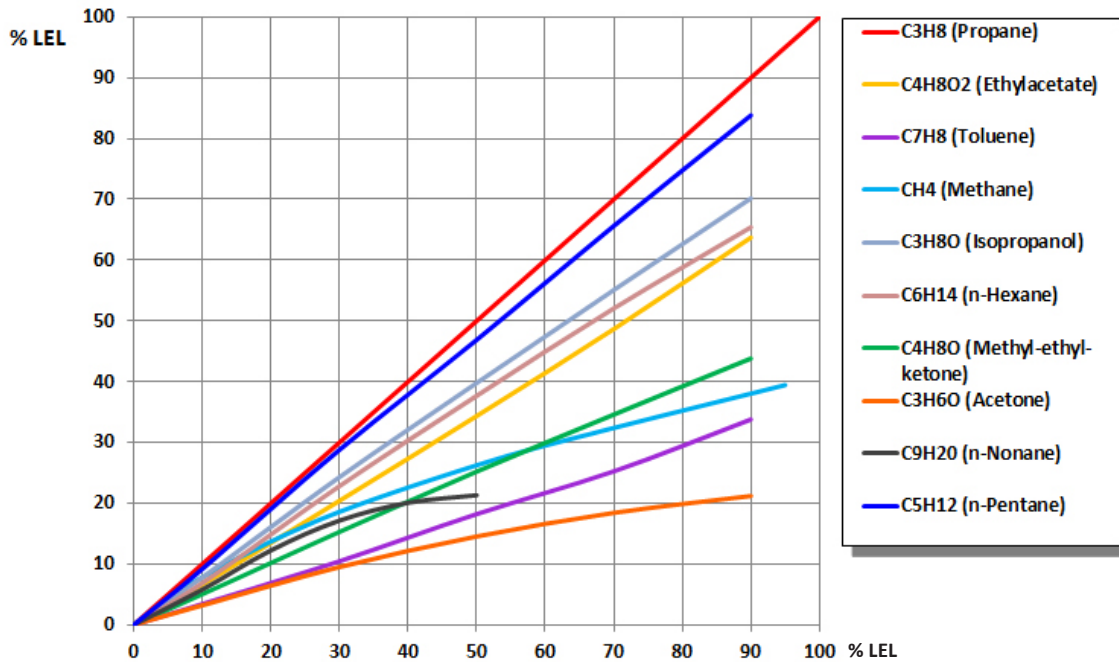

Figure 12: Relative responses of GfG MK 231-5 (3.33 μm) NDIR combustible gas sensor (propane scale) to various other detected gases. The C-H bonds in hydrocarbon molecules and the O-H bonds in alcohols (such as isopropanol) show good absorbance to IR radiation at 3.33 μm. The more bonds in the molecule, the more opportunities for absorbance. Methane (CH_4), which has only four C-H bonds, shows a lower response than larger hydrocarbon molecules like pentane (C_5H_{12}), which has 10 C-H bonds.
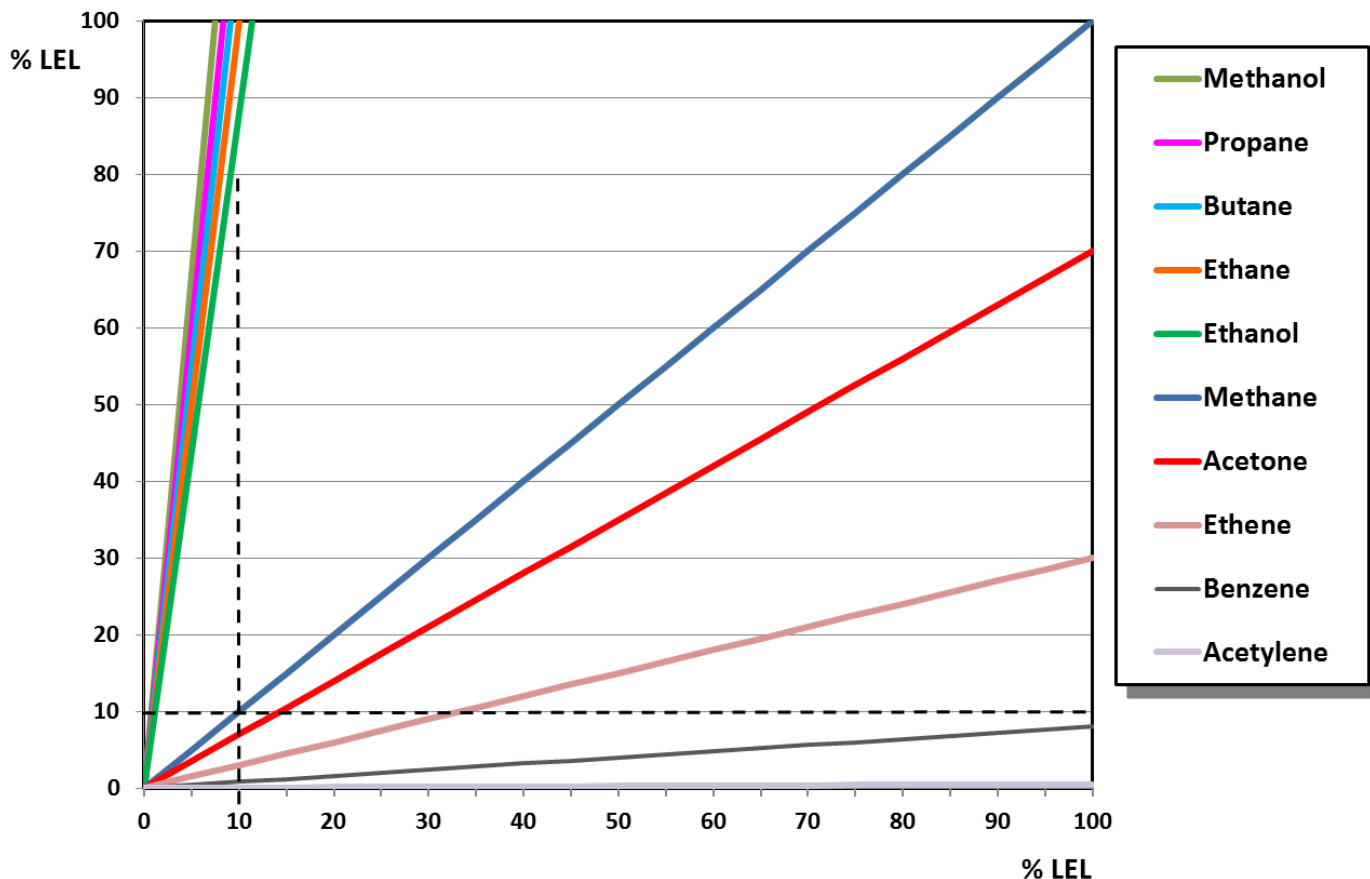
Figure 13: Linearized relative responses of GfG MK 231-5 (3.33 µm) NDIR combustible gas sensor (methane scale) to various other gases. Alliphatic hydrocarbons like propane, butane and ethane, as well as alcohols like methanol and ethanol have a higher relative response compared to methane . Ethene, (which has a C=C double bond), shows a lower relative response of about 0.7 compared to methane. Benzene has an even lower relative response of about 0.08 compared to methane. Acetylene (which has a C≡C triple bond) has a relative response so low that it cannot be measured at this wavelength.

to achieve the same strength of signal), but it means that the sensor is physically larger.

As a consequence of these design considerations, the performance characteristics of NDIR sensors can differ significantly between manufacturers. However, all NDIR sensors share certain performance characteristics.

What is the best wavelength for measurement?

