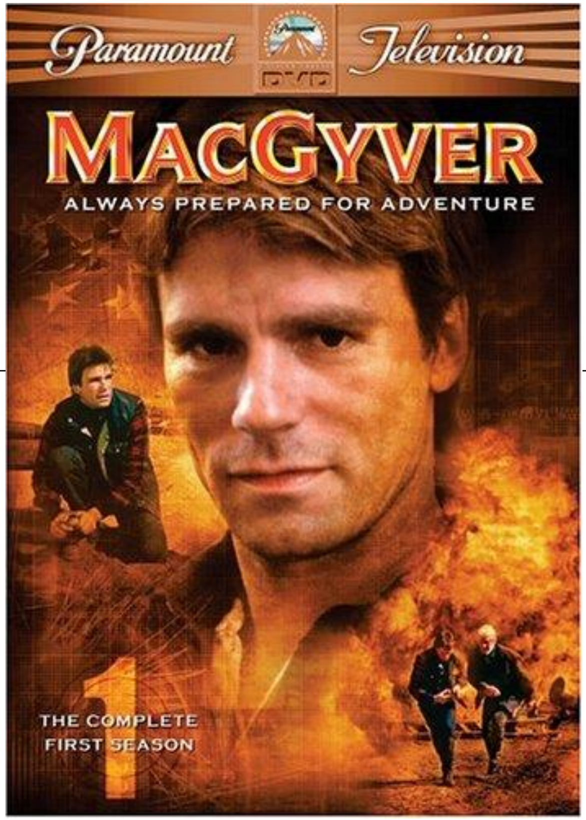

MacGyver Gas Detection

Getting out of “sticky” situations using the sensitivities and cross-sensitivities of common sensors

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4/2018

Sometimes it isn't easy

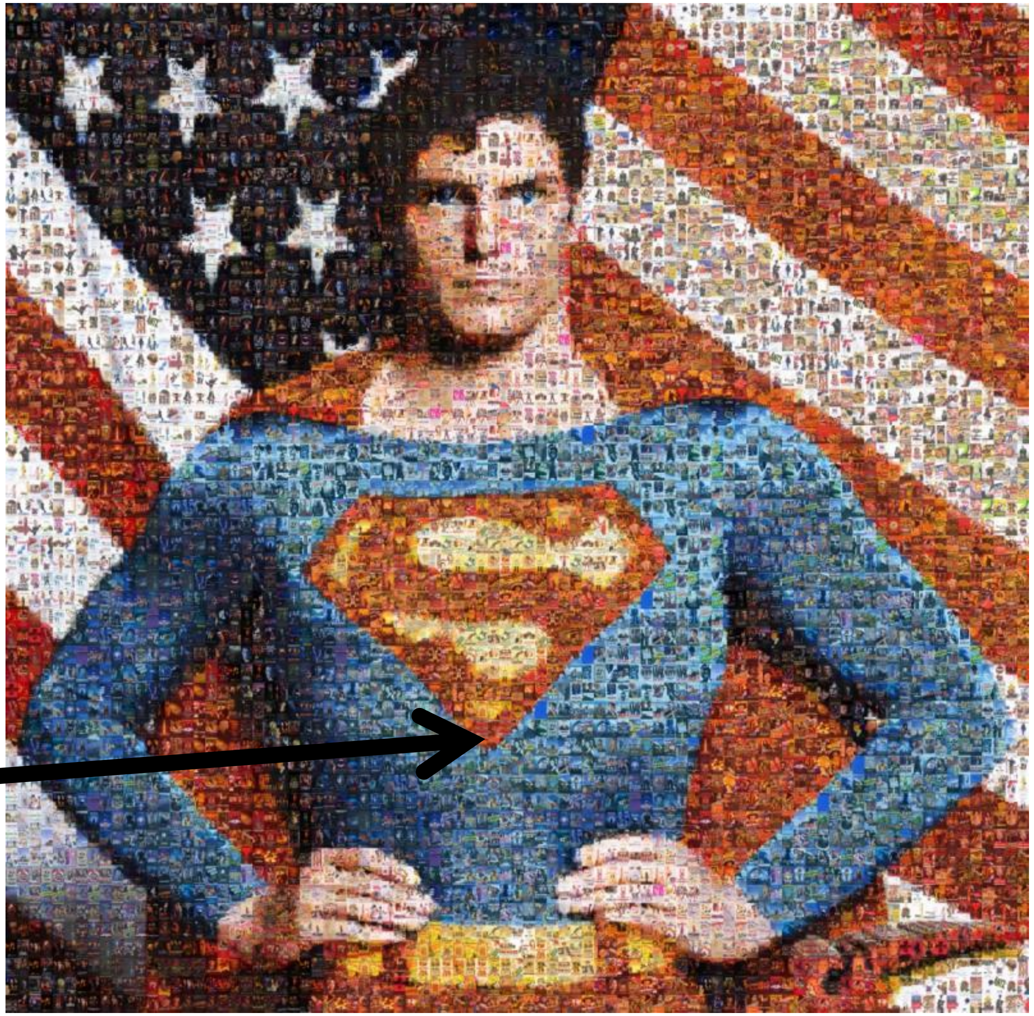
- Easy gas detection is lovely
- It's a Carbon Monoxide (CO) incident
- You turn off the furnace and the CO levels go down
- You turn the furnace back on and the CO levels go back up
- Problem SOLVED
- But sometimes it isn't this easy
- This is not the "EASY" gas detection course
- In this class we will discuss strategies that can help to solve the more complicated gas detection challenges

