

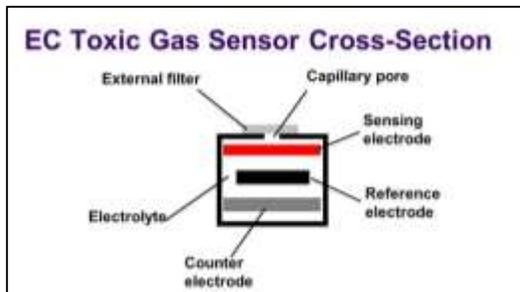
Getting the Most from Toxic Gas Sensors

Understanding and using the toxic gas sensors found in portable handheld detectors

Toxic gas sensors are commonly found in handheld gas detectors used in industry for confined space entry, and in potentially strenuous activities like hazardous materials (hazmat) response. Understanding how these sensors work, how they can fail and how to use them effectively in all circumstances is the key to extracting maximum value from them. Some electrochemical sensors include: Ammonia (NH₃), Carbon Monoxide (CO), Chlorine (Cl₂), Chlorine Dioxide (ClO₂), Ethylene Oxide (EtO), Hydrogen Cyanide (HCN), Hydrogen Sulfide (H₂S), Nitric Oxide (NO), Nitrogen Dioxide (NO₂), Phosphine (PH₃) and Sulfur Dioxide (SO₂).

How Electrochemical (EC) toxic gas sensors work

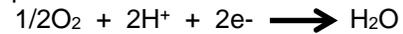
Basically, the EC sensor is a battery that turns concentrations of the gas of interest into a current output in proportion to the concentration of the gas, usually at part per million (ppm) levels. EC sensors are similar to dry cell batteries in construction. Gas diffuses into the sensor through a very small capillary hole and then reacts at the surface of the sensing electrode. The sensing electrode is made to catalyze a reaction specific to the toxic gas. EC sensors are often called "3-wire" sensors as they have a sensing, reference and counter electrodes. Use of selective external filters further limits cross-sensitivity for NEW SENSORS.



For example, carbon monoxide is oxidized at the sensing electrode:

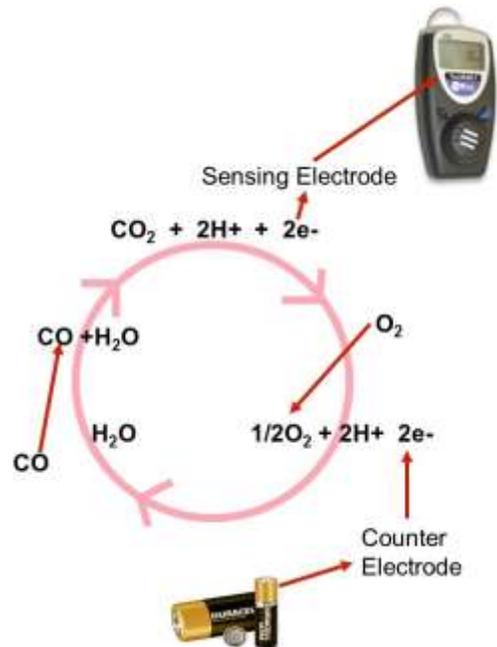


The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:



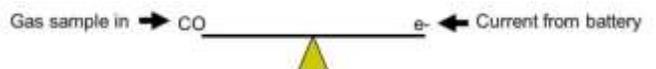
EC Sensors are a Regenerative Process

Unlike "fuel cell" oxygen sensors which have a one-way trip from lead to lead oxide, electrochemical toxic gas sensors are more of a circular process. Chemical comes in, reacts, generates electrical current, uses up water and then current from the battery is returned to the sensor to regenerate water in the presence of oxygen. It's a regenerative or circular process as long as you stay within the operating parameters (specs) of the sensor.



Stay within the operating parameters and you stay in balance

Another way to look at EC sensors is that



they are like a "see-saw." Under normal operation the amount of toxic gas in can be

Getting the Most from Toxic Gas Sensors

balanced by the electrical current added back in at the counter electrode:

Exceed the operating parameters & destroy the balance (& possibly the cell)

However, if the sensor is exposed to too much toxic gas (or sometimes interferent) it MAY not be able to balance back out. This may exceed the “maximum over-range” of the sensor or “Sensor IDLH.”



Sensor specifications help to define this and many other areas of sensor performance.

Understanding sensor specifications and how they might impact decision-making

Just like humans, sensors can stand to be exposed to certain levels of chemicals. Even too much of a “good” thing can kill sensors just like drinking too much water at one sitting can be fatal to humans. Understanding your sensors’ limitations will help you make better decisions and perhaps help you get more information from them. Sensor limitations are defined in sensor specifications published by monitor and sensor manufacturers. Sensor specs may vary from instrument specs as aspects of an instrument can impact sensor performance. EC sensors are typically designed to monitor at or below TWA levels of chemicals at “standard” environmental conditions, excursions outside of these “normal” conditions can lead to unusual readings and even damage to the sensor(s).

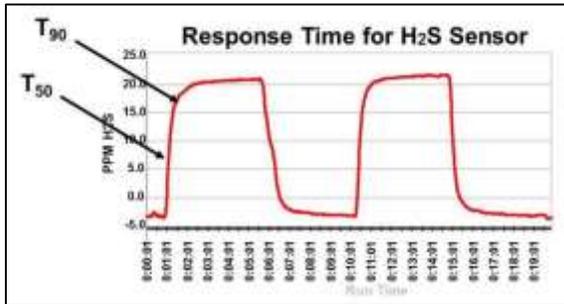
- **Range:** The normal operating concentration of a sensor where the best linearity is found. Exceeding the normal operating range may result in erroneous readings and long recovery times, but should not permanently damage the sensor as long as the Max Overload is not exceeded.
- **Max Overload:** The highest concentration that the electrochemical cell can stand before it is potentially irreversibly harmed. This rating is like the “Sensor IDLH” (Immediately Dangerous to Life & Health). Exceeding this value will likely give erroneous readings and cause permanent damage to the sensor.
 - **A big white cloud of ammonia will most likely kill an ammonia sensor.**

Electrochemical ammonia sensors can “see” relatively small amounts of ammonia without being exhausted; like a dry-cell battery, an electrochemical ammonia sensor only lasts a fixed period of time, measured in ppm/hours.

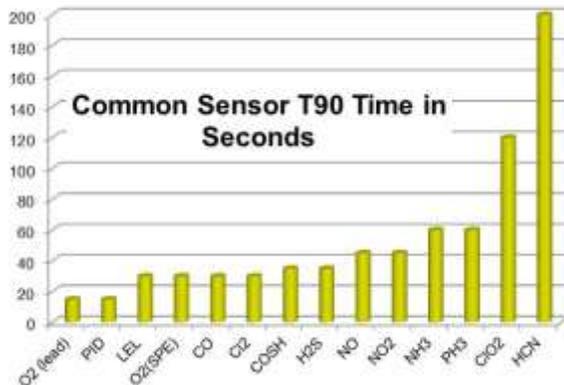
- Suppose an ammonia cell is rated for 20,000 ppm/hours, this means it can be exposed to 10,000 hours of 2 ppm ammonia or 1000 hours of 20 ppm but once 20,000 ppm/hours is reached the cell is dead. In addition to fixed life expectancy, electrochemical sensors have maximum overload ratings that are relatively low. For many ammonia sensors this “Sensor IDLH” is only 200-300 ppm. This is the root of the reliability problem with electrochemical ammonia sensors because they are quickly used up in the presence of large ammonia leaks and they cannot be used to help locate the leak.
- **Resolution:** The least significant digit on the display or the minimum amount of chemical that the sensor can “see,” aka: “Increment of measurement.” Typically most EC sensors offer 1 or 0.1 ppm resolution. Resolution requirements can change as exposure limits progress, for example the Threshold Limit Value (TLV) for H₂S was 10 ppm and it has changed to 1 ppm. While 1 ppm resolution was sufficient with the 10 ppm exposure limit, 0.1 ppm resolution is required with the 1 ppm exposure limit because with only 1 ppm resolution one jumps from 0 to alarm with no warning.
- **Limit of Detection (LOD):** The minimum amount of gas or vapor that the detector can accurately measure. This does not necessarily agree with the resolution of the meter and often is NOT as good as the meter’s resolution.
- **Response Time:** Time for a sensor to reach its final stable reading. Typically called T₉₀, or time to 90% of response and usually expressed in seconds. **Sensors don’t respond instantly, it is common to have to wait 30 or more seconds to respond, depending on the sensor and the sample draw.** The common O₂ (Oxygen), LEL (Lower Explosive Limit),

Getting the Most from Toxic Gas Sensors

CO, H₂S and PID (Photoionization Detector) typically found in today's "5-gas detector" all respond in less than 30 seconds after the gas gets to the sensors.