The wavelength ranges most frequently used for combustible gas measurement are near 3.33 µm or 3.4 µm (micrometers). A filter is used to limit the band of wavelengths that are used for measurement. The active detector in an NDIR combustible gas sensor measures the amount of infrared light absorbed at this wavelength range. A reference detector measures the amount of light at another wavelength where there is no absorbance. Methane and molecules with double bonds (such as butadiene and ethene) or a benzene ring (such as toluene or benzene) show stronger absorbance at 3.33 µm than they do at 3.4 µm, while saturated hydrocarbons such as propane and butane show stronger absorbance at 3.4 µm. (Figure 10)

While catalytic Wheatstone bridge type LEL sensors are more sensitive to small saturated hydrocarbon molecules like methane and propane than to larger molecules like pentane or nonane; the opposite is true for NDIR sensors. It is the chemical bonds in the molecules being measured that actually

absorb the infrared light. Since larger molecules have more chemical bonds holding the atoms in the molecule together, they provide more opportunities for infrared radiation to be absorbed. Thus, NDIR sensors are actually more sensitive, not less sensitive, to large saturated hydrocarbons like nonane and decane. (Figures 12 and 13)

NDIR sensors cannot measure a gas unless the bonds in the molecules absorb IR at the measurement wavelengths. It is primarily the "stretch" vibrational modes of the C-H bonds in combustible gas molecules that absorb infrared light near 3.33 µm and 3.4 µm. Methane (CH_4) has only four C-H bonds., while pentane (C_5H_{12}) has 12 C-H bonds. It makes sense that the relative response of the NDIR sensor to pentane is greater than the response to methane. Certain other chemical groups, such as the -OH bonds in alcohol molecules, also absorb well in thiese same wavelength ranges.