Integrating Gas Detection Techniques

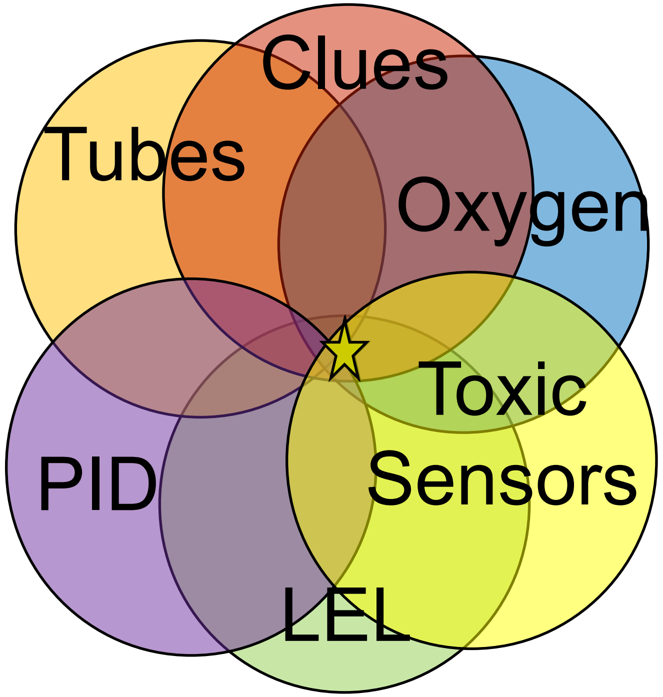
- Typically multiple clues are required to come to a conclusion
- One way to think of this is to think about layering detection technologies and clues to solve the problem
- Each detection technology adds another angle to the problem to get closer to the solution
- You can get more out of your meter than just the individual 4 or 5 sensors if you think orthogonally!

Integrating Gas Detection Techniques

- “I’ve got a whole bunch of pictures I’ve got to take to make up the big picture”



Integrating Gas Detection Techniques



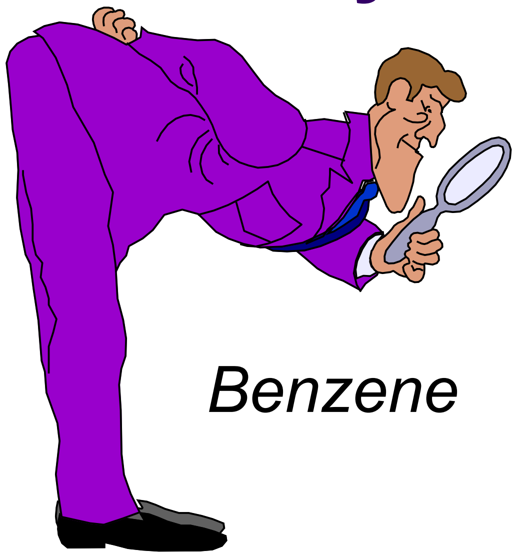
☆ =The Real Answer

- Throughout this course we will use Venn diagrams to illustrate the layering or integration of gas detection techniques
- Each circle represents the range of chemicals seen by a sensing technique
- Colored circles in the following examples indicate a positive response for that technology
- By overlaying multiple detection techniques we can zoom in on the solution
- Your sensors are a team not individuals, sometime just one sensor does the job but other times you need the entire team to "win"
- Use multiple techniques until you feel comfortable with the solution
- ***If you get confused, "Add a circle" don't feel limited to the circles depicted here***

Thimk! (yes I know I misspelled it)

- Detectors are essentially dumb devices that sense and output a number
- They are highly dependent upon the person using device to interpret number and make an educated assumption on what it means
- Even in the future represented by Star Trek, they still gave the Tricorder to the smartest guy on the spaceship!

