

AP1016: Understanding CO₂ sensors and their applications

Carbon dioxide is one of the most frequently overlooked of all toxic gases. Even to refer to CO₂ as a toxic gas is a surprise to many safety professionals.

Carbon dioxide is the fourth most common gas present in the earth's atmosphere, with an average ambient concentration (in fresh air) of about 350 ppm. Carbon dioxide is one of the most common by-products of living organisms. With every exhaled breath we produce and release CO₂ into the atmosphere (with an average concentration in exhaled breath of about 3.8%). According to one USDA study, an average person produces about 450 liters (900 grams) of CO₂ per day.

Liquid and solid carbon dioxide (dry ice) are widely used as refrigerants, especially in the food industry. Carbon dioxide is also used in many industrial and chemical industry processes. Carbon dioxide is particularly associated with the beer and wine making industries, where it is produced by yeast during the fermentation process that converts sugar into alcohol. Carbon dioxide in the headspace of fermentation vessels can easily reach 50% by volume or even higher concentrations. Carbon dioxide is also widely used in the oil industry, where it is commonly injected into oil wells to decrease the viscosity and aid in the extraction of oil from mature fields. It is also one of the most common atmospheric hazards encountered in confined spaces.

Carbon dioxide is a primary by-product of bacterial decomposition. As with people, "aerobic" or oxygen using bacteria produce carbon dioxide as a primary metabolic by-product. In many confined spaces there is a direct relationship between low concentrations of oxygen and elevated concentrations of CO₂. In the case of a confined space where CO₂ is generated as a by-product of aerobic bacterial action, a concentration of 19.5% O₂ (the hazardous condition threshold for oxygen deficiency in most jurisdictions) would be associated with an equivalent concentration of at least 1.4% (= 14,000 ppm) CO₂. This is substantially higher than the generally accepted workplace exposure limit for CO₂ (5,000 ppm calculated as an 8-hour TWA).

The true concentration of CO₂ could be substantially higher if the oxygen deficiency is due to displacement rather than consumption of the oxygen in the confined space. Fresh air contains only 20.9% oxygen by volume. The balance consists

mostly of nitrogen, with minor or trace concentrations of a wide variety of other gases including argon, water vapor and carbon dioxide. Because oxygen represents only about one-fifth of the total volume of fresh air, every 5% of a displacing gas that is introduced into a confined space reduces the oxygen concentration by only 1%. As an example, consider an oxygen deficiency due to the introduction of dry ice into an enclosed space. In this case a reading of 19.5% O₂ would not be indicative of 1.4% CO₂, it would be indicative of 5 X 1.4% = 7.0% (= 70,000 ppm) CO₂.

The bottom line is that if you wait until the oxygen deficiency alarm is activated, and the deficiency is due to the presence of CO₂, you will have substantially exceeded the toxic exposure limit long before leaving the affected area.

In spite of these considerations, in the past the majority of atmospheric monitoring programs have treated CO₂ as only a "simple asphyxiant". An asphyxiant is a substance that can cause unconsciousness or death by suffocation (asphyxiation).



Figure 1: Compact multi-sensor instruments are capable of providing direct CO₂ measurement during confined space and other atmospheric monitoring procedures



