There is no Antidote for Lack of Oxygen

With each breath we prove the importance of oxygen. Our life depends on it. Each time we take in a breath of air, we take in approximately 20% oxygen and 80% nitrogen. Under normal atmospheric pressures, the higher partial pressure of oxygen (O_2) in a breath of "fresh" air means that the oxygen diffuses from our lungs into our blood stream and then is carried throughout our body. Without this oxygen, the cells in our body will quickly die. While Chemical Warfare Agents (CWAs) are very toxic, there are antidotes for them and some other toxic gases and vapors. If oxygen is removed from the atmosphere that we are breathing, without the restoration of oxygen we will quickly die. There is no other antidote.

Humans Can't Sense Oxygen

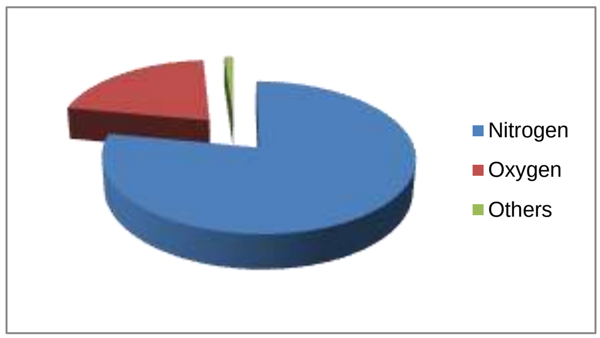
Because humans cannot sense oxygen deficient environments, we must use and understand detection technologies that will allow us to properly sense oxygen depleted environments. In this white paper we will discuss:

1. The importance of knowing the oxygen concentration in both deficient and enriched environments.
2. How to use oxygen as a "broadband" indicator that other gases have entered the environment.
3. The common types of oxygen sensors used in personal/handheld detectors.
4. Describe the failure modes, and their causes, of oxygen sensors.

"Fresh Air"

In a short hand way, air is often referred to as 20% oxygen and 80% nitrogen. But in reality air is a more complex mixture of the following gases:

- This mixture or matrix of gases is what is considered "normal" air. Changes to this mixture can be hazardous to our health and may affect other sensors. For example:
- Air has a molecular weight (MW) of 29, as lower MW gases are substituted into the matrix it can affect the performance of some oxygen sensors.
- High levels of water (H_2O) vapor can affect PID performance
- Oxygen is required for catalytic bead Lower Explosive Limit (LEL) and electrochemical toxic gas sensors to operate, below 12-14% oxygen catalytic bead LEL sensors become unreliable due to lack of oxygen for their oxidative process
- Nitrogen is important for zeroing Thermal Conductivity (TC) sensors, as the concentration of nitrogen changes the TC sensor output will change
- We can't zero carbon dioxide sensors in air because there is always a background level of carbon dioxide..



Nitrogen	N_2	78%
Oxygen	O_2	20.90%
Argon	Ar	0.93%
Water	H_2O	0-3%
Carbon Dioxide	CO_2	340 ppm
Neon	Ne	18.2 ppm
Helium	He	5.2 ppm
Methane	CH_4	2 ppm
Krypton	Kr	1.1 ppm
Hydrogen	H_2	0.5 ppm
Nitrous Oxide	N_2O	0.5 ppm
Xenon	Xe	0.09 ppm
Volatile Organic Compounds	VOCs	<1 ppm

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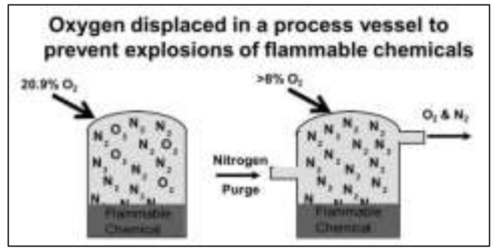
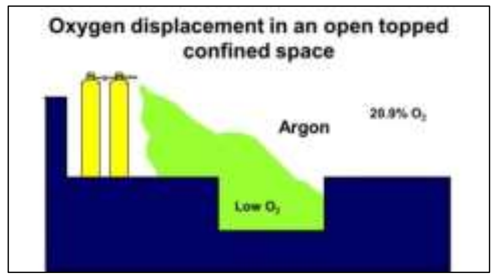
Oxygen Deficiency

According to the OSHA (US Occupational Safety and Health Administration) rule contained in 29CFR1910.146 or "the Confined Space Standard" air is oxygen deficient whenever the concentration is less than 19.5%. This provides protection for normal workers both at sea level and at normal higher elevations. The movement of oxygen from the lungs into the bloodstream isn't driven by concentration, but rather by partial pressure of oxygen (PO2) which at sea level is 20.9% of 760 mm/hg or 158.8 mm/hg. Causes of oxygen deficiency can include:

- **Displacement:** A gas is added to the atmosphere that displaces the normal atmosphere and reduces the oxygen content. One example of this is adding an inert gas like nitrogen to vessels containing flammable liquids to get the oxygen levels below the point that will support combustion (typically less than 8%). This process is called "inerting" and is common in processing of flammable chemicals, aircraft wing-tanks and shipboard fuel tanks. Entering inerted vessels can be quickly fatal. We can also see oxygen displacement in open topped spaces when a gas that is heavier than air, like argon or carbon dioxide, can collect.