Any chemical groups in the molecule that depress or reduce the "stretch" vibrational mode reduce the overall absorbance of IR light at these wavelengths. For instance, ethane (C_2H_6) shows stronger absorbance than ethene (C_2H_4). The presence of the carbon-carbon double bond (C=C) in the ethene molecule reduces the stretch vibrational mode. Although ethene is still detectable, it has a lower relative response. The presence of the benzene ring in an aromatic molecule like toluene molecule (C_7H_8) reduces absorbance even more significantly. (Figure 13)

Although acetylene (C_2H_2) has two C-H bonds, the presence of a triple bond between the two carbon atoms so reduces absorbance that it renders the molecule unmeasurable at 3.33 µm or 3.4 µm. However, the C≡C triple bond shows strong absorbance at a wavelength of 2.3 µm. (Figure 8)

Unfortunately, while acetylene absorbs strongly at 2.3 µm, most other commonly encountered combustible gases do not, making the wavelength a poor choice for general LEL measurement. It's worth noting that while the NDIR LEL sensors in portable instruments use a single wavelength range to measure gas, some fixed IR sensors have multiple detectors that measure at up to four different wavelengths. This allows the system to calculate a total combustible gas concentration that includes acetylene as well as the other gases detected at the typical 3.3 µm or 3.4 µm measurement wavelengths.

Absorbance of infrared light is proportional to the concentration of measurable gas in the sensing chamber of the sensor. However, the absorbance is not linear per concentration unit. Instruments equipped with NDIR sensors for combustible gas measurement generally include a library
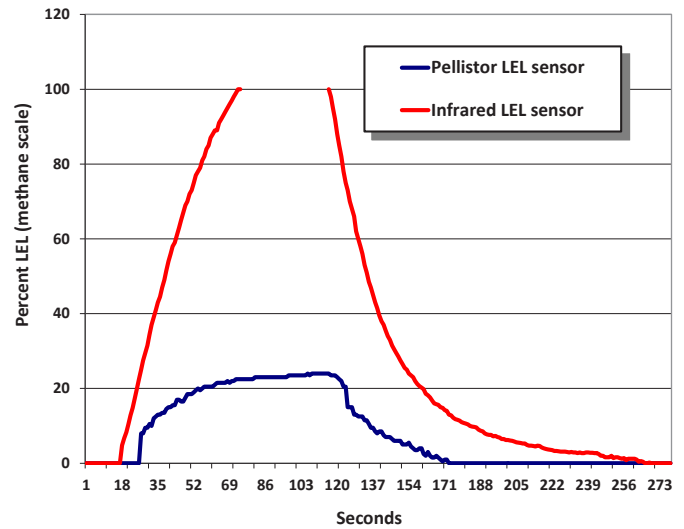

Figure 14: Relative response of pellistor and infrared sensors to n-hexane. Both sensors were calibrated to 50% LEL methane (CH_4), then exposed to 50% LEL n-hexane (C_6H_{14}). The uncorrected readings for the pellistor sensor are much lower than the true concentration (50% LEL); while the uncorrected readings for the IR sensor are more than twice as high as the true concentration, (in fact, the readings exceeded the over-range limit of 100% LEL).
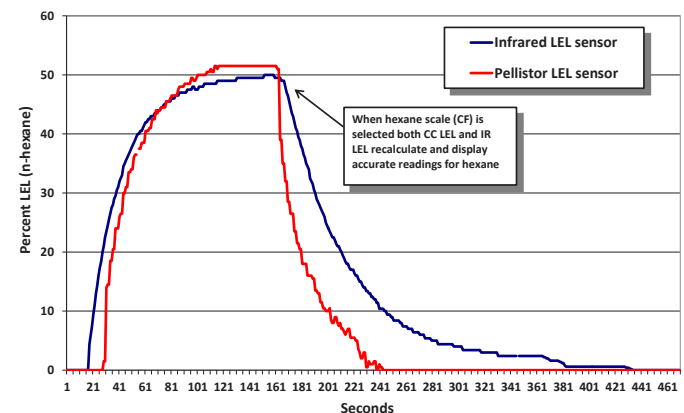

Figure 15: Response of n-hexane calibrated pellistor and IR sensors to 50% LEL n-hexane. The readings for both sensors are now very close to the true 50% LEL concentration applied. The initial response of the IR sensor is slightly quicker than the response of the pellistor sensor. However, the time to the final stable response (t100) is virtually identical for both sensors, (about 150 seconds).

of response curves. Since the response curves are not linear, and are shaped quite differently for methane versus most other detectable gases, instruments utilize a design specific "lookup table" of values to convert readings from one scale to another. For maximum accuracy, NDIR sensors need to be individually programmed by the manufacturer with a sensor specific lookup table. (Figure 13)

For methane or natural gas measurement it is generally best to use the methane scale. For measurement of alcohols and saturated hydrocarbons (such as ethane, propane, butane, pentane, hexane, nonane, etc.), it is generally better to operate the instrument on the propane scale, since the relative responses of these gases and vapors are fairly similar to each other. (Figure 13)

For unsaturated gases such as ethylene or benzene, direct calibration to the gas of interest, or using the appropriate curve from the lookup table "library" in the instrument's memory is normally the best approach.