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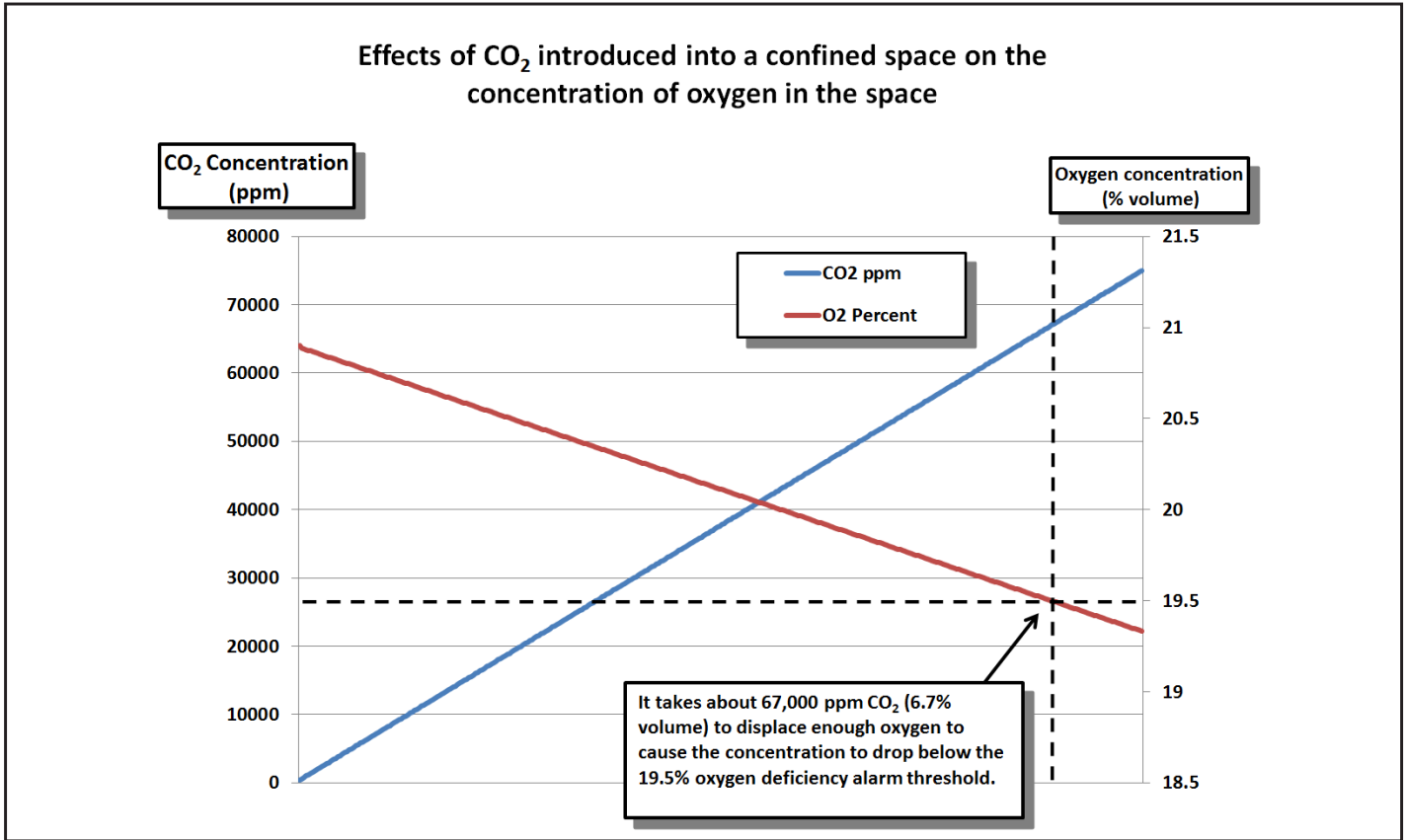


Figure 2: Every 5% of displacing gas introduced into a confined space reduces the O₂ concentration by about 1%.

Asphyxiants which have no other health effects are referred to as “simple” asphyxiants. Because CO₂ was not considered to be a toxic hazard, rather than directly measuring the CO₂ in the confined space or workplace environment, it was seen as adequate to simply measure the oxygen concentration. This attitude is changing as it becomes more feasible (and affordable) to directly measure CO₂ by means of compact, portable multi-sensor gas detectors equipped with miniaturized infrared sensors for the direct measurement of this gas.

- **Carbon dioxide is a toxic contaminant with strictly defined workplace exposure limits**

Carbon dioxide is listed as a toxic contaminant with strictly defined occupational exposure limits in almost every country. The most widely recognized exposure limits for CO₂ reference an 8-hour Time Weighted Average (TWA) of 5,000 ppm, with a 15-minute Short Term Exposure Limit (STEL) of either 15,000 ppm or 30,000 ppm. The following table lists several of the most commonly cited workplace exposure limits:

Standard / Country	8-hour Time Weighted Average	15-minute Short Term Exposure Limit
USA NIOSH REL	5,000 ppm	30,000 ppm
USA OSHA PEL	5,000 ppm	None Listed
ACGIH® TLV®	5,000 ppm	30,000 ppm
United Kingdom WEL	5,000 ppm	15,000 ppm

Carbon dioxide is heavier than air, with a density of 1.5 times that of fresh air. When carbon dioxide is released into an enclosed or confined space it tends to settle to the bottom of the space, reaching the highest concentration in the lowest parts of the space. Because of this tendency to settle, as CO₂ is produced it can reach higher and higher concentrations in localized regions of the space (such as the head space immediately above the liquid in fermentation vats).