- **Microbial action:** Oxygen consuming (aerobic) bacteria that use up the oxygen in the atmosphere are often found in sewers.
- **Oxidation:** Chemical processes that use oxygen consume the oxygen in the atmosphere. One common example is rust. Large water tanks and barges made of steel will rust when exposed to water. The rusting action stops when the oxygen in an enclosed space is entirely consumed.
- **Combustion:** A fast form of oxidation where a fire or explosion consumes the oxygen in an enclosed space.
- **Absorption:** Large amounts of some chemicals will preferentially absorb oxygen.

Dry Ice Kills in a Meat Packing Plant

As part of his job a worker had to go into an open pit at a meat packing plant to clean out the waste in the pit. Upon entering the pit the worker quickly succumbed due to low levels of oxygen. The investigation demonstrated that there was low oxygen in the pit because dry ice was used to help the flash freeze processing of the meat. Dry ice sublimates to carbon dioxide which is heavier than air and settled in the pit to create the low oxygen environment.

Symptoms of Oxygen Deficiency

Oxygen is required to sustain life. As oxygen levels go down not only is it harder for us to breath, but it becomes increasingly difficult to make good decisions because less oxygen is going to our brain. Symptoms of oxygen deficiency can have very fast on-set. While many people can hold their breath for a minute or more, if one doesn't recognize that the atmosphere is lacking oxygen they will continue to breathe "normally." The lungs are not a one-way oxygen transfer system; oxygen transfer is driven by the partial pressure of oxygen. In normal conditions the partial pressure of oxygen in the alveoli is higher than the blood, so oxygen will diffuse from the alveoli to the blood stream. But if the partial pressure of oxygen in the blood stream is higher than it is in the alveoli of the lungs, as it could be if one breathes in an oxygen depleted atmosphere, the oxygen will transfer from the blood-stream to the lungs and quickly rob one of precious oxygen.

20.9 %	Oxygen content in normal "fresh" air
19.5 % - 12 %	Impaired judgment, increased pulse and respiration, fatigue, loss of coordination
12 % - 10 %	Disturbed respiration, poor circulation, worsening fatigue, decreased mental awareness symptoms within seconds to minutes
10 % - 6 %	Nausea, vomiting, inability to move, loss of consciousness, and death
6 % - 0 %	Convulsions, gasping respiration, cessation of breathing, cardiac arrest, symptoms immediate, death within minutes

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Oxygen Enrichment

High levels of oxygen can proportionally increases the rate of many chemical reactions. It can cause ordinary combustible materials to become flammable or explosive. The Apollo 1 command module fire in 1967 was allegedly caused by Velcro becoming explosively combustible in an oxygen enriched environment. According to one expert "Things get strange above 30% Oxygen."

- A candle in a pure oxygen environment burns VERY quickly
- Mix liquid oxygen with kerosene, which isn't normally thought of as being flammable or explosive, and you have rocket fuel
- Road asphalt saturated with liquid oxygen will explode under the slightest pressure and behave much like a landmine

OSHA's Confined Space Standard, 29 CFR 1910.146, specifies that any atmosphere over 23.5 % is oxygen enriched. Some other codes are more stringent. One of the most conservative approaches is to use 22% oxygen as take action point. But anytime an atmosphere is oxygen enriched or if organic materials are still outgassing oxygen from a liquid oxygen spill, it is best to wait until levels have returned to normal before returning the area to normal usage.

Enriched Oxygen Examples

One doesn't have to work for NASA to encounter enriched oxygen atmospheres. One of the most common ways to encounter enriched oxygen is in applications of Liquid OXygen or "LOX." LOX has an expansion ratio of 1:861 at standard atmospheric temperature and pressure. So a little spill will make a lot of oxygen. Because LOX is an efficient way of transporting and storing oxygen, it is found in places that use a lot of oxygen (like medical and industrial processes). While once contained to hospitals and big chemical plants, cryogenic liquid cylinders of LOX can now be found used for home medical treatments and even used to bubble oxygen into 200 gallon live fish totes. Because LOX has become more common in our communities we have to be more vigilant about enriched oxygen atmospheres.