Diffusion units may take longer to respond because the gas has to diffuse into the meter and through a dust filter before it gets to the sensors. Pumped units should be faster responding because they deliver the gas to the sensor. Some sensors, like HCN, take significantly longer to respond.



- CHEATERS ALERT: Sometimes people will provide response times that are not T₉₀s to make their sensors appear better than their competitors. In two competitive bid situations T₅₀s and T₆₅s were provided to make one manufacturer appear better than the other. Largely the electrochemistry for one chemical species of sensor will have VERY similar response times to the competitor's same chemical species because the chemistry and physics are similar.
- For sensors like LEL and PID response time (and recovery time) can vary with the vapor pressure of the gas/vapor being sampled. These sensors will take longer to respond to lower vapor pressure chemicals and they will

recover slower to these chemicals. Because of this, the gas is defined in the specification of these sensors, typically methane for LEL sensors and isobutylene for PID.

- **Sample tubing will effect response time:** Response time increases on pumped monitors when extension tubing is used. As a rule of thumb with a safety margin, for most monitors drawing 250-500 cc/min through 1/8" tubing add at least 1 second of lag time for every 10' of tubing. Response time will increase for larger bore tubing because there's more volume of atmosphere to move through it. Always check your meter's pump or your squeeze-bulb for strong flow through the tubing because older pumps may not be up to the task, or the tubing connections may leak. Check with manufacturer on maximum tubing to be used, only under unusual situations should more than 25' of tubing be used
- **Sample tubing will affect response time for pumped units**

| Nominal | | | | | | Delay Time @ ~250-300 cc/min | | |
|---------|-------|-------|-------|-------|-------------|---------------------------------|-----|--|
| in | in | | cm | | Seconds per | | | |
| OD | OD | ID | OD | ID | 1' | 10' | 30' | |
| 1/8 | 0.125 | 0.063 | 0.318 | 0.159 | 0.1 | 1 | 5* | |
| 4 mm | 0.157 | 0.110 | 0.400 | 0.260 | 0.4 | 4 | 11 | |
| 3/16 | 0.188 | 0.127 | 0.476 | 0.323 | 0.5 | 5 | 15 | |
| 1/4 | 0.250 | 0.190 | 0.635 | 0.483 | 1.1 | 11 | 33 | |
| 5/16 | 0.313 | 0.248 | 0.794 | 0.630 | 1.9 | 19 | 57 | |
| 3/8 | 0.375 | 0.311 | 0.953 | 0.790 | 3.0 | 30 | 90 | |
| 1/2 | 0.500 | 0.438 | 1.270 | 1.107 | 5.9 | 59 | 178 | |

| Nominal | | | | | | Delay Time @ ~500 cc/min | | |
|---------|-------|-------|-------|-------|-------------|-----------------------------|-----|--|
| in | in | | cm | | Seconds per | | | |
| OD | OD | ID | OD | ID | 1' | 10' | 30' | |
| 1/8 | 0.125 | 0.063 | 0.318 | 0.159 | 0.1 | 1 | 4* | |
| 4 mm | 0.157 | 0.110 | 0.400 | 0.260 | 0.2 | 2 | 7 | |
| 3/16 | 0.188 | 0.127 | 0.476 | 0.323 | 0.3 | 3 | 9 | |
| 1/4 | 0.250 | 0.190 | 0.635 | 0.483 | 0.7 | 7 | 20 | |
| 5/16 | 0.313 | 0.248 | 0.794 | 0.630 | 1.1 | 11 | 34 | |
| 3/8 | 0.375 | 0.311 | 0.953 | 0.790 | 1.8 | 18 | 54 | |
| 1/2 | 0.500 | 0.438 | 1.270 | 1.107 | 3.5 | 35 | 106 | |

* Corrected for decrease in flow rate due to pressure drop in tubing
Ref: RAE Systems TR-118

- **Sample tubing can absorb chemicals:** Always use sample tubing that will not absorb the chemicals that may be present, otherwise the tubing can reduce and even eliminate the sensor response. Soft, flexible "Tygon" tubing is the most common tubing supplied and used with gas monitors, but it is not appropriate for use with many gases. Corrosive and reactive gases such as NH₃, Cl₂, ClO₂, HCl, HCN and NO₂ may be absorbed by Tygon tubing as a sponge would absorb

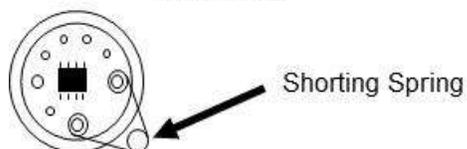
Getting the Most from Toxic Gas Sensors

water. Low vapor pressure chemicals such as diesel, jet fuel, phenols and even CWAs will adhere to and absorb into Tygon tubing. **In atmospheres where these classes of chemicals exist, or ANYTIME one is sampling an unknown atmosphere through tubing then non-reactive, non-absorbent tubing such as Teflon should be used.** CO, H₂S, PH₃, SO₂ and NO are ok with Tygon.

Make sure that water isn't sucked into tubing or that moist environments condense in the tubing. Reactive gases like NH₃ and HCl can be absorbed into the water, reducing or eliminating response. Water can block flow and can destroy sensors and meters. Always watch for moisture in your sample line when drawing a sample for a space that may have liquid in it or may be hot enough that the tubing will act as a condenser.

- **Bias & Equilibration:** Some electrochemical sensors like NO and NH₃ for some manufacturers may require a bias voltage to detect the gas (while most do not). Equilibration is the time a new sensor requires to stabilize prior to use (aka: warm up time). Biased sensors require about 6 hours to equilibrate after installation for the baseline to become stable enough to calibrate. Unbiased sensors require only about 10 minutes to stabilize. Once installed, sensor bias stays on even when the meter is off. Therefore, even biased sensors are ready for immediate use when the instrument is turned on again. But equilibration time is needed if the battery becomes completely drained.
 - Unbiased sensors are shipped with a shorting spring across the electrodes to avoid an accidental bias. The spring should be removed before installation.

Bottom view



- Sensor warmers can be used to maintain bias on NO and NH₃ sensors and thus avoid long equilibration times when swapping these sensors into a Multi-gas instrument.



- **Temp Range:** Normal operating temperature of the sensor. Sensors are chemical processes, cooling them down will slow up the process and heating them up will speed up the process. Storing detectors outside in the winter may provide low readings. Storing detectors in hot cars in the summer may provide high readings and dry out the sensors. Allowing meter to return to normal operating temperature typically will restore readings. **Freezing or cooking your sensors could kill them!**
- **Pressure Range:** Normal operating pressure of the sensor. Often this is "Atmospheric" pressure of 14.7 PSIA $\pm 10\%$. Some sensors may exhibit transient alarms due to fast pressure changes. For example, a cross-country jet landing at Boston, MA is effectively descending from 5000 feet to sea level in just a few minutes and detectors traveling on this plane will take up to 30 minutes to adjust to the pressure change. However if one had driven from 5000 feet to sea level the pressure would have acclimated slowly and no false alarms due to pressure change would have been noticed. This is because the sensor needs to acclimate to pressure changes through a tiny capillary hole that is designed to limit the flow of gas into the sensor. Large and quick pressure changes can overwhelm the capillary's ability to adjust to the changes. As a guideline, ***If your ears pop, your sensors may need some time to equilibrate, remember that they often have to balance pressure through a tiny capillary hole***
- **Operating Humidity:** Normal operating humidity. Typically EC sensors operate best in 15-90% relative humidity "non-condensing" atmospheres, but they may

Getting the Most from Toxic Gas Sensors

be able to tolerate short term excursions in atmospheres outside of these humidity parameters. Condensing humidity can put a film of water over the top of the sensor which will block the diffusion mechanism, lowering or preventing a reading from the sensor. As a guideline, ***If your glasses fog, moisture could be condensing on your sensors.*** Consistently high humidity can dilute electrolyte. Consistently low humidity will dry out the electrolyte.