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While present as a natural component in fresh air, at higher concentrations exposure symptoms include headaches, dizziness, shortness of breath, nausea, rapid or irregular pulse and depression of the central nervous system. Besides displacing the oxygen in fresh air, high concentrations of CO₂ may exacerbate or worsen the symptoms related to oxygen deficiency, and interfere with successful resuscitation. Even moderately elevated concentrations associated with poorly ventilated indoor spaces can produce physiological symptoms. According to NIOSH chronic exposure to elevated indoor CO₂ concentrations have been linked with the following symptoms:

Concentration	Symptom
250 – 350 ppm	Normal background concentration in outdoor ambient air
350 – 1,000 ppm	Concentrations typical of occupied indoor spaces with good air exchange
1,000 – 2,000 ppm	Complaints of drowsiness and poor air
2,000 – 5,000 ppm	Headaches, sleepiness, and stagnant, stale, stuffy air. Poor concentration, loss of attention, increased heart rate and slight nausea may also be present
5,000 ppm	Workplace exposure limit (as 8-hour TWA) in most jurisdictions
> 40,000 ppm	Exposure may lead to serious oxygen deprivation resulting in permanent brain damage, coma and even death

According to NIOSH concentrations of 40,000 ppm or higher should be regarded as immediately dangerous to life and health. Exposure to very high concentrations (e.g. exposure to 6% volume CO₂ for several minutes or 30% volume CO₂ for 20-30 seconds), has been linked to permanent heart damage, as evidenced by altered electrocardiograms.

Concentrations greater than 10% are capable of causing loss of consciousness within 15 minutes or less.

- **How NDIR (non-dispersive infrared) CO₂ sensors detect gas**

The most widely used technique for real-time measurement of carbon dioxide is by means of non-dispersive infrared (NDIR)

sensors that measure CO₂ as a function of the absorbance of infrared light at a specific wavelength.

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. Vibrational modes are dictated by the nature of the specific bonds that hold the molecule together. The larger the molecule, the greater the number of modes of movement. Each mode represents vibrational motion at a specific frequency. The modes are always the same for a specific molecule. Chemical bonds absorb 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.

Specific molecules absorb infrared radiation at precise wavelengths. When infrared radiation passes through a sensing chamber containing a specific contaminant, only those wavelengths that match one of the vibration modes are absorbed. The rest of the light is transmitted through the chamber without hindrance. The presence of a



Figure 3: IR CO₂ sensors detect gas as a function of absorbance of infrared light at a specific wavelength

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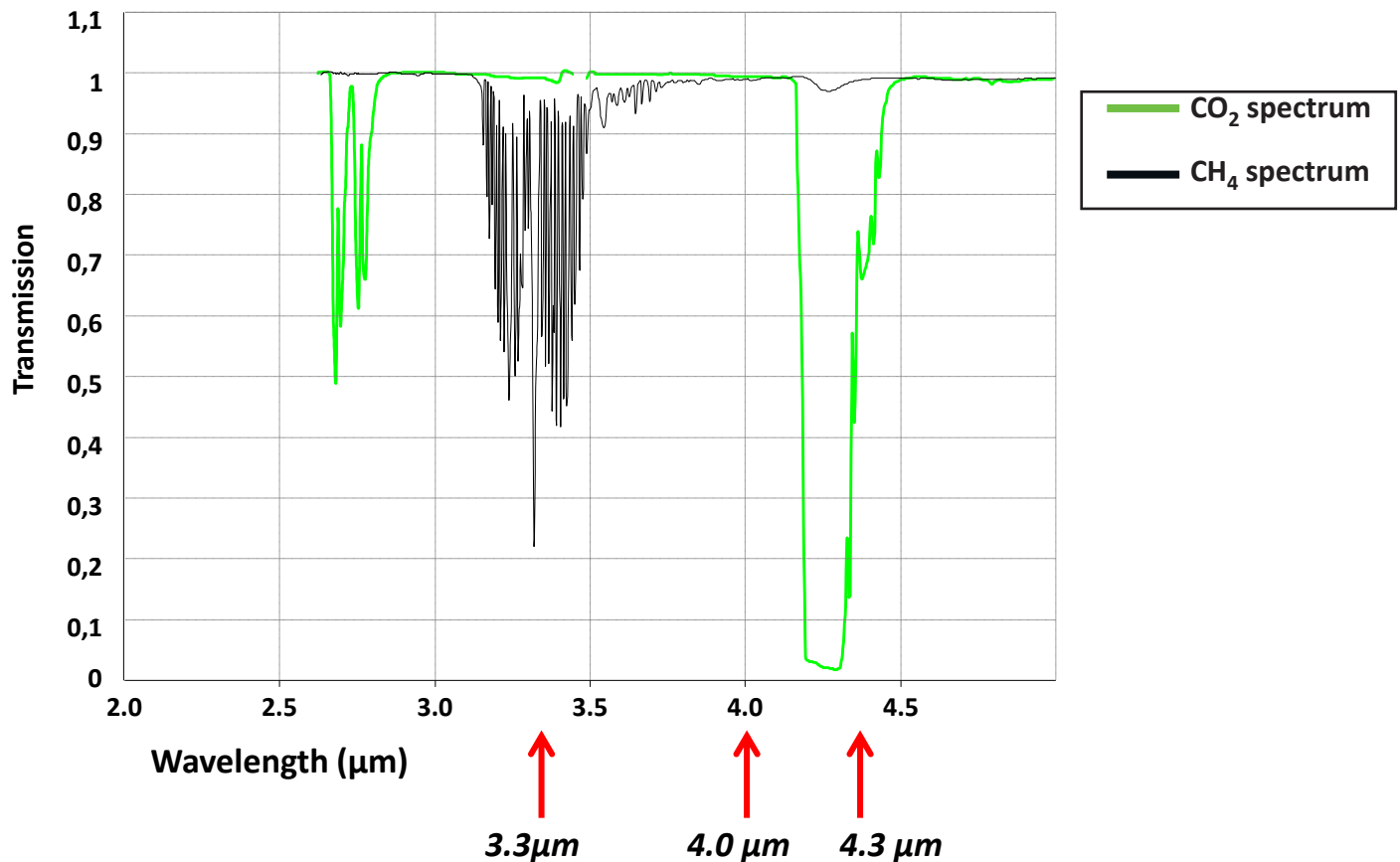