Absorbance by water vapor at 3.33 µm and 3.4 µm is comparatively modest, limiting the effects of humidity interference at these measurement wavelenghts. However, since water still absorbs some IR light at these wavelengths, the sensor should be zeroed in the ambient atmosphere in which the instrument will be used before each day's use.   As long as the humidity is relatively stable, performing a fresh air calibration adjustment in the ambient atmosphere is enough to "zero out" the effects of humidity on readings (Figure 8).

As with all sensors used to measure gas, in order to be measured the gas has to successfully reach the part of the sensor where the gas is detected. Some NDIR sensors, (including the sensors used in GfG instruments) are intrinsically safe devices that do not include a flame arrestor. NDIR sensors that do not include a flame arrestor or sinter are excellent for the LEL range measurement of the large molecules in combustible liquid vapors from diesel, jet fuel, kerosene, turpentine and crude oil.

NDIR LEL sensors that include a flame arrestor are subject to the same limitations as other types of sensors which include a barrier that prevents or limits the diffusion of large molecules into the sensor. Even though the molecules absorb well at the measurement wavelength, if they are unable to reach the optical sensing chamber they cannot be measured.
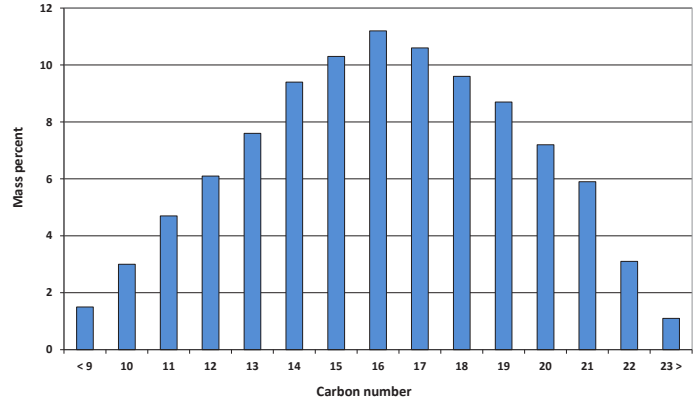

Figure 16: Typical carbon number distribution in No. 2 Diesel Fuel (liquid). Less than 1.5% of diesel molecules are small enough to be measurable by means of a typical pellistor LEL sensor. Less than 4% of molecules present as vapor (STP) are small enough to be measured.
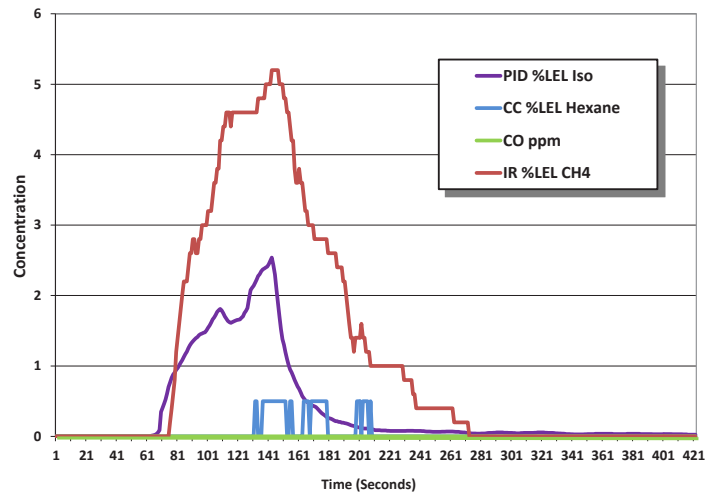

Figure 17: Response of PID, catalytic (pellistor) %LEL, IR %LEL and CO sensors exposed to diesel vapor. The IR LEL sensor shows the most accurate response, while the catalytic LEL sensor barely shows any response at all. PID is the best detection technology for low range ppm detection.

NDIR combustible gas sensors have a number of other advantages when compared to pellistor type sensors. NDIR sensors are not equipped with external flame arrestors that slow or limit the entry of large hydrocarbon molecules into the sensor. (Figures 12 and 13) NDIR sensors do not require oxygen. They are also not subject to damage due to exposure to sensor poisons. Finally, unlike pellistor type sensors, they can be used for measurement of high concentration combustible gas above the 100% LEL concentration.

One of the most important limitations of NDIR combustible gas sensors is that they cannot be used for measurement of diatomic gases such as oxygen (O_2), nitrogen (N_2) and hydrogen (H_2). In applications where H_2 may be potentially present, the instrument should be equipped with a type of sensor designed to respond to H_2, such as a pellistor LEL sensor or an electrochemical sensor capable of measuring H_2 in the desired range.