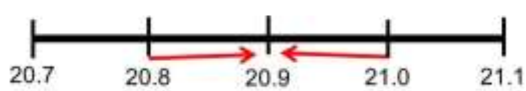
Oxygen Sensors as a "Broad-band" Toxic Sensor

If no other sensing technology will "see" a toxic gas/vapor in an atmosphere, the oxygen sensor provides a way to "see" it via oxygen displacement.

- Air is 20.9% or 209,000 ppm oxygen (O_2)
- Air is 78% or 790,000 ppm nitrogen (N_2)
- A decrease in O_2 concentration from 20.9% to 20.8% means that there may be as much as 5000 ppm of "something else" in the air.
    - Decreasing from 20.9 to 20.8% Oxygen is a decrease in oxygen of 1000 ppm, but Air is 20% O_2 so that means that the other 80% of N_2 must be displaced too.
    - 20/80 = 1000/x then x is 4000 and 4000+1000= 5000
    - Every 0.1% Oxygen drop is as much 5000 ppm of "something else."
    - Every 1000 "oxygens" leave with 4000 "nitrogens" for a total of 5000.
    - It doesn't matter if the diluting gas is chlorine or nitrogen, the effect is the same.

Oxygen sensor "Dead Band"

Many gas monitor manufacturers put a "dead-band"around 20.9% oxygen, forcing the detector to read "20.9" when the real readings may be jumping around a little. This is done to give users more "confidence" in the oxygen sensor readings in normal 20.9% scenarios. For example if the manufacturer has implemented a 0.2 % oxygen dead-band all potential readings between 20.8% and 21.0% are forced to read 20.9%. This can reduce the perceived "jumpiness" of oxygen sensors but it can reduce their effectiveness as a broad-band toxic sensor. Dead band values are not typically published in detector specifications but 0.2% seems to be a minimum value and some detectors may have dead-band values as high as 0.3% meaning that one would not see a change in the detector reading even though O_2 was decreasing from 20.9 to 20.6%.



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On a meter that has a 0.2% dead-band, if the oxygen sensor jumps from 20.9 to 20.7 you won't notice 5000 ppm of "something else" you might only see the first 10,000 ppm of it. While oxygen is only a gross broad band sensor sometimes is all you've got. Assuming that oxygen is not being consumed, if oxygen drops AT ALL you have a LOT OF SOMETHING else in the air, so much so that ***you should expect response from most electrochemical sensors if only as a reading from cross-sensitivity***

Oxygen consumption

Now that you've learned the rule of 5000, note that the exception to the rule is when oxygen is consumed without a contaminant being added to the atmosphere:

- **Chemical Oxidation:** Rust may be the most common form of this and it makes enclosed spaces made of or containing steel/iron and water particularly dangerous. The ferrous metals will oxidize in the presence of water and oxygen until the oxygen is totally consumed at which point the system becomes stable and rusting ceases.
- **Combustion:** A faster form of oxidation usually accompanied by flame/smoke. In addition to consuming oxygen, combustion produces many byproducts (some may be toxic) so this is a case where the drop in oxygen will be accompanied by an increase in toxicity.
- **Absorption/Adsorption:** Some chemicals can absorb/adsorb oxygen. Perhaps the most common adsorbent is activated carbon as found in a filtration system. Damp curing concrete will also absorb oxygen from air.
- **Metabolism:** Many living organisms consume oxygen. In closed systems that contain organisms, from aerobic bacteria to people, the oxygen will be consumed. Metabolism produces many byproducts (some may be toxic) so this is a case where the drop in oxygen may be accompanied by an increase in toxicity. Carbon dioxide is the chief toxic by-product of human respiration.

Types of Oxygen Sensors

While there continue to be innovations in oxygen sensor design for portable products, the oxygen sensors most commonly used in most of today's handheld meters break down into one of the following types:

1. **Electrochemical "Fuel Cell"** sensors (using either capillary or membrane diffusion limiting mechanisms)
2. **Solid polymer electrolyte (SPE)** or "nafion" sensors (using a capillary diffusion limiting mechanism)

Fuel Cell Oxygen Sensors

The oxygen sensor generates electrical current proportional to the oxygen concentration. Oxygen entry into the cell must be limited or else it would be quickly used up by the 20.9% oxygen in air. Think of the oxygen sensor as a coffee cup where the coffee is the electrolyte mixture. With the lid off the oxygen will get to the electrolyte and consume it quickly. But if you put a lid with a sip hole on the coffee cup then it limits the entry of oxygen to the coffee "electrolyte." One could also put oxygen permeable "glad-wrap" over the top of the coffee cup to limit the entry of oxygen. In a real oxygen sensor, entry is typically limited by one of two means:

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1. **Capillary pore**: similar to the sip hole on a coffee cup, this is the most common fuel cell oxygen sensor. It gives direct reading of % volume. A hole that is about the size of a human hair limits the flow of oxygen into the sensor.
2. **Membrane:** Similar to the "glad-wrap" over the coffee cup, this O_2 permeable membrane provides direct measurement of partial pressure of oxygen. The rate at which oxygen diffuses into the sensor is limited by a membrane. While reading in partial pressure the output of these sensors is typically converted into percent volume on the handheld detector.