- **Drift:** Amount sensor output will change over a period of time (typically month) expressed in %. The greater the drift spec the more calibration is required.
- **Storage Life:** The recommended maximum time a sensor should be stored in its original packaging before being installed in an instrument.
- **Storage Temp:** The recommended temperature to store sensors prior to use. Freezing sensors may rupture them. Storing them in too warm an environment may cause them to fail prematurely.
- **Operating Life:** the expected useable life of the sensor after it is installed, as long as "Storage Life" is not exceeded
- **Warranty:** The time from shipment up to which the manufacturer will replace a sensor free of charge, or at reduced charge, in case of failure. The Warranty period is generally equal to or less than the Operating Life. Watch out for "pro-rated" sensor warranties where you only get credit for the number of months of warranty not used rather than getting a completely new sensor. For example, if a \$240 sensor with a 2 year pro-rated warranty fails at month 23, the user is only going to get a \$10 credit towards the purchase of a new sensor. A sensor with a Storage Life of 6 months, Operating Life of 2 years and Warranty of 2 years, stored for ½ year before installation, is expected to be useable for up to 2½ years from the date of shipment, even though the warranty expires 1½ years after it is installed.
 - As long as sensors pass their calibration test, they are good to use even after their warranty has expired.
 -

at a moment's notice may choose to change out sensors at the end of their warranty period.

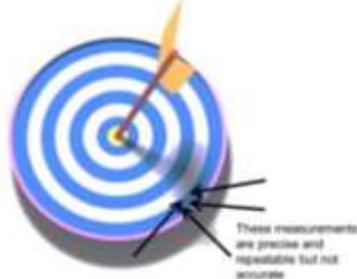
- **Calibration Gas Concentration:** This is the recommended calibration gas value for a sensor. A low value might not give a stable calibration and high values might use up sensor prematurely.
- **Calibration Flow Rate:** The recommended calibration gas flow rate. Some sensors require a higher flow rate because components of the detector may absorb these gases. A low gas flow may result in not enough gas reaching the sensor resulting in a poor calibration. In real-time usage with these reactive gases in the air, the detector absorbs them from the atmosphere. But when calibrating with these gases one must account for the fact that the detector will absorb some. Chlorine and ClO₂ sensors are very dependent on gas flow for a stable calibration and some manufacturers recommend 1000 cc/min for 2 min even on pumped units. One should also be careful calibrating NO, PH₃, NH₃ and HCN which some manufacturers recommend a 1000 cc/min flow.
 - **Manufacturers have reasons for the numbers used in calibration specs, follow them!**
- **Accuracy:** The percent (%) agreement between the instrument reading and the true concentration.
 - **+/-10% of reading:** If the reading is 50 ppm the real concentration is between 45-55 ppm.
 - **+/-10% of reading or 2 ppm:** The error is the higher of 10% or 2 ppm.
 - If the reading is 9 ppm then the real concentration could be between 7-11 ppm which is +/- 2 ppm (rather than 8-10 ppm if using +/-10%).
 - If the reading is 50 ppm then +/- 10% (+/- 5 ppm) would be the accuracy not +/- 2 ppm.
- **Precision/Repeatability:** The maximum percent variation between repeated independent readings on a sensor under identical conditions.

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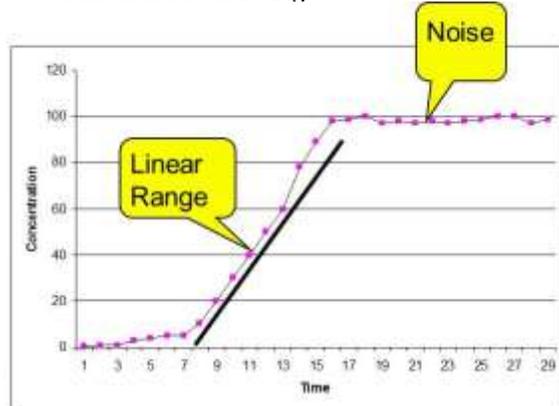
that require their meters to be available

Getting the Most from Toxic Gas Sensors

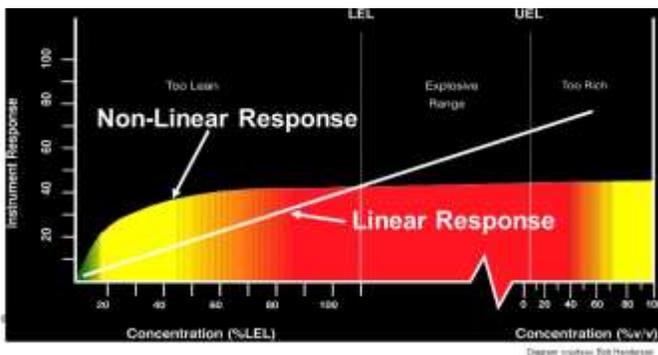
- Accuracy vs. Precision:** Accuracy describes how consistent the readings are with the actual concentration while precision describes how much readings agree with each other. In archery “accuracy” describes the closeness of the arrows to the bulls-eye; “precision” describes how close the arrows are to each other. One can have a high degree of precision but all the arrows could be in a tight group on the outer ring of the target.
- Recovery time:** The time necessary for the sensor to recover after exposure to a gas. Sometimes recovery time is MUCH longer than response time.
- Linearity:** How well the sensor concentration response curve matches a straight line. The more linear a sensor is the more accurate it is across its measurement range. When constructing a house one would chose a metal tape measure over a rubber one. A linear sensor is like the metal tape measure, it’s reliable across its entire measurement range.



- Linear range:** The portion of the concentration range where the instruments response matches a straight line. Some products have extended ranges where they are not linear.
- Noise:** Random fluctuations in signal that are independent of the concentrations being



Resolution: 1 ppm
Response Time (t90): 30 sec
Bias & Equilibration: Bias off; 10 min after installation
Max Overload: 500 ppm
Temp Range: -4 °F to 113°F (-20°C to 45°C)
Pressure Range: Atmospheric ±10%
Operating Humidity: 15-90% non-condensing
Drift: < 2% signal/month
Storage Life: 6 months in sealed container
Storage Temp: 32 °F to 68°F (0 °C to 20°C)
Operating Life: 2 years in air
Warranty: 2 years from date of shipment
Calibration Gas: 10 ppm H₂S, balance N₂
Calibration flow rate: 400 cc/min



H₂S Sensors Specifications Summarized

Having discussed sensor specifications, let’s summarize them for a common H₂S sensor:

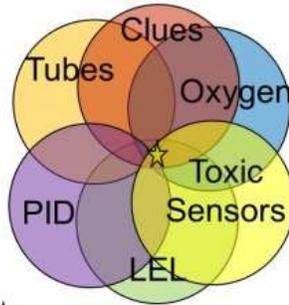
H₂S Car Suicide

A dead body was found in car with a note on the window advising of high levels of H₂S using the “Detergent” suicide method of mixing an acid with a sulfur containing cleansing compound. Following the Detergent suicide recipe, first responders have shown that concentrations of H₂S can go into the percent by volume levels (1-10%=10,000-100,000 ppm). These levels can exceed the **range**, **linear range** and **max overload** specifications of all H₂S sensors.

- Clues:** Body in car with note on the window

Getting the Most from Toxic Gas Sensors

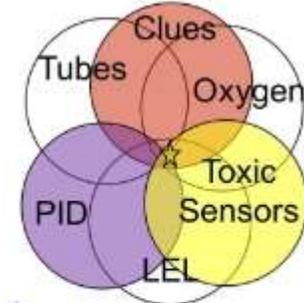
- **Oxygen:** ~15.9-20.7%, **permanent sensor damage possible**
- **Toxic Sensors:** H₂S EC sensor going to over-range at 100-500 ppm, expect some response from the CO sensor, **permanent sensor damage possible** because of exceeding the sensor "Max Overload" specification
- **LEL:** could get some reading at high levels (~4 CF), **permanent sensor damage possible because large amounts of H₂S are a known poison**
- **PID:** up to 15,000 ppm (~3.3 CF)
- **Tubes:** good bet for high readings of H₂S



★ = Lots of H₂S

colorimetric tubes or sampling with lab testing was recommended

- **Clues:** Refinery clean-up with strong H₂S smell
- **Oxygen:** no change in reading
- **Toxic Sensors:** 199 ppm reading on H₂S sensor
- **LEL:** no reading (LEL = 4% or 40,000 ppm) possible clue that there are low or no VOCs
- **PID:** 240 ppm in isobutylene units or 792 in H₂S units (CF = 3.3)
- **Tubes:** not used but would have been the next step



★ = 100-792 ppm of H₂S present

Oil Refinery Remediation H₂S

An excavator operator at a refinery clean-up wore a datalogging 5-gas detector along with supplied air. The datalog graph showed a perfectly straight line at 199 ppm of H₂S. The user's supervisor called the detector's manufacturer's representative who said that this indicated that they had maxed out the H₂S circuit on the meter because it's only rated to 100 ppm H₂S and while the electronics had 99 ppm of over-range, it wouldn't go any higher than 199. The lack of sensor **noise** was the first clue something was wrong. In the real world one would not see a perfect straight line of 199 on a datalog graph. Clearly we are out of the **linear** range of the H₂S sensor which was 0-100 ppm. This data is questionable but we certainly have more than 100 ppm and may have more than 200 ppm H₂S. PID data from the same meter showed 240 ppm in Isobutylene units. There was no LEL reading and H₂S is a LEL inhibitor. Using a PID correction factor for H₂S of 3.3, the concentration if it were just H₂S is 792 (240 x 3.3 = 792). PID measures total VOCs including H₂S so part of the signal could be VOCs but this at least gives us a theoretical upper boundary for the H₂S concentration. We can be pretty sure that we had a lot of H₂S and it could be 100-790 ppm (IDLH = 100 ppm). So it's possible that the **max overload** of 500 ppm of H₂S was exceeded. Further testing using