Examples of sensor configurations optimized for specific applications:

- ## Confined space monitoring for shipyards

Two categories of combustible gas hazards are of special concern during shipyard and maritime confined space entry procedures; the heavy fuel vapors from the diesel, bunker and fuel oil used to power the ship's engines; and hydrogen gas produced by the electrolysis of metals when exposed to seawater or moisture. Pellistor type LEL sensors are not effectively able to measure combustible vapor molecules larger than nonane (C_9H_{20}), which has nine carbon atoms. The average size of the molecules in diesel fuel is 16 carbons. Less than 1.5% of the molecules in diesel fuel are small enough to be effectively measured by this type of sensor. (Figures 14 and 15) Pellistor sensors used in this type of environment are also frequently damaged due to exposure to sensor poisons. In addition, in many cases the monitor must be used to obtain samples from compartments and spaces that have been purged with an inert gas such as nitrogen or CO_2 to remove the oxygen.

Pellistor sensors cannot be used for monitoring combustible gas in oxygen deficient atmospheres unless equipped with dilution fittings or a second pump used to introduce enough fresh air into the sample for the pellistor sensor to be able to oxidize and properly detect the gas. Pellistor sensors are also incapable of providing dependable LEL range measurement for diesel, bunker and fuel oil vapors.

Figure 18: Sampling inerted vessels often requires very long sample lines. Use of an attachable motorized sampling pump allows the G460 from GfG Instrumentation pictured above to be located up to 300 feet away from the point where the sample is obtained.
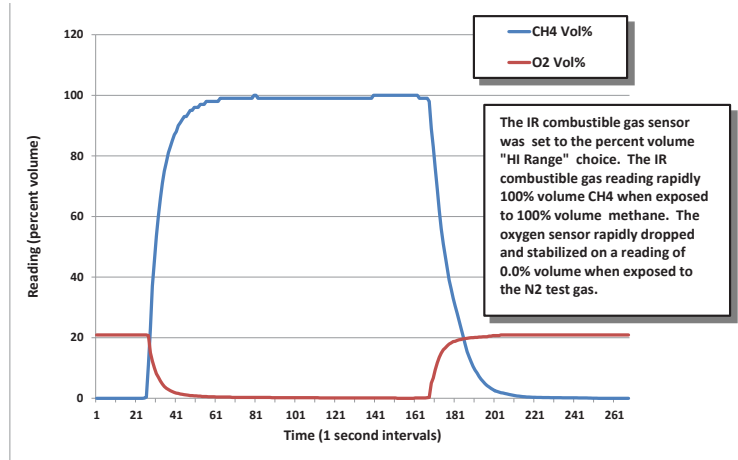

Figure 19: Response of "high range" (percent volume) infrared (IR) LEL and O_2 sensors exposed to 100% volume methane (CH_4). The IR combustible gas sensor was set to the percent volume "HI Range" choice. The IR combustible gas reading rapidly reached 100% volume CH_4 when exposed to pure methane. The oxygen sensor rapidly dropped and stabilized on a reading of 0.0% volume when exposed to the oxygen free CH_4 gas.

The optimal configuration for this application would be an instrument equipped with an oxygen sensor, an NDIR sensor for LEL range combustible gas measurement, a PID for ppm range VOC measurement, and an electrochemical hydrogen sensor for LEL range (1 – 4% volume) H_2 measurement. The instrument should have an available motorized sampling pump for sampling from remote or inerted spaces. (Figure 16)

- **High range measurement of natural gas from "sour" (high H2S content) natural gas wells**

The natural gas from many of the older fields in North America is often extremely "sour"; with H_2S concentrations up to 30,000 ppm or even higher. It is sometimes necessary for workers wearing appropriate PPE and respiratory protection (pressure demand SCBA) to enter areas where the concentration of combustible gas is above the explosion limit, and where the H_2S concentration routinely exceeds 3,000 ppm. It is often necessary to use multi-sensor instruments as "leak detectors" capable of measuring the natural gas in both the LEL and the percent volume ranges. Although TCD sensors are excellent for the measurement of high range methane in air, they cannot detect large hydrocarbon and VOC molecules, and (if they include a catalytic pellistor sensor or mode of operation) are vulnerable to sensor poisons such as H_2S.
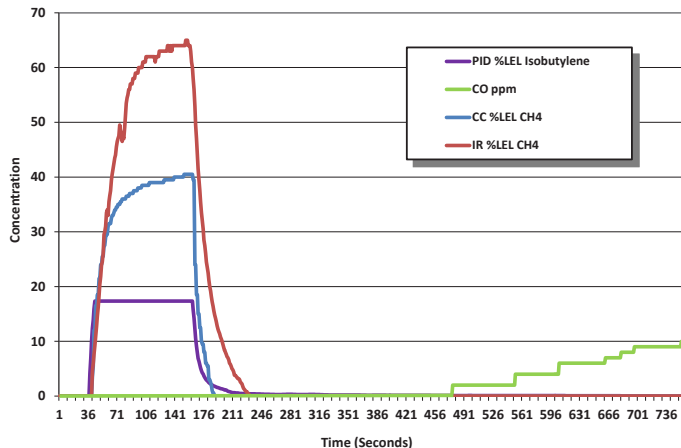