Regardless of the diffusion mechanism, oxygen enters the sensor then:

Oxygen is reduced to hydroxyl ions at the cathode:

$O_2 + 2H_2O + 4e- \longrightarrow 4OH-$ (basic environment)

Hydroxyl ions oxidize the (lead) anode:

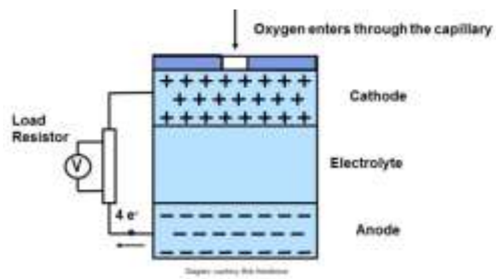
$2PB + 4OH- \longrightarrow 2PbO + 2H_2O + 4e-$

Overall cell reaction:

$2PB + O_2 \longrightarrow 2PbO$

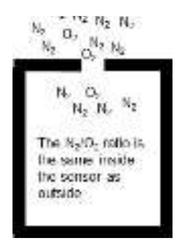
The fuel cell oxygen sensor is a one-way, 26 (or 13) month trip from lead to lead oxide. Life is entirely determined by how much oxygen gets into the sensor. The more oxygen gets in, the faster the sensor is used up and dies. So these sensors will die faster when routinely used in an oxygen enriched atmosphere and they may live longer when used in inerted atmospheres.

Capillary Fuel Cell Oxygen Sensors



The capillary fuel cell oxygen sensor is the most common oxygen sensor type in portable gas detectors. It provides for a true percent volume measurement. This is due to the "battle" between nitrogen and oxygen molecules trying to get through the capillary.

- O_2 has a MW of 32 and N_2 has a MW of 28 so they are in relative balance in the battle to get in the capillary
- This results in a true % volume reading because the ration of oxygen to nitrogen inside the sensor is the same as it is outside of the sensor.
- Minor fluctuations in pressure and barometric pressure will not change the sensor reading. Although large pressure changes can cause pressure transients as the sensor slowly equalizes pressure through the capillary pore.
- At the top of Everest it will still read 20.9%



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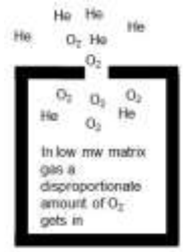
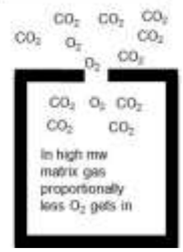
Matrix effect on Capillary Oxygen Sensors

Capillary sensors are much more common in personal gas monitors than membrane oxygen sensors, but sometimes they can have issues. Matrix gases other than nitrogen can affect capillary oxygen sensor readings:



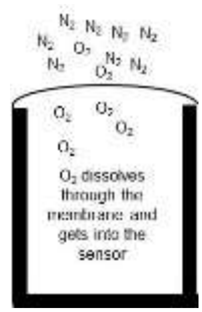


- Matrix gases with lower molecular weight than N_2 (like He with a MW of 4) will increase O_2 sensor readings because O_2 wins the battle into the capillary
  - The battle to get into the capillary pore is like a wrestling match, and the big fat (high MW) guy wins and preferentially enters the sensor.
- Matrix gases with a higher molecular weight than nitrogen (like carbon dioxide with a MW of 44) should decrease oxygen sensor readings because the carbon dioxide wins the battle into the capillary.
  - High levels of carbon dioxide in the aqueous electrolyte (water) produces carbonic acid which neutralizes the hydroxyl ions (OH-) and can slow down the chemical reaction.
- This effect depends on the molecular weight difference in the matrix gas that is applied to the sensor if it has been previously calibrated in air:
  - **Hydrogen:** with a molecular weight of 2, if nitrogen in air is replaced by hydrogen, oxygen readings will increase.
  - **Helium:** with a molecular weight of 4, if nitrogen in air is replace with helium, oxygen readings will increase.
  - **Ammonia:** with a molecular weight of 17, if the nitrogen is replaced with ammonia, oxygen readings will increase
  - ***Note that oxygen readings can increase even though the actual concentration may not be increasing.***
  - Generally speaking both the oxygen and the nitrogen are replaced so the oxygen levels will go down although the oxygen drop may be delayed.