Figure 4: Infrared transmittance spectra for methane and carbon dioxide. IR sensors usually measure CO₂ at a wavelength of 4.3 μm (= 4,300 nm). IR CO₂ sensors usually use 4.0 μm (= 4,000 nm) as the reference since neither CO₂ or water absorbs much IR light at this wavelength. Combustible gases like methane are usually measured around 3.3 μm (= 3,300 nm).

particular chemical group within a molecule thus gives rise to characteristic absorption bands. Since most chemical compounds absorb at a number of different frequencies, IR absorbance can provide a "fingerprint" for use in identification of unknown contaminants.

Alternatively, for some molecules it may be possible to find an absorbance peak at a specific wavelength that is not shared by other molecules likely to be present. In this case absorbance at a particular wavelength can be used to provide substance-specific measurement for a specific molecule. Carbon dioxide has such an absorbance peak at a wavelength of 4.3 microns (μm). Absorbance of infrared light at this wavelength is proportional to the concentration of CO₂ present in the sensing chamber of the sensor. The absorbance is not linear per concentration unit, but is mathematically predictable and easily calculated by microprocessor equipped portable gas detectors.

Miniaturized NDIR CO₂ sensors include an infrared light source (typically a tungsten filament lamp) capable of emitting light in the desired wavelengths. Optical filters are used to limit the light transmitted through the sensing chamber to a narrow range of wavelengths. Most NDIR CO₂ sensors are dual detector systems that provide both a reference and an active signal. Pyroelectric detectors capable of measuring absorbance at the specific wavelengths of interest are used to provide the measurement and reference signals. The active detector in a CO₂ sensor measures the amount of light in the 4.3 μm range that reaches the detector after passing through the sensing chamber. The reference detector measures the amount of light at another wavelength (or range of wavelengths) where there is no absorbance for the gas of interest. The greater the concentration of CO₂, the greater the reduction in the amount of light that reaches the active detector when compared to the reference signal.

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Figure 5: Infrared CO₂ sensors are also available for use in continuously operational “fixed” detection systems.

In the past, infrared based instruments have tended to be bulky, expensive, and required a high level of operator expertise to obtain accurate readings. A new generation of miniaturized NDIR sensors has permitted the development of infrared based instruments for an ever widening variety of atmospheric hazards including carbon dioxide, Freons®, ammonia, and methane, as well as generalized hydrocarbon combustible gas detection.

The regulations are already changing. Recent fatalities in the wine industry in California and Oregon have heightened concerns, and increased the obligation for direct CO₂ measurement during workplace procedures that may expose workers to this contaminant in the wine making industry. In Germany and Austria regulations already require direct measurement of CO₂ during most confined space entry procedures. It is clear that with the increased availability, and increasingly affordable cost of miniaturized NDIR CO₂ sensors, more and more atmospheric monitoring programs will include the direct measurement of this dangerous atmospheric contaminant.

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