Figure 20: Response of standard pellistor (catalytic) LEL, O2, PID and CO sensors exposed to 50% LEL (9,000 ppm) isobutylene. The PID was calibrated to isobutylene. The LEL sensor was calibrated to methane (CH4). The relative response of the LEL sensor to isobutylene is about 0.8. The maximum over-limit concentration of the PID is 1,700 ppm. Readings above this concentration are logged at this maximum value. Note the delayed response of the CO sensor to this very high concentration of VOC vapor.
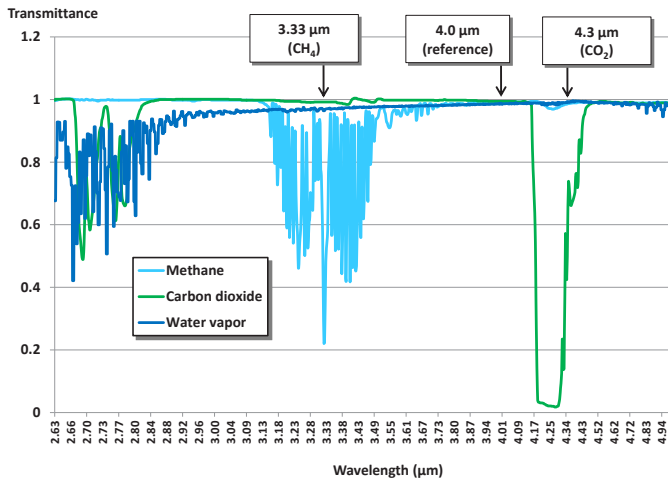

Figure 21: Transmittance spectra of methane and carbon dioxide. Dual-channel IR combustible gas / CO2 sensors actually measure absorbance at three wavelengths. Combustible gas is measured at 3.33 µm. CO2 is measured at 4.3 µm. A single reference wavelength (4.0 µm) is used for both measurement channels.
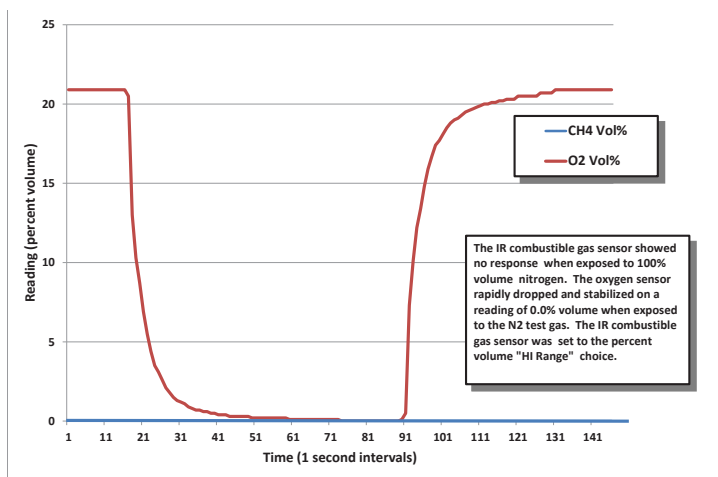

Figure 22: Response of infrared (IR) combustible gas and oxygen sensors exposed to 100% volume nitrogen (N2). The IR combustible gas sensor showed no response when exposed to 100% volume nitrogen. The oxygen sensor rapidly dropped and stabilized on a reading of 0.0% volume when exposed to the N2 test gas. The IR combustible gas sensor was set to the percent volume "HI Range" choice.

The optimal configuration is an instrument with an oxygen sensor and a dual range NDIR sensor capable of monitoring both in the 1 – 100% LEL as well as in the 1 – 100% volume range. (Figure 17) Because infrared sensors are not subject to damage due to sensor poisons (like H_2S), not having to purchase replacement sensors generally saves instrument users more than the cost of purchasing the more expensive NDIR sensor to begin with.

Important note: Carbon monoxide sensors include protective internal or external filters, but once they are saturated, the sensors show a strong response to VOC vapors and hydrocarbon gases such as hexane. (Figure 18) While the effects of this cross sensitivity may not be significant in low range concentrations, high concentrations of VOC vapor may make it impossible to use an instrument that has been equipped with a CO sensor.