- Response = Response in N_2 (air) x $\sqrt{28/mw}$
  - Where mw = average molecular weight of the new matrix gas
  - 28 = molecular weight of nitrogen
- For example, for a sensor calibrated in air and used to measure in 80% helium/20% nitrogen mix:
  - Average molecular wt. = 0.8(4) + 0.2(28) = 8.8
  - Response = Response in N_2 (air) x $\sqrt{28/8.8}$ = 1.78
  - Therefore the reading will be 78% higher in the He/N_2 mix and would need to be divided by 1.78 to obtain the true reading.

Membrane Fuel Cell Oxygen Sensors

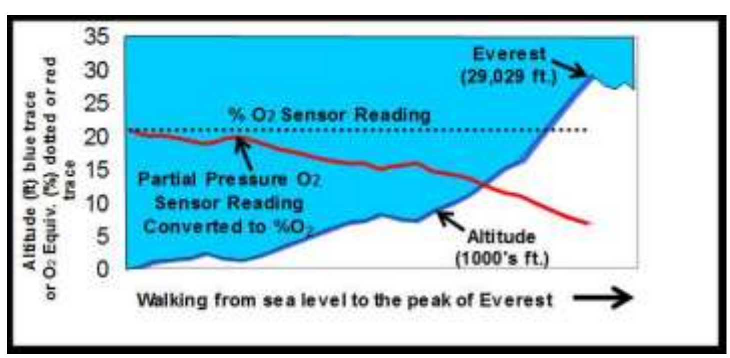
In a membrane fuel cell oxygen sensor there is a very thin, plastic oxygen permeable membrane over the top of the sensor which is a solid barrier in which the oxygen molecules must dissolve into in order to reach the sensing electrode.



- Entry into the cell is driven by the differential of oxygen partial pressure across an oxygen permeable membrane
- This results in a partial pressure reading which is usually corrected to %Oxygen in the detector's electronics
- Minor changes in pressure and barometric pressure can change the sensor readings unless it is corrected for pressure

Oxygen Deficiency-Partial Pressure

Imagine that one walks from sea level to the top of Mt. Everest with two detectors calibrated at sea level . This graphic shows that while the % volume oxygen sensor (dotted black line) always reads 20.9% oxygen despite the altitude (blue line), the partial pressure oxygen sensor reading converted to % oxygen (solid red line) decreases with altitude. There is more distance between oxygen molecules at altitude versus sea-level, put another way



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there is a lower partial pressure of oxygen at altitude, but they are still in the same ratio or concentration of 20.9%.

The partial pressure oxygen sensor is commonly used in monitoring oxygen in gases used in underwater diving applications where partial pressure and matrix effects of dilutant gases are of concern. For example helium is often used to replace nitrogen in air for deep diving applications where nitrogen narcosis is possible and a capillary oxygen sensor will not be accurate when changing from air (a nitrogen/oxygen matrix) to a helium/oxygen matrix.

Volume versus Partial Pressure at the Top of Mount Everest

At the top of Everest (29,029 ft.), the standard barometric pressure is 34kPa (253 mmHg), this means that there is 33% of the oxygen available at sea level and a meter using the partial pressure membrane oxygen sensor would read only 6.9% if it had been calibrated at sea level and was not corrected for pressure changes while the % volume capillary oxygen sensor would still read 20.9%.

In 2012 Hurricane Sandy hit the northeast coast of the United States with a record low eye pressure of about 940 millibars

- Sandy's ATM pressure was 940 millibars = 13.6 psia = 0.928 ATM
- 20.9% of Sandy's ATM pressure = 20.9% x .928 ATM = 19.4% Partial Pressure of oxygen (PO2) corrected for Sandy's ATM Pressure
- So, Sandy's PO2 (19.4%) was below OSHA's IDLH of 19.5%, or about the same as climbing to about 2060 feet
- If a partial pressure oxygen sensor was not compensated or re-zeroed during this record low, it would read 19.4% Oxygen and be in low oxygen alarm.