Think of yourself as a detective!



Carbon Disulfide

Ammonia

Carbon Monoxide

Styrene

Benzene

PERC

Xylene

Detectors need Detectives to come to the right conclusion

- This course provides gas detectives with a tool kit to use both in everyday and unusual circumstances
- While some of the examples may seem unlikely, it is hoped that by documenting them they can rest in the back of the gas detective's brain for those times when the detective has to rise to the challenge

Agenda

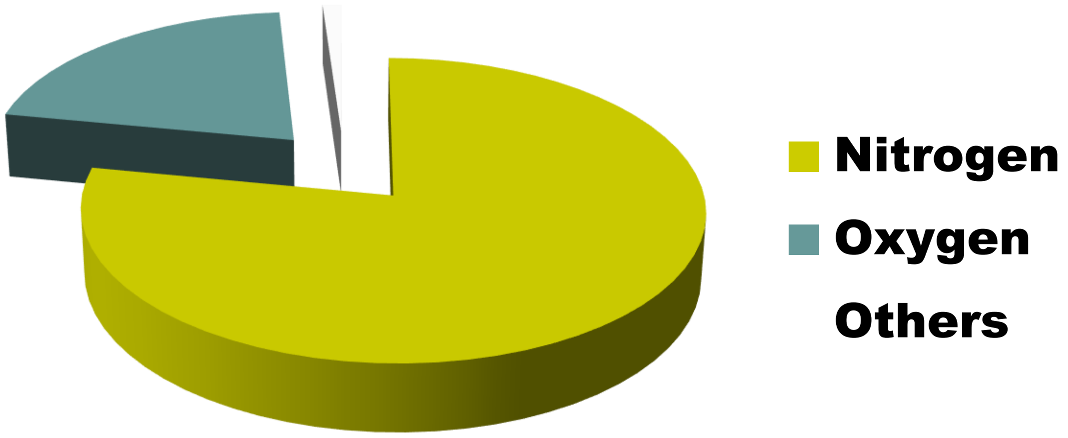
- Oxygen
- Combustible Gases & Vapors
- Toxic Gases & Vapors
- PIDs
- Putting it all together

Oxygen

- Lack of Oxygen is more acutely fatal than even the most toxic gases and vapors, even CWAs
- There is no antidote for lack of oxygen
  - Causes:
  - Displacement (by what?)
  - Microbial action
  - Combustion
  - Absorption
- Oxygen can be the ultimate “broad-band” toxic sensor and detects gross contaminants even when all other sensors fail you

Composition of “fresh air”

In a short hand way air is about 20% oxygen and 80% nitrogen



Oxygen Drops from 20.9-20.8%

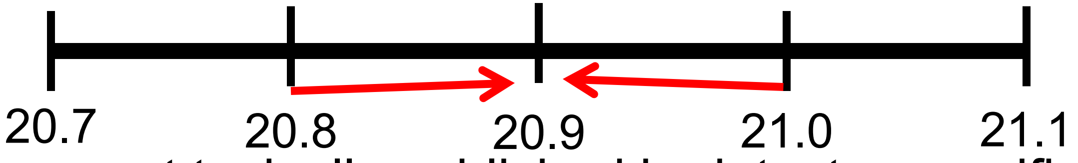
How much of “something else” has entered this room?

Oxygen sensors as a “broad-band” toxic sensor or the “Rule of 5000”

- 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 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 detector 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
- For example if the manufacturer has implemented a 0.2 % oxygen dead-band all potential readings between 20.8-21.0 are forced to read 20.9%



  - 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%

If Oxygen Decreases AT ALL you may have a LOT OF SOMETHING ELSE!

- While dead-band can reduce the perceived "jumpiness" of oxygen sensors but it can reduce their effectiveness as a broad-band toxic sensor
- 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 and oxygen readings

- Many living organisms consume oxygen
- In closed systems that contain organisms, from bacteria to people, the oxygen may 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