Electrochemical Toxic Sensors

Advantages

- + Continuous Readings
- + Proven Technology
- + Reasonably Specific
- + Cross-sensitive

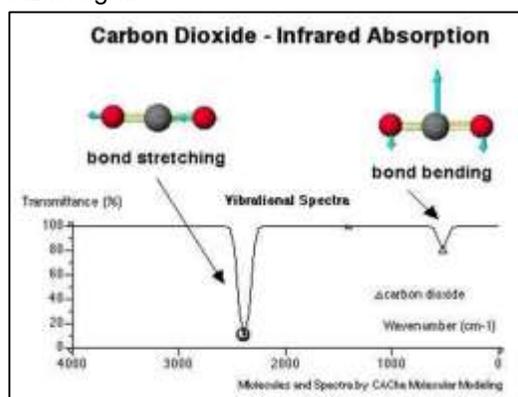
Disadvantages

- "Exotic" sensors can be expensive to purchase and to calibrate
- "Exotic" sensors typically have 1 year life
- Cross-sensitive

Getting the Most from Toxic Gas Sensors

CO₂ can't be detected by an EC sensor

There are no electrochemical (EC) sensors for Carbon Dioxide (CO₂). Non Dispersive InfraRed (NDIR) sensors are the accepted standard for real-time monitoring of CO₂. NDIR sensors use the absorption of infrared light to make gas measurements. The amount of IR light absorbed is proportional to the concentration of CO₂ which is typically measured in ppm. The energy of the photons is not enough to cause ionization, and thus the detection principle is very different from that of a photoionization detector (PID). Ultimately, the energy is converted to kinetic energy, causing the molecules to speed up and thus heat the gas. The O-C-O bonds in CO₂ absorb NDIR light:



Essentially the NDIR sensor looks for the “shadows cast” by O-C-O bonds when IR light is shined through gases/vapors with O-C-O bonds. The darker the shadow the higher the concentration of carbon dioxide.

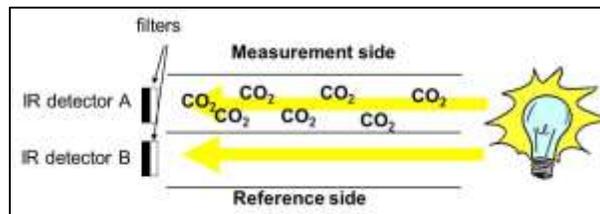


How the NDIR sensor works

Light passes through the gas sample and is absorbed in proportion to the amount of O-C-O bonds present. The filter in front of the detector removes all the light except that corresponding to O-C-O bonds. The reference detector

provides a real-time signal to compensate the variation of light intensity due to ambient or sensor changes.

$$\text{Concentration} = \text{Detector B} - \text{Detector A}$$



Collapsed man in a basement

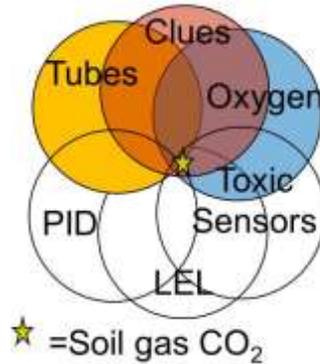
EMS responded to a call of a man collapsed in a basement with a possible heart attack. He had gone down to re-light an extinguished pilot light on his heater. The 5-gas detector readings in the basement showed O₂ as low as 13% in the low lying areas but no other sensors showed changes. When removed from the basement the man recovered fully. Detector readings in the outside cut-out to the basement entrance were <19.5% because the detector was in O₂ alarm. Further investigation showed that the house was built on an old dump and was collapsing into the dump, the basement floor was collapsing and the heater was even hanging from its pipes. Steel columns had been punched through holes in the basement floor to hold up the house. A carbon dioxide (CO₂) colorimetric tube went full scale at over 5000 ppm demonstrating there is a lot of CO₂ in the air.

Natural decomposition in the ground can generate large amounts of CO₂ which sometimes is called “soil gas.” While this rarely pushes its way into homes, in this case the steel columns went through holes in the basement floor which provided a means for the CO₂ to travel into the basement. The house provides a low pressure zone drawing the gas from the high pressure soil into the house which is known as the “Stack Effect.” If it was all CO₂ in the area with 13% oxygen that would be 39.5% CO₂ in the air (20.9-13=7.9; 7.9 x 5000 = 395,000 ppm/10,000 = 39.5%). No wonder the pilot light on the heater went out. The IDLH for CO₂ is 40,000 ppm, TWA is 5000 ppm, it is no wonder that the man collapsed. This is one reason the Germans require CO₂ in their confined space detectors.

Getting the Most from Toxic Gas Sensors

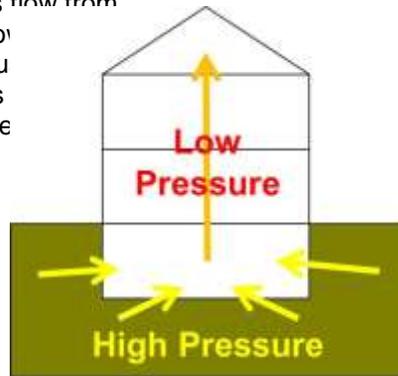
Clues: man down in a basement

- **Oxygen:** as low as 13% meaning as much as 39.5% of “something else” in the air
- **Toxic sensors:** CO and H₂S sensors show no changes, only an NDIR CO₂ sensor would help
- **LEL:** no change, non-flammable
- **PID:** no change, not ionizable with a 10.6eV lamp
- **Tubes:** CO₂ tubes are very helpful



Why high levels were in the house if it was coming from the soil?

Gases and vapors flow from high pressure to low pressure. In a house the soil represents high pressure zone the basement represents a low pressure zone. So the gas/vapor will flow from the soil into the basement and is drawn upward via “stack effect.”



Understanding sensor cross-sensitivities

Every sensor has a cross-sensitivity. It can see gases other than the specified gas that are not filtered out and can react with the electrolyte. These can also be called “interferents” The interferent gas can either decrease the signal (negative cross-sensitivity) or increase the signal (positive cross-sensitivity). Cross-sensitivity values may vary between batches of EC sensors because cross-sensitivity is not typically controlled during the manufacturing process. EC sensors are primarily designed for the industrial TWA monitoring market. When exposed to large concentrations of other gases/vapors (above IDLH levels or when oxygen measurements are below 20.9%) one should start to expect cross-sensitive responses. **For safety concerns, a negative**

cross-sensitivity may present more risk than a positive one, as it will diminish the response to the target gas and so prevent an alarm

A CO Sensor cross-sensitivity chart

| Gas | Concentration | Response# |
|------------------|---------------|-----------|
| H ₂ S | 24 ppm | 0 ppm |
| SO ₂ | 5 ppm | 0 ppm |
| Cl ₂ | 10 ppm | 0-1 ppm |
| NO | 25 ppm | 0 ppm |
| NO ₂ | 5 ppm | 0 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 5 ppm | 0-1 ppm |
| H ₂ | 100 ppm | 40 ppm |
| Ethylene | 100 ppm | 16 ppm |
| Acetylene | 250 ppm | 250 ppm |
| Ethanol | 200 ppm | 1 ppm |
| Ethylene Oxide | 125 ppm | ≥40 ppm |
| Propane | 100 ppm | 0 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Isobutylene | 1000 ppm | 7 ppm |
| Hexane | 500 ppm | 0 ppm |
| Toluene | 400 ppm | 0 ppm |
| Nitrogen | 100% | 0-4 ppm |

* Cross-sensitivity chart for example only, consult your manufacturer for specific cross-sensitivities

- **Note:** High levels of polar organic compounds including alcohols, ketones, and amines give a negative response on this sensor

The previous chart is a representative chart that shows theoretical cross-sensitivity on a new sensor (this chart is for reference only, please consult your manufacturer for the specific cross-sensitivities of their EC sensors). Used sensors show increasing response to VOCs and other interferents. So cross-sensitivity increases with age. But it's not just how much time that has passed it's also how much chemical has stressed the sensor. So a one year old CO sensor that hasn't seen high levels of CO or any appreciable levels of interferents will probably have less increase in cross-sensitivity than a two day old CO sensor that was used on an all-day long ethanol spill on the first day that it was in the detector.