Fuel Cell Oxygen Sensors Compared

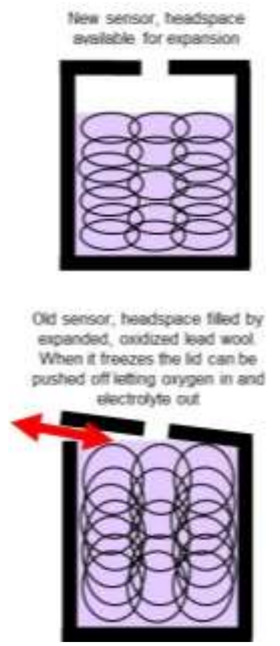
Capillary

- Most Common in handheld detectors
- Reads % Volume
- + Reading doesn't change with pressure
- − Affected by molecular weight of matrix gases
- − Acid gases like carbon dioxide can get in the sensor and can affect performance
- RAE, ISC, MSA, Draeger

Membrane

- Less Common in handheld detectors
- Read % Volume corrected from partial pressure
- + Unaffected by changes in matrix gases
- + Membrane is selective to oxygen and prevents neutralization from acid gases like carbon dioxide

- Reading may change with pressure
- RKI, Draeger (0-100% sensors only)



Fuel Cell Oxygen Sensor Failure Modes

- Once all the available surface area of lead anode is converted to lead oxide the sensor will not produce any more output.
- Electrolyte leakage due to physical damage such as dropping or freezing.
- Desiccation (drying out) in hot dry environments such as storage in hot environments consistently over 120ºF (49ºC) like in the trunk of a car in the summer.
- Blockage of capillary pore/coating of the membrane by liquids or dirt.
- Freezing an oxygen sensor can "pop" the top on older sensors because the aqueous electrolyte freezes, expands and causes the sensor to burst. This is often found with older sensors stored at extremely low temperatures (<0ºF,< -18ºC) because the electrolyte is not pure water it will freeze until significantly below 32ºF (0ºC). Lead oxide is bigger than the lead wool. As the sensor ages and the lead wool is converted to lead oxide it needs to expand and room is provided in the sensor for this expansion. However, frozen water will expand also. So if a new sensor is exposed to extremely low temperatures sensors it may freeze but its electrolyte may not expand enough to rupture the sensor. In older sensors, where the lead wool has expanded to lead oxide, freezing a sensor could result in the electrolyte expanding enough to rupture because the room for expansion has been used up. When this happens, upon thawing one might see very high oxygen readings because the diffusion limiting capillary or membrane has been circumvented and oxygen is pouring into the sensor. It will quickly get used up. The concern in this situation is for the sensor board, because the caustic electrolyte can spill onto the sensor board, and other boards, requiring their replacement.
- Electrolyte neutralized by exposure to high levels of carbon dioxide in the aqueous electrolyte (water) produces carbonic acid which neutralizes the hydroxyl ions (OH-) and shuts down the chemical reaction
  - Such levels are only found in breweries, bottlers and dry ice plants.
  - Exhaling into your monitor WILL NOT HURT the oxygen sensor.

Fuel Cell Oxygen Sensor Summary

<u>Advantages</u>

- + Proven technology
- + Fail safe (they typically fail to zero)
- + Required for properly measuring combustibility

<u>Disadvantages</u>

- − Always "on" with limited and finite life span (<26 months)
- − Contain toxic heavy metal (lead)
- − Leaking electrolyte can ruin meter
- − Only can detect gross levels of TICs

Solid Polymer Electrolyte (SPE) Oxygen Sensors

Also known as an "oxygen pump" or "nafion" sensors, these sensors offer longer potential life. They avoid the leakage problems associated with traditional "Fuel Cell" Oxygen sensors containing lead wool and liquid electrolyte and they eliminate lead. This makes the SPE sensor "RoHS" (Restriction of Hazardous Substances Directive) compliant which is a European standard that provides for "the restriction of the use of certain hazardous substances in electrical and electronic equipment." Fundamentally this standard seeks to reduce the amount of toxic metals like lead and tin in electronics.

Oxygen enters the sensor through a capillary and is reduced to water at the cathode by the following reaction:

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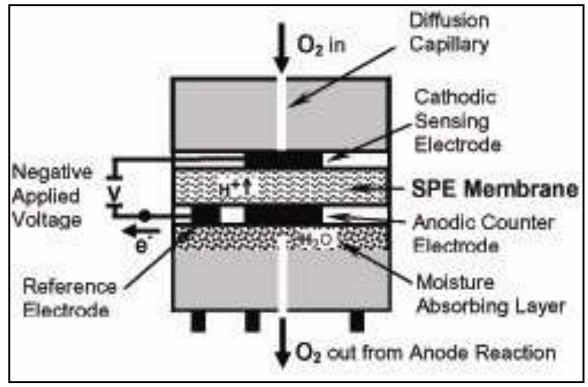
$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

In the other half-cell, water is oxidized to oxygen, and protons are released:

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

The protons travel across the SPE (nafion) membrane, and oxygen is vented through a second opening on the bottom side of the sensor ***Humidity is absorbed from the ambient air*** and is stored in a water-absorbing layer, this layer and the SPE membrane are moist, but not wet, and therefore the sensor cannot leak. This makes the SPE oxygen sensor kind of like an "air plant" because it gets its moisture from air. But this can lead to problems when this sensor is implemented in excessively dry climates. The amount of current necessary to reduce the incoming oxygen at the sensing electrode is proportional to the concentration of oxygen in the atmosphere being sampled. The net reaction of oxygen entering the top and leaving the bottom gives rise to the common name of ***"oxygen pump"*** for this type of sensor.