It is generally best to use a dedicated instrument that does not include a CO sensor when the instrument is routinely used in atmospheres with high background VOC concentrations. An alternative is to use a CO sensor equipped instrument, but to turn the CO sensor off while the instrument is being used in this application.

• Instruments at oil refineries used to measure ppm range VOC vapors, LEL hydrogen (H_2), C1-C9 hydrocarbons (methane through nonane), carbon monoxide and hydrogen sulfide

Industrial hygienists at refineries routinely deal with a wide range of toxic VOCs such as hexane, toluene, xylenes and benzene as well as the vapors associated with the products produced for sale (e.g. diesel, gasoline, jet fuel, etc.).

It is widely understood by hygienists that it is not enough to depend on readings from the LEL sensor to determine whether or not a hazardous condition exists due to the presence of toxic concentrations of VOC vapors. The optimal instrument in this case is equipped with a standard % LEL pellistor sensor (which is capable of detecting all of the C1–C9 hydrocarbons as well as hydrogen), an oxygen sensor, a PID and a dual channel electrochemical "COSH" sensor capable of providing independent readings for both CO and H_2S.

• Instrument used to measure O_2 and % LEL combustible gas in procedures that include vessel inertion at an oil refinery

In order to reduce the risk of explosion, it is a common practice at many refineries and chemical plants to replace the oxygen in the atmosphere of tanks and vessels with an inerting gas such as nitrogen or carbon dioxide. Typically, two readings are of equal importance during inertion procedures. The oxygen concentration must remain below a certain threshold (at many facilities the threshold is 2.0% volume oxygen). The second reading is a direct measurement of the amount of combustible gas present in the atmosphere in the vessel. The types of combustible gases encountered often include hydrogen.

As previously discussed, pellistor type LEL sensors can be used for this purpose, but only when the instrument includes provision for introducing enough fresh air into the sample for there to be sufficient oxygen for the LEL sensor to accurately detect gas. Monitoring of inerted vessels has been done in the past at many refineries by means of a specialized instrument equipped with a pellistor LEL sensor and two internally housed pumps. One pump is used to pull the sample through a hose and probe assembly back to the instrument. The second pump is used to dilute the sample with fresh air from a location outside of the vessel. The instrument recalculates the readings shown on the instrument display to make up for the effects of introducing the fresh air into the sample.

These specialized instruments are "lunch box" type monitors too large to be worn, and are typically left outside of the vessel in an area far enough away that air drawn into the instrument by the second pump is contaminant free and can safely be used for sample dilution. Problems experienced by users of this specialized instrument include difficulty maintaining the proper dilution ratio due to filter loading, and damage to the pellistor sensors due to exposure to sensor poisons such as H_2S. As always, the flame arrestor in the pellistor sensor limits the ability of the sensor to detect hydrocarbon gases larger than nonane (C_9H_{20}).

The optimal solution is an instrument equipped with an oxygen sensor with an "inverted" alarm activated by the concentration climbing above 2.0% volume, an IR %LEL combustible gas sensor (which does not require oxygen to detect gas), and a 1 – 4.0 % volume range electrochemical hydrogen sensor (the LEL concentration for H_2 is 4.2% volume). The instrument should also be equipped with an attachable (or internal) motorized pump for sampling the atmosphere in the vessel through a hose and probe assembly. Since it is not necessary to dilute the sample with fresh air in order to obtain readings, it is not necessary to position the instrument in a contaminant free area remote from where the readings are being obtained.

• Instrument used to monitor atmospheres at landfills

Landfill monitoring applications involve a number of unique requirements. The anaerobic decomposition of the organic material in the buried trash has the potential for generating massive quantities of methane and carbon dioxide, as well as potentially lethal concentrations of hydrogen sulfide.

Carbon dioxide is much heavier than air, and can easily accumulate in excavations, trenches and other localized areas. Besides the danger to workers, these localized areas of oxygen deficiency may not contain enough O_2 for pellistor LEL sensors to accurately detect combustible gas. It should be noted that CO_2 is not a "simple asphyxiant" that harms workers only by displacing oxygen. Carbon dioxide is a recognized toxic gas, with an exposure limit of 5,000 ppm (8 hour TWA) in most jurisdictions.

Another concern is the high concentrations of combustible gas that may be present. Landfill instruments need to be able to measure in the percent volume as well as percent LEL ranges. Yet another consideration is that landfill instruments are often used to obtain readings from "bore holes" drilled into the buried material. This type of usage requires the instrument to be available for use with a motorized pump.