Getting the Most from Toxic Gas Sensors

When to look for cross-sensitivities

There is an old saying "When you hear stampeding hooves think horses not zebras."



But sometimes when you can't find the horses and you've been trying real hard, it is time to start looking for the zebras. There is a saying in detection "one man's noise is another man's sensor" and sometimes cross-sensitivities can be used to our benefit. Cross-sensitive responses may be expected **anytime** oxygen reads less than 20.9% and there is not an obvious reason that oxygen should be consumed.

Methanol Tank Truck Rollover

The day after responding to a day-long clean-up because of a methanol tank truck rollover, the hazmat team's instrument specialist called his manufacturer's representative because the CO and H₂S sensors in his 5 gas detector were "acting funny." This multigas detector was exposed to a high level of methanol the entire day before due to the spill. Both the CO and



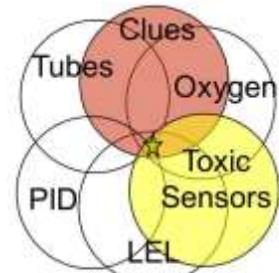
Photo by Abby Taylor, Hournatoday.com

H₂S sensors were giving "Neg" or negative alarms. Reading the sensor spec sheet it said "**Note:** High levels of polar organic compounds including alcohols, ketones, and amines give a negative response." So it appears that the day-long exposure caused methanol to build up in the EC sensors which caused them to give a negative reading. The detector was programed

to know that negative readings are impossible so it gave a "Neg" alarm. ***This situation is dangerous because a negative alarm means that if CO or H₂S were present, the sensors would go into alarm LATE because of the negative condition of the sensors.*** The methanol in the sensor would effectively be subtracting from any signal generated by CO or H₂S gas getting to the sensor.

It was recommended that they put their detector into calibration mode to silence the sensor alarms. Running the detector 24 hours on its charger cleared the methanol interferent or "poison" from the sensor. If after 24 hours the sensors calibrate go ahead and continue to use them. But calibrate more often for a while to make sure they are all right and they probably had greater cross-sensitivities in their future uses. If the sensors don't calibrate or if they remain unstable then they need to be replaced.

- **Clues:** methanol tank truck rollover the day before
- **Oxygen:** no change in reading
- **Toxic sensors:** NEG alarm from both CO and H₂S sensors
- **LEL:** strong reading throughout the methanol incident (CF = 1.5)
- **PID:** no reading, methanol isn't ionizable with a 10.6eV lamp
- **Tubes:** none used



★ = Toxic sensors poisoned by methanol

Food Warehouse CO

When a gas detection sales representative visited a food warehouse maintenance room he had 80 ppm CO indicated on his 5-gas detector. He asked the maintenance staff if they used propane forklifts (a common source of CO) but was told that they used battery powered forklifts. The maintenance room was located within the battery charging area. The lead acid batteries used to power the forklifts generate hydrogen when charging.

From the CO sensor cross-sensitivity chart below, we can see that the CO sensor is

Getting the Most from Toxic Gas Sensors

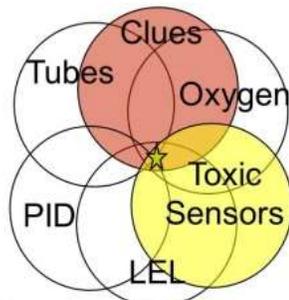
about a 40% hydrogen sensor because 100 ppm of H₂ produces 40 ppm of response on the CO sensor. So the 80 ppm indicated CO on the detector translates to 200 ppm hydrogen or about 0.5% of LEL. The 5-sensor detector had

| Gas | Concentration | Response# |
|------------------|---------------|-----------|
| H ₂ S | 24 ppm | 0 ppm |
| SO ₂ | 5 ppm | 0 ppm |
| Cl ₂ | 10 ppm | 0-1 ppm |
| NO | 25 ppm | 0 ppm |
| NO ₂ | 5 ppm | 0 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 3 ppm | 0-3 ppm |
| H ₂ | 100 ppm | 40 ppm |
| Ethylene | 200 ppm | 20 ppm |
| Acetylene | 350 ppm | 350 ppm |
| Ethanol | 200 ppm | 1 ppm |
| Ethylene Oxide | 125 ppm | ≥40 ppm |
| Propane | 100 ppm | 0 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Isobutylene | 1000 ppm | 7 ppm |
| Hexane | 500 ppm | 0 ppm |
| Toluene | 400 ppm | 0 ppm |
| Nitrogen | 100% | 0-4 ppm |

* Cross-sensitivity chart for example only, consult your manufacturer for specific cross-sensitivities

no LEL reading; LEL of H₂ is 4% by volume (40,000 ppm), 1% of LEL is just 400 ppm Using a correction factor of 1.2, 1% of LEL hydrogen is just 333 ppm in methane units. So it's not surprising that the LEL sensor read 0 because the amount of hydrogen present was too small for the LEL sensor to see it. When they checked with a CO colorimetric tube it registered no CO reading. So the clues, CO sensor reading and the lack of a colorimetric CO response lead us to the conclusion that the CO reading on monitor was due to hydrogen cross-sensitivity on the CO sensor.

- **Clues:** Warehouse w/ battery powered forklifts
- **Oxygen:** no change in reading
- **Toxic Sensors:** 80 ppm reading on CO if H₂ it's approximately 200 ppm,
- **PID:** no reading on PID
- **LEL:** no reading on LEL (CF = 1.1)
- **Tubes:** no reading on CO tube



★ = Probably Hydrogen gas from forklift batteries

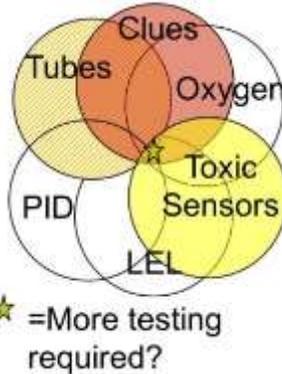
“CO” found during House Renovation

As part of a house renovation, CO monitors were installed as a house was being converted from electric to gas heat. The household CO sensors went into alarm as soon as they were turned on, even though the furnace was not hooked up to gas line. Portable CO sensors from multiple manufacturers were used but all gave the same high readings. The occupants were not symptomatic of CO toxicity and when blood was drawn from them there was no CO found. So this really rules out CO in the house. Colorimetric CO tubes gave a low CO reading, about 10% of the reading on the portable CO sensors when sampling from the same place. That is, if the CO sensors read 50 ppm the CO tube only read 5 ppm. If it was CO we would expect the tube to match the sensors within 10%. That is if the CO sensors read 50 ppm then the CO tubes should read 45-55 ppm. But because the tube only read 10% of the sensor we suspect that it is a cross-sensitive gas not CO. The first thought was maybe the workers left a leaking acetylene torch because acetylene gas will be detected by CO sensors and the CO tube was about 10% cross-sensitive to acetylene. But there were no acetylene tanks in the house. PID, LEL, Oxygen and H₂S sensors saw no change in readings. When sample tubes were driven into the ground around house they gave high CO & FID readings. It seems that some soil gas was drawn into the house by the “stack effect” and it appears that the gas that it was to blame for setting off the CO sensors. However the identity of the gas remains a mystery.

Getting the Most from Toxic Gas Sensors

Because the PID didn't see anything and the FID did see something it would appear that it is some flammable gas or vapor with an ionization potential above the PID's 10.6eV lamp yet still seen by the CO sensor, the FID and the CO tube.