SPE Oxygen shares many Capillary Effects

As the SPE sensor uses a capillary to limit oxygen response, it should demonstrate the same capillary effects as the capillary fuel cell sensor. It is a % volume sensor and it should have the same affects from changing molecular weights in matrix gases. But because the SPE does not have a basic aqueous electrolyte it should not suffer neutralization effects from acid gases such as carbon dioxide.

SPE Oxygen Sensor Summary

Advantages

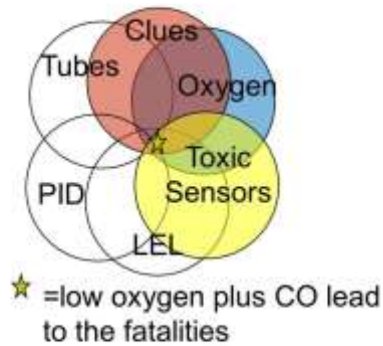
- + Potential of much longer life span (~5 years)
- + Do not contain significant amounts of toxic compounds and are RoHS compliant
- + No electrolyte to leak out
- + Light weight
- + Fail safe
- + Required for properly measuring combustibility

Disadvantages

- − Still relatively unproven technology
- − Can fail in excessively dry climates
- − Higher power consumption
- − Slightly slower response (30 vs. 15 seconds)
- − Only can detect gross levels of TICs

The story of Unstable Oxygen Sensors

Two people (one a senior state official) were found dead in a ground floor apartment on a cold February in a former Soviet Union state. Carbon Monoxide poisoning from a natural gas heater was suspected. CO was when the heater was running in the apartment but not enough to immediately lethal (~300 ppm). A multi-point wireless gas on system was used to monitor inside and outside of the apartment confirm CO poisoning was the culprit. Multiple detectors were inside and outside of the apartment. The three oxygen sensors apartment read 20.7, 20.8 and 20.6%. Using the rule that every drop in oxygen means that there is 5000 ppm of "something else" in the air these readings indicate 15,000, 10,000 or 20,000 ppm of "something else" in the apartment. While one oxygen



sensor reading 20.7% may be a "flakey sensor," three tell you something is going on. From this data, it was found that the heater was drawing oxygen from a very tightly sealed apartment and make up air was being drawn in through the flue because the stack was missing. When the security detail started their cars to keep warm, high levels of CO were generated in the alley next to the apartment and this was drawn into the apartment through the broken flue. The fatalities were due to a combination of low oxygen levels and elevated CO.

- **Clues:** two fatalities in apt.
- **Oxygen:** depressed oxygen levels indicate "something else" is there
- **Toxic:** CO sensors are elevated but not lethal
- **LEL:** no change in reading
- **PID:** no change in reading
- **Tubes:** none used

The story of the Slow Oxygen Sensor

HazMat was called to a university kitchen because of complaints of dizziness, weakness and nausea when workers entered a walk-in freezer/refrigerator. When HazMat arrived they found nothing abnormal in the refrigerated section but the door to the combination unit was open allowing for ventilation prior to arrival, they made entry into the refrigerated portion of the freezer wearing SCBA and turnout gear and found nothing using a 4 gas meter and PID. They doffed their gear to question the kitchen supervisor and those complaining of weakness and nausea who provided them with no additional clues. While looking at the combination freezer/refrigerator they noticed plastic slats separating the two walk in units. They remotely sampled the freezer section of the unit by putting the gas meter through the slats and saw no change in the meter readings. After sampling with their meter, they entered the freezer unit by walking though the slats and began to survey further. At about 12 feet into the freezer section the two members of the entry team felt "funny" and "light headed." Within a few seconds of the on-set of symptoms the 4 gas meter indicated a low oxygen environment (<19.5% oxygen), and went into alarm. This was about 60 seconds after entering the room and was 30 seconds after the entry team members felt the effects.

When questioned again, the supervisor told Hazmat about a pallet of dry ice being stored in the freezer for the university beauty pageant they had scheduled for the weekend. Dry ice sublimates into carbon dioxide (CO_2). Based upon the fact that the oxygen sensor went into alarm after entering the freezer section, this means it was measuring less than 19.5% oxygen. Therefore, the entry team was exposed to more than IDLH levels of carbon dioxide based upon the following math:

- TWA 5,000 ppm, 0.5% by volume JUST 20.8% oxygen
- STEL 30,000 ppm, 3% by volume JUST 20.3% oxygen
- IDLH 40,000 ppm, 4% by volume JUST 20.1% oxygen
- 19.5% oxygen means that there was 7% (20.9-19.5 = 1.4, 14 x 5000 = 70,000 or 7% by volume) carbon dioxide in the freezer, nearly twice IDLH

The freezer/refrigerator was classified as a confined space until the pallet of dry ice was removed.