The optimal solution is a G460 equipped with a dual-channel infrared sensor that measures absorbance at two different wavelengths, 3.33 μm for combustible gas, and 4.3 μm for CO_2 (Figures 19 and 20). (The same 4.0 μm reference wavelength is used for both channels.) The infrared sensor is "dual-range" as well as dual-channel. Combustible gas can be measured in either of two user-selectable ranges; 1 – 100% LEL or 1 – 100% volume. The instrument should also be equipped with substance-specific sensors for measuring O_2, CO and H_2S. The G460 also needs to be equipped with an attachable motorized pump for sampling the atmosphere in the vessel through a hose and probe assembly.

Summation:

No single type of sensor is perfect for all applications. The four basic sensors (LEL / O_2 / CO / H_2S) used in most multi-sensor instruments are a good start, but may not be capable of properly monitoring for the presence of all potential hazards. Table 1 (following page) summarizes the advantages and limitations of each type of sensor discussed. Table 2 provides specific examples of sensor configuration choices by application.

The key to success is understanding the monitoring environment, and the specific benefits and limitations of the sensors selected.

Table 1: Sensors for measurement of combustible gas and VOCs

	Able to detect LEL range C1 – C5 hydro-carbon gases (methane, ethane, propane, butane, pentane and natural gas)	Able to detect LEL range C6 – C9 hydro-carbon gases (hexane, hep-tane, octane, nonane)	Able to accurately detect LEL range heavy fuel vapors (e.g. diesel, jet fuel, kerosene, etc.)	Able to detect heavy fuel vapors in low ppm range (e.g. diesel, jet fuel, kerosene, etc.)	Able to use in low oxygen atmospheres	Vulnerable to sensor poisons (e.g. silicones, phosphine, tetraethyl lead, H2S, etc.)	Able to use for high range combustible gas measurement (100% LEL and higher)	Able to measure H_2
Standard catalytic (pellistor) type LEL sensor	Yes	Yes	No	No	No	Yes	No	Yes
NDIR combustible gas sensor	Yes	Yes	Yes	Yes*	Yes	No	Yes	No
PID (with standard 10.6 eV lamp)	No	Yes**	Yes**	Yes	Yes	No	No	No
Electrochemical H2 sensor	No	No	No	No	Yes	No	No	Yes
Thermal Conductivity Sensor	Yes	Yes	No	No	Yes***	No****	Yes	Yes

*   Because of their logarithmic output curve, NDIR sensors show the most sensitivity at the lowest concentration of measured gas. An NDIR combustible gas sensor with 0.1% LEL resolution over 0 – 5% LEL provides 50 ppm step-change resolution for methane. Because the LEL concentration is so much lower, the same sensor would provide 11 ppm step change resolution for n-hexane.

**   Although PIDs are able to detect a wide variety of VOC vapors, the ability of the PID to measure LEL range concentrations is limited by the full range of the PID. The 10% LEL concentration for most VOC gases ranges between 1,000 and 3,000 ppm.   A PID with a full range of 2,000 ppm would only be able to detect maximum concentrations of 6% to 20% LEL, depending on the VOC being measured.

***   Only if the exact composition of the oxygen deficient atmosphere is known and the instrument is properly calibrated for use in this mixture.

**** TCD sensors that include a catalytic bead or operation mode are vulnerable to sensor poisons as long as the catalytic bead is under power.

Table 2: Examples of possible sensor configurations optimized for specific applications*

	Confined space monitoring for municipal, water and wastewater	Confined space monitoring for shipyards	High range CH$_4$ from "sour" (high H$_2$S) natural gas wells	Oil refinery confined space instrument	Instrument used to measure O$_2$ and %LEL gas in inerted vessels	Landfill monitor
Type of hydrocarbon and / or VOC being measured	%LEL CH$_4$, O$_2$, CO and H$_2$S	Heavy fuel and VOC (diesel, bunker, JP-8, solvents), natural gas and H$_2$	%LEL and high-range %Vol. CH$_4$	%LEL C1 - C9 gases, ppm range VOC, %LEL H$_2$, CO and H$_2$S	%LEL C1 - C9 gases in low O$_2$ atmosphere, ppm range VOC, CO and H$_2$S	%LEL and high-range %Vol. CH$_4$ and O$_2$
Standard catalytic (pellistor) type LEL sensor	Yes	No	No	Yes	No	No
NDIR combustible gas sensor	No	Yes	Yes	No	Yes	Yes
PID (with standard 10.6eV lamp)	No	Yes	No	Yes	No	No
Electrochemical H$_2$ sensor	No	No	No	No	No	No
Electrochemical CO sensor	Yes	Yes	No	Yes	Yes	Yes
Electrochemical H2S sensor	Yes	Yes	Yes	Yes	Yes	Yes
O$_2$ sensor	Yes	Yes	Yes	Yes	Yes	Yes

*   The listed sensor configurations only represent one possible solution for a specific application. The presence of additional conditions or requirements may completely change the optimal sensor configuration.