- **Clues:** CO alarms, asymptomatic occupants
- **Oxygen:** no change in reading
- **Toxic Sensors:** CO in alarm for multiple sensor manufacturers, but all CO sensors are chemically similar
- **LEL:** nothing but FID got low levels of something
- **PID:** no reading
- **Tubes:** if it was CO we would expect agreement between the tube and the sensor, when the tube reads 10% of the sensor reading then we think possible cross-sensitivity
- Clearly more testing was needed

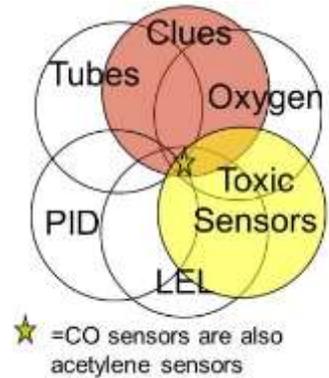


Firehouse CO detectors

All the permanent and portable CO detectors in a firehouse went into alarm. They checked the heater room but no CO was coming from the heater. They looked to see if the batteries from the vehicles in the equipment bay were cooking off and producing hydrogen but they were fine. When they removed all of the vehicles from the equipment bay the CO alarms went away. They brought the equipment back in until they had CO alarms again. Upon further investigation they found that the acetylene tank in the heavy rescue truck was leaking. Looking on the following CO sensor cross-sensitivity chart we can see that 250 ppm of acetylene produces 250 ppm of response on the CO sensor. Put another way, this means that in the case of this manufacturer a CO sensor is an acetylene sensor.

| Gas | Concentration | Response# |
|------------------|---------------|-----------|
| H ₂ S | 24 ppm | 0 ppm |
| SO ₂ | 5 ppm | 0 ppm |
| Cl ₂ | 10 ppm | 0-1 ppm |
| NO | 25 ppm | 0 ppm |
| NO ₂ | 5 ppm | 0 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 5 ppm | 0-1 ppm |
| H ₂ | 100 ppm | 40 ppm |
| Acetylene | 250 ppm | 250 ppm |
| Propane | 100 ppm | 1 ppm |
| Ethylene Oxide | 125 ppm | 140 ppm |
| Propene | 100 ppm | 0 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Isobutylene | 1000 ppm | 7 ppm |
| Hexane | 500 ppm | 0 ppm |
| Toluene | 400 ppm | 0 ppm |
| Nitrogen | 100% | 0-4 ppm |

- **Clues:** All CO monitors in alarm but no good source
- **Oxygen:** no change in reading
- **Toxic Sensors:** CO sensors are 1 to 1 cross-sensitive to acetylene,
- **LEL:** either not used or no reading, low readings picked up by CO detector wouldn't be seen by LEL sensor
- **PID:** not used, wouldn't see acetylene
- **Tubes:** would have been nice to use right from the start to help eliminate CO



Carbon Dioxide in a Corn Silo

A fire department responded to 2 men down in a corn silo with water in it. The multigas detector showed high levels of CO and the user thought that high CO "must be CO₂ cross-sensitivity because the grain was fermenting." CO sensors are NOT cross-sensitive to CO₂ at all. Because the corn was wet perhaps the next place to look are the gases/vapors produced by fermentation. Common fermentation gases and vapors include: ethanol, lactic acid, hydrogen. Less common ones include: butyric acid (which smells like vomit) & acetone (which smells sweet). Finally silage "greens" in corn can lead to elevated levels of NO/NO₂. Looking at the following CO sensor cross-sensitivity chart we can find a number of suspects for

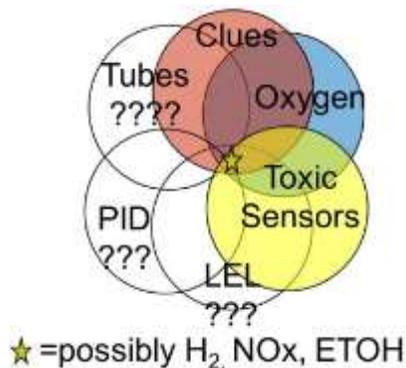
Getting the Most from Toxic Gas Sensors

the CO sensor response. 25 ppm of NO will not produce a response on a new CO sensor, but 26 would probably produce 1 ppm. 5 ppm of NO₂ does not produce a response on a new CO sensor, but 6 ppm probably would make 1 ppm. Hydrogen and ethanol both will produce response on a CO sensor.

| Gas | Concentration | Response# |
|------------------|---------------|-----------|
| H ₂ S | 24 ppm | 0 ppm |
| SO ₂ | 5 ppm | 0 ppm |
| Cl | 20 ppm | 0 ppm |
| NO | 25 ppm | 0 ppm |
| NO ₂ | 5 ppm | 0 ppm |
| NH ₃ | 5 ppm | 0-2 ppm |
| H ₂ | 5 ppm | 0-2 ppm |
| H ₂ | 100 ppm | 40 ppm |
| Chlorine | 100 ppm | 16 ppm |
| Acetylene | 150 ppm | 250 ppm |
| Ethanol | 200 ppm | 1 ppm |
| Ethylene | 225 ppm | 210 ppm |
| Propane | 300 ppm | 0 ppm |
| Isobutylene | 300 ppm | 0 ppm |
| Isobutylene | 3000 ppm | 7 ppm |
| Hexane | 500 ppm | 0 ppm |
| Toluene | 400 ppm | 0 ppm |
| Nitrogen | 200% | 0.4 ppm |

- **Clues:** Corn silo with two victims
- **Oxygen:** in alarm (<19.5%) meaning that at least 70,000 ppm (14 x 5000 ppm) or 7% of something else is there, that's a lot of something else which would be expected to induce a cross-sensitive response on an EC sensor
- **Toxic Sensors:** high reading on CO, could be from cross-sensitive to oxides of nitrogen NO_x, hydrogen, ethanol or other organics with an old CO sensor
- **PID:** no data, if zero strongly suspect hydrogen. Hydrocarbons and a little of NO_x will show here
- **LEL:** no data, but could pick up ethanol (CF = 1.7) or H₂ (CF = 1.1)
- **Tubes:** would have been nice to run a CO tube to rule it out

“



TWA Meter” Confused by IDLH Atmosphere

Well before dawn on a hot summer morning, a HazMat team reported to a dwelling with multiple un-responsive occupants that were taken to hospital. They got the following readings after the victims had been removed from the building:

- Oxygen: 20.6% (meaning 15,000 ppm of “something else” is there)
- CO: more than 750-900 ppm
- H₂S: ~24 ppm
- ppb PID: 1500-2000

The house was well sealed with multiple window mounted AC units set to recirculate. No obvious source of a lot CO was identified, although there was a gas stove and hot water heater in the dwelling. It appears that rat poison had been spread in the basement/crawl space and these areas were wet from rain water leakage. Because of the rat poison, phosphine (PH₃) was suspected because when some rat poisons get wet they produce PH₃. PH₃ has a very distinctive “dead fish” odor at extremely low (ppb) levels and while responders were fully masked throughout the response there were no reported odors. A PH₃ sensor was used and readings were as high as 8 ppm. Victim blood gas confirmed high CO and all were put in hyperbaric chambers providing solid confirmation that high levels of CO were present. Let's look at the CO exposure limits:

- TWA: 50 ppm (OSHA)
- IDLH: 1200 ppm

If not an IDLH environment the atmosphere in the house certainly was over the TWA for CO and near IDLH for CO. The readings were probably lower than the victims experienced because they were made after a bunch of firefighters in turnout gear and SCBA had entered the building to remove the victims.

The next day it was learned that there was an ambulance call to the same house about midnight, hours before the multiple victim call. There was an unresponsive victim in the foyer of the building when the medics arrived. There wasn't enough room in the foyer to treat this victim so they set their medic bag down and dragged the victim onto the front porch. Downloading the datalog from the CO detector on the medic bag the next day showed that it went full scale to 1200 ppm. That's the highest that CO detector would

Getting the Most from Toxic Gas Sensors

read so there was at least IDLH levels of CO in the foyer. There may have been even more because with the oxygen sensor dropping from 20.9% to 20.6% it indicates that we may have as much as 15,000 ppm of total contamination.

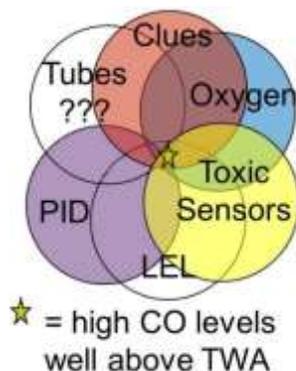
- Every 0.1% drop in oxygen readings means that as much as 5000 ppm of “something else” is in the air.

Most detectors and especially EC sensors are designed for the industrial environment in which staying at or below TWA values (the OSHA “speed limit”) is the primary concern. When exposed to concentrations near or above IDLH levels these “TWA” meters can get “stressed” leading to some “crazy” sensor readings.

Checking the cross-sensitivity charts for the H₂S and PH₃ sensors show that their readings are consistent with cross-sensitivity from the high levels of CO seen at the scene. Put another way, there may not have been any H₂S or PH₃ present. The next detection technology to think of in this call should have been colorimetric tubes, they can handle higher ranges of CO than the EC sensors that are best at TWA levels. Tubes could have been used to help rule out the presence of H₂S and PH₃.

When detectors are stressed like they were in this call, calibration should certainly be performed post call and with increased frequency subsequently **until it can be established by consistent calibration data that the sensor(s) have not been permanently stressed.** HazMat response IS NOT a TWA job and can stress detectors designed for the industrial TWA environment beyond their design parameters.