Oxygen sensors should respond quickly. There are two contributing factors that can account for the delayed response of the oxygen sensor:

1. CO_2 with a MW of 44 is significantly heavier than air with a MW of 29. Prior to entering the freezer section the CO_2 would be towards the floor and the metering may not have picked this up. Upon entering the freezer section the responders mixed the CO_2 into the air.
2. Because of its higher molecular weight CO_2 will beat out O_2 for the battle into the O_2 sensor capillary. This allows the CO_2 to react with the aqueous electrolyte to produce carbonic acid. This acid works to neutralize the basic KOH electrolyte and slow oxygen sensor response and in extreme amounts can ruin the sensor. Normal oxygen sensor response time is about 15-20 seconds. It seems that CO_2 exposure can delay capillary fuel cell O_2 sensor readings for 2-3 minutes. Ultimately a high molecular weight matrix gas like CO_2 should produce lower than actual readings on the O_2 sensor.

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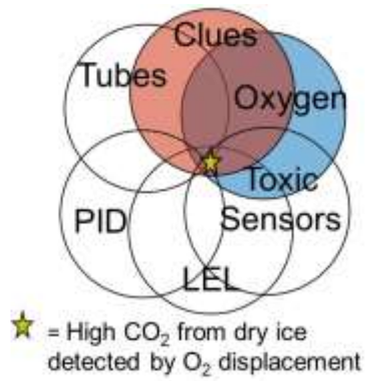
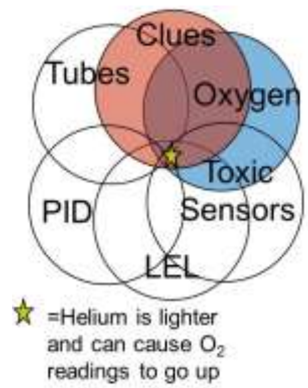


- **Clues:** food freezer before homecoming, workers complaints of dizziness, light-headedness and nausea. Further questioning identified dry ice in the freezer
- **Oxygen:** delayed response to low oxygen levels cause by CO_2 displacement
- **Toxic:** nothing indicated, could have used NDIR carbon dioxide sensor
- **LEL:** no change in reading
- **PID:** no change in reading
- **Tubes:** could have used a CO_2 tube

Oxygen Sensor Reads Higher

Teenage girls found deceased in a car with a cylinder of helium visible. Initial metering around the door seals of the car showed a slight increase of oxygen before levels dropped to near zero when the sample probe was pushed into the closed car. It was found that the oxygen sensor used was capillary based and the lighter molecular weight of helium relative to oxygen was responsible for the slight initial increase in oxygen levels.



- **Clues:** car with victims and helium balloon cylinder in it
- **Oxygen:** goes up and then goes down when probe is fully into the car
- **Toxic:** nothing indicated
- **LEL:** no change in reading
- **PID:** no change in reading
- **Tubes:** none recommended

Oxygen Sensor Summary

Advantages

- ✚ Continuous Readings
- ✚ Proven Technology
- ✚ Specific
- ✚ Required for properly measuring combustibility

Disadvantages

- − Only can detect gross levels of TICs

About the Author

Christopher Wrenn is the Vice President of Americas Sales for AEssense Corp., a Silicon Valley developer and manufacturer dedicated to providing innovative technological solutions for plant growers worldwide. Previously Chris was Sr. Director of Sales and Marketing for Environics USA, a provider of sophisticated gas & vapor detection solutions for the military, 1st responder, safety and homeland security markets. Chris was also a key member of the RAE Systems team, helping to grow RAE's revenues from $1M/yr to nearly $100M/yr in the above mentioned markets.

Chris has extensive experience teaching gas and vapor detection and has been a featured speaker at more than 100 international conferences. He has written numerous articles, papers and book chapters on gas/vapor detection. Mr. Wrenn has received the following awards:

- 2011 "Outstanding Project Team Award," in recognition of outstanding service and dedication to the Real Time Detection Registry Team presented by the AIHA (American Industrial Hygiene Association) President
- 2015, received the James H. Meidl "Instructor of the Year" award at The Continuing Challenge, Sacramento, CA presented by CA State Fire Marshal

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- 2016, received the "Level A Award" from the International Hazardous Materials Response Team Conference "For your Leadership Service and Support to the Hazardous Response and Training Program."

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