- **Clues:** multiple victims in hyperbaric chambers who tested positive for elevated CO levels in their blood
- **Oxygen:** 20.6% indicates as much as 15,000 (3 x 5000) of something else is there
- **Toxic Sensors:** more than 750 ppm reading on CO, 24 on H₂S and 8 on PH₃. Checking cross-sensitivity charts we find that the H₂S and PH₃ readings are consistent with high CO levels



- **PID:** 1500-2000 ppb is 1.5-2.0 ppm which really is a low reading and isn't inconsistent with 15,000 ppm of “something else”
- **LEL:** no data,
- **Tubes:** would have been great because they are a great IDLH detection tool for CO

CO Sensor Cross-sensitivity Summary

Because they are one of the most common EC sensors fielded we seem to have the most cross-sensitivity issues with CO sensors. Here's a summary of the common cross-sensitivities of CO sensors:

- Hydrogen:
 - Charging lead-acid batteries in cars, golf carts or tractors
 - Nuclear power plant containment buildings
 - Self-heating meals (like MREs)
 - Some manufacturers offer special CO sensors that are not cross-sensitive to hydrogen but they are more expensive
- Acetylene: CO sensors ARE acetylene sensors
- Hydrocarbons: this is usually less of a problem because some manufacturers supply charcoal filters to fit above the CO sensor to help prevent this. But in one case a gallon of acetone spilled on a carpet set off the household AND the fire department CO monitors.



Getting the Most from Toxic Gas Sensors

Clan Lab: Using Cross-Sensitivity to your advantage

In the clan lab application it is common to see ammonia (NH₃) and phosphine (PH₃) sensors fielded as part of multi-sensor detection products. These EC sensors are reasonably specific and are sensitive enough for TWA alarm limits. However, these EC sensors have a limited life of a year, they are expensive to purchase and require frequent calibrations with expensive and short lived calibration gases. In the case of phosphine, one measurement option is to use PH₃ cross-sensitivity on an H₂S sensor. Even when it is possible to purchase a specific phosphine sensor (PH₃) an H₂S sensor may do in a pinch. As it is much less expensive to own an H₂S sensor for detecting PH₃ than a dedicated PH₃ sensor, for some it may be a better choice:

- H₂S sensor: 2 year sensor for \$195 + \$295 for 4 gas mix calibration gas good for 2 years = \$240/year
- PH₃ sensor: 1 year sensor for \$295 + \$280 for PH₃ cal. gas good for 4-6 months = \$855/year

From the following cross-sensitivity chart, the H₂S sensor is 80% cross-sensitive to PH₃ but has poor NH₃ cross-sensitivity.

| Gas | Concentration | Response |
|------------------|---------------|---------------|
| CO | 300 ppm | <1.5 ppm |
| SO ₂ | 5 ppm | about 1 ppm |
| NO | 35 ppm | <0.7 ppm |
| NO ₂ | 5 ppm | about 1 ppm |
| H ₂ | 100 ppm | 0 ppm |
| HCN | 10 ppm | 0 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 5 ppm | about 4 ppm |
| CS ₂ | 100 ppm | 0 ppm |
| Methyl sulfide | 100 ppm | 9 ppm |
| Ethyl sulfide | 100 ppm | 10 ppm* |
| Methyl mercaptan | 5 ppm | about 2 ppm |
| Ethylene | 100 ppm | < 0.2 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Toluene | 10000 ppm | 0 ppm* |
| Turpentine | 3000 ppm | about 70 ppm* |

* Cross sensitivity chart for example only, consult your manufacturer for specific cross sensitivities

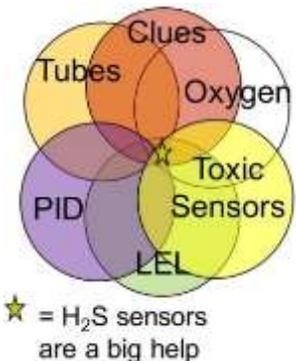
The following cross-sensitivity chart shows that CO sensor has some PH₃ cross-

| Gas | Concentration | Response# |
|------------------|---------------|-----------|
| H ₂ S | 14 ppm | 0 ppm |
| SO ₂ | 5 ppm | 0 ppm |
| Cl ₂ | 10 ppm | 0-1 ppm |
| NO | 35 ppm | 0 ppm |
| NO ₂ | 5 ppm | 1 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 5 ppm | 0-1 ppm |
| H ₂ | 100 ppm | 0 ppm |
| Ethylene | 100 ppm | 15 ppm |
| Acetylene | 250 ppm | 350 ppm |
| Ethanol | 200 ppm | 1 ppm |
| Ethylene Oxide | 125 ppm | 240 ppm |
| Propane | 100 ppm | 0 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Isobutylene | 1000 ppm | 7 ppm |
| Hexane | 500 ppm | 0 ppm |
| Toluene | 100 ppm | 0 ppm |
| Nitrogen | 100% | 0-4 ppm |

* Cross sensitivity chart for example only, consult your manufacturer for specific cross sensitivities

sensitivity but poor NH₃ cross-sensitivity

- **Clues:** clan lab
- **Oxygen:** no change in reading
- **Toxic Sensors:** H₂S sensor will read for PH₃ so 10 ppm of PH₃ will read 8 ppm on the H₂S sensor. CO helps a little because 10 ppm PH₃ will read ~1-2 ppm
- **LEL:** will pick up high levels of PH₃ but it will permanently ruin the sensor
- **PID:** with a CF of 3.9 the PID isn't sensitive enough for PH₃ which has a low TWA of 0.3 ppm, and long term PH₃ exposure will develop a coating on the lamp
- **Tubes:** PH₃ and NH₃ tubes are just some two that could be used



Other places to find Phosphine

- Grain fumigation in both rail cars and silos
- Shipping container fumigations
- When some "rat" poisons get wet they may off gas phosphine
- When some rat poisons are ingested for chemical suicide the vomit can off-gas phosphine and in the case of death the body bag may be found to contain phosphine

Getting the Most from Toxic Gas Sensors

EC sensor cross-sensitivity can work for you

A military wanted to protect troops from as many Toxic Industrial Chemicals (TICs) as possible. They only wanted “detect to warn.” Using sensor cross-sensitivities they could protect from a wide range of threats.

- The only danger with this implementation is that cross-sensitivities are not controlled at time of manufacture, but the good news is that cross-sensitivities tend to increase with age so as the detectors get older they will alarm more.

| OVERALL | VOC SENSOR | | CO SENSOR | | H ₂ S SENSOR | |
|-------------------|------------|---------|-----------|---------|-------------------------|---------|
| | Detected | Alarmed | Detected | Alarmed | Detected | Alarmed |
| Acrolein | YES | No | No | No | YES | No |
| Acrylonitrile | YES | No | No | No | YES | No |
| Ammonia | YES | No | No | No | No | No |
| Benzene | YES | YES | No | No | YES | No |
| Carbon Dioxide | YES | No | YES | No | YES | YES |
| Chlorine | No | No | No | No | No | No |
| Chloroform | YES | No | No | No | No | No |
| Dimethylamine | YES | YES | YES | No | YES | No |
| Ethylene Oxide | YES | YES | YES | YES | YES | No |
| Formaldehyde | YES | No | No | No | No | No |
| Hydrochloric Acid | YES | No | No | No | YES | No |
| Hydrogen Cyanide | YES | No | No | No | No | No |
| Hydrogen Fluoride | YES | No | YES | No | No | No |
| Methyl Bromide | YES | YES | No | No | No | No |
| Methyl Chloride | YES | YES | No | No | No | No |
| Phosgene | YES | No | YES | No | No | No |
| Phosphine | YES | No | YES | YES | YES | YES |
| Toluene | YES | YES | No | No | YES | No |

- 18 target chemicals
- PID (alarming @50 ppm), CO (@35 ppm) and H₂S (@10 ppm)
- Detected: 17 chemicals
- Alarmed: 8 chemicals

Leaking Refrigeration System

An old apartment building was being renovated and as an old, unused refrigerator was being removed from an apartment, a line was cut. This line leaked something into the area that sickened people and smelled badly like sulfur. Typically a halocarbon refrigerant like “Freon” wouldn’t smell or sicken people. On initial entry the 5-gas detectors showed high levels of H₂S at upper levels of the building where the refrigerator was found. But arriving hazmat didn’t find any sewer openings to produce H₂S gas. Upon searching the

building hazmat found a sulfur dioxide (SO₂) tank in the basement of the building. This tank was plumbed to a building wide refrigeration system. SO₂ is an early refrigerant that is also found in old “monitor style” refrigerators. Reading the H₂S sensor cross-sensitivity chart below, H₂S sensors are cross-sensitive to SO₂ at a 5-1 ratio. So 10 ppm on an H₂S sensor means 50 SO₂, the TWA of SO₂ is 2 ppm and IDLH is 100 ppm. H₂S sensor readings were reported to be as high as 100 ppm which would be equivalent to 500 ppm of SO₂ or 5 times IDLH. No wonder people were sickened. PIDs cannot “see” SO₂ so cannot be used to sniff for the source.

| OVERALL | VOC SENSOR | | CL SENSOR | | HCN SENSOR | |
|-------------------|------------|---------|-----------|---------|------------|---------|
| | Detected | Alarmed | Detected | Alarmed | Detected | Alarmed |
| Acrolein | No | No | No | No | No | No |
| Acrylonitrile | No | No | No | No | No | No |
| Ammonia | YES | No | YES | No | No | No |
| Benzene | YES | YES | No | No | YES | No |
| Carbon Dioxide | No | No | No | No | YES | YES |
| Chlorine | YES | No | YES | YES | No | No |
| Dimethylamine | YES | YES | No | No | No | No |
| Ethylene Oxide | YES | No | No | No | No | No |
| Hydrogen Cyanide | YES | No | No | No | YES | YES |
| Hydrogen Fluoride | No | No | No | No | YES | YES |
| Methyl Bromide | YES | YES | No | No | YES | YES |
| Methyl Chloride | YES | No | YES | YES | No | No |
| Phosphine | YES | No | No | No | YES | YES |
| Toluene | YES | YES | No | No | YES | YES |

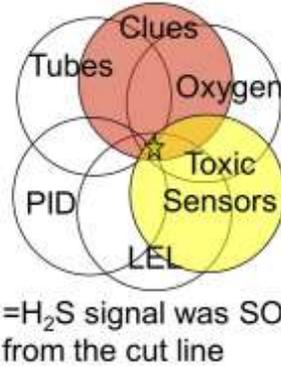
- 14 target chemicals
- PID (alarming @50 ppm), Cl₂ (@0.5 ppm) and HCN (@4.7 ppm)
- Detected: 12 chemicals
- Alarmed: 10 chemicals
- With their lower alarm limits, Cl₂ and HCN sensors are inherently cross-sensitive so they can alarm for more gases/vapors.

Getting the Most from Toxic Gas Sensors

| Gas | Concentration | Response |
|------------------|---------------|---------------|
| CO | 300 ppm | 100 ppm |
| SO ₂ | 5 ppm | about 1 ppm |
| NO | 35 ppm | < 0.7 ppm |
| NO ₂ | 5 ppm | about 1 ppm |
| H ₂ | 100 ppm | 0 ppm |
| HCN | 10 ppm | 0 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 5 ppm | about 4 ppm |
| CS ₂ | 100 ppm | 0 ppm |
| Methylsulfide | 100 ppm | 9 ppm |
| Ethylsulfide | 100 ppm | 10 ppm* |
| Methyl mercaptan | 5 ppm | about 1 ppm |
| Ethylene | 100 ppm | ≤ 0.2 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Toluene | 10000 ppm | 0 ppm* |
| Turpentine | 3000 ppm | about 70 ppm* |

* Cross-sensitivity chart for example only; consult your manufacturer for specific cross-sensitivities

- **Clues:** Renovation causes a leak, HazMat finds an SO₂ cylinder
- **Oxygen:** no change in reading
- **Toxic Sensors:** H₂S sensors are cross-sensitive to SO₂ at a 5-1 ratio, 10 ppm on an H₂S sensor means 50 SO₂, the TWA of SO₂ is 2 ppm and IDLH is 100 ppm
- **LEL:** no reading
- **PID:** can't read SO₂
- **Tubes:** none used, but an SO₂ tube could have been used for confirmation



Using Cross-sensitivity to approximate scale

In the last example the cross-sensitivity chart showed that 5 ppm SO₂ produced 1 ppm of response on the H₂S sensor. So the H₂S sensor is 20% cross-sensitive to SO₂:

$$1_{\text{H}_2\text{S}}/5_{\text{SO}_2} = 0.20 \text{ or } 20\%$$

To get the reading in units of SO₂:

- Divide by the H₂S reading by 0.20:
10ppm/0.20 = 50 ppm
- Or multiply the reading by the reciprocal of the percentage which in this example is
1/0.20 = 5, 5 x 10 ppm_{H₂S} = 50 ppm_{SO₂}

NOTE: sensor cross-sensitivity is not continuously monitored and controlled for by manufacturers and only provides an APPROXIMATION of the cross-sensitive

gas/vapor concentration, but sometimes that's all you got! One should always confirm with colorimetric tubes.

Gas Delivery Truck

A gas delivery truck driver hears cylinders/bottles fall as he is driving. He pulls over when he thinks he hears gas leaking. He tells the arriving hazmat team that he thinks the leaking cylinders could be chlorine, ethylene oxide (EtO) or hydrogen. The CO sensor will detect both EtO (~40% response), H₂ (~40% response), and even Cl₂ (~10% response) as seen in the following CO sensor cross-sensitivity chart:

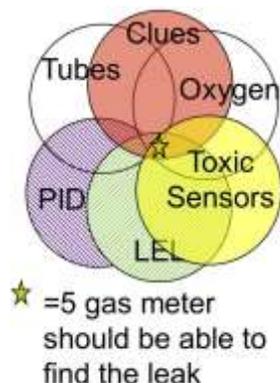
| Gas | Concentration | Response# |
|------------------|---------------|-----------|
| H ₂ S | 24 ppm | 0 ppm |
| SO ₂ | 5 ppm | 0 ppm |
| Cl ₂ | 10 ppm | 0-1 ppm |
| NO | 35 ppm | 0 ppm |
| NO ₂ | 5 ppm | 0 ppm |
| NH ₃ | 50 ppm | 0 ppm |
| PH ₃ | 5 ppm | 0-1 ppm |
| H ₂ | 100 ppm | 40 ppm |
| Ethylene | 100 ppm | 10 ppm |
| Acetylene | 250 ppm | 250 ppm |
| Ethanol | 100 ppm | 0 ppm |
| Ethylene Oxide | 125 ppm | 340 ppm |
| Propane | 100 ppm | 0 ppm |
| Isobutylene | 100 ppm | 0 ppm |
| Isobutylene | 1000 ppm | 7 ppm |
| Hexane | 500 ppm | 0 ppm |
| Toluene | 400 ppm | 0 ppm |
| Nitrogen | 100% | 0-4 ppm |

* Cross-sensitivity chart for example only; consult your manufacturer for specific cross-sensitivities

Using all the sensors on a 5-gas detector we can get a better picture of which gas is leaking. If we get signal from the CO sensor, PID and LEL sensor then it's ethylene oxide because that's the only gas that can be seen by all three sensors. If the CO sensor and LEL see it then it's probably hydrogen because the PID can't see hydrogen. If only the CO sensor responds it's probably chlorine because the PID and LEL sensors can't see chlorine. However, even these "unusual" gases can be detected by a common 5-gas detector.

Getting the Most from Toxic Gas Sensors

- **Clues:** Driver tells HazMat he thinks something's leaking
- **Oxygen:** no change in reading
- **Toxic Sensors:** Cl₂ sensor will work on Cl₂, but CO sensor will detect both EtO (~40%), H₂ (~40%), and even Cl₂ (~10%), H₂S doesn't help
- **LEL:** won't see Cl₂ but may see EtO and H₂ in high concentrations
- **PID:** with 10.6ev lamp may see EtO at high levels but won't pick up Cl₂ or H₂
- **Tubes:** Specific tubes would work



Solving Cross-Sensitivity Issues

1. **Detective work:** what are the clues telling you?
2. **Sensors:** What are ALL your sensors telling you?
 - If oxygen has dropped AT ALL you have A LOT of something there and you should expect cross-sensitivities
 - PIDs and LEL can work together to provide clues
 - Consider the possibility of cross-sensitivities
 - Consider using cross-sensitivity to your advantage
3. **Verify with different technology:** colorimetric tubes are excellent tools for this
4. **Calibrate:** Calibration is "confidence in a can." Carry calibration gas with you if you can.

Toxic gas sensors are a workhorse technology for protection from gases in applications ranging from industrial confined space entry to HazMat. However, designed for the everyday industrial environment they can be damaged or provide erroneous readings when the environment strays from "normal" and sensor specifications define what's normal for EC sensors. Like many sensing technologies EC sensors have cross-sensitivities. Users of EC sensors should be aware when and where they might run into cross-sensitivities and understand that while EC cross-sensitivity might be misleading, it can also be a benefit. While a workhorse technology, EC sensors

should be used with all clues and sensors available to come to a more complete answer to gas detection challenges.

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
- 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."