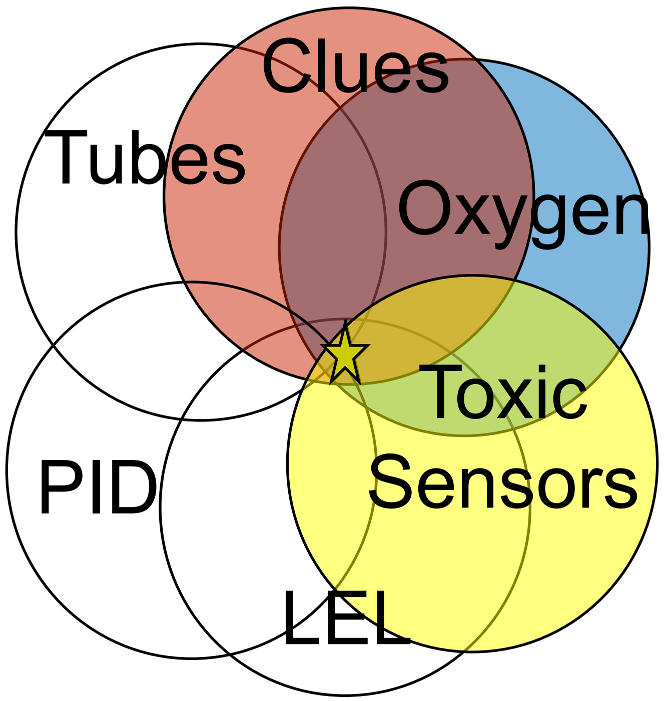
Unstable Oxygen Sensors

- Two found dead (one the prime minister) in a ground floor apartment on a cold February in a former soviet union state
- CO poisoning from a natural gas heater was suspected
- CO was found when the heater was running in the apartment but not enough to be immediately lethal (~300 ppm)
- A multi-point wireless gas detection system was used to monitor in and outside of the apartment to confirm CO poisoning was the culprit
- Detectors were placed inside and outside of the apartment
- 3 oxygen sensors in the apartment read 20.7, 20.8 and 20.6% indicate 15,000, 10,000 or 20,000 ppm of “something else” is there
  - One oxygen sensor reading 20.7% may be a “flakey sensor,” three tell you something is going on

Unstable Oxygen Sensors

- 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
- The fatalities were due to a combination of low oxygen levels and elevated CO

Unstable Oxygen Sensors



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

☆ =low oxygen plus CO lead to the fatalities

O_2: 20.6, LEL: 0, CO: 300, H_2S: 1.5, PID: 0

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 made entry 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 detector and PID.
- They doffed PPE to question the kitchen supervisor and those complaining of weakness and nausea
- While looking at the combination freezer/refrigerator they noticed plastic slats separating the two walk in units

Slow Oxygen Sensor

- They remotely sampled the freezer section of the unit by putting the 4 gas detector through the slats and saw no change
- They entered the unit by walking though the slats and began to survey further into the unit
- At about 12 feet the two members of the entry team felt “funny” and “light headed.” Within about a few seconds the 4 gas detector indicated a low O_2 environment, and went into alarm. This was about 60 seconds after entering the room and was 30 seconds after the entry team members felt the affects.
- When questioned the supervisor told Hazmat about the pallet of dry ice being stored in the freezer for the university beauty pageant they had scheduled for the weekend.

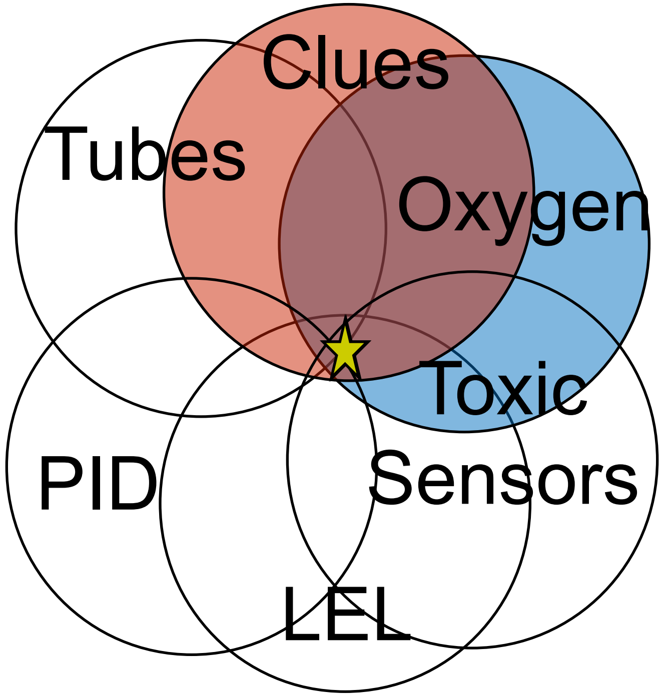
Slow Oxygen Sensor

- 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
  - Because the detector was in low oxygen alarm they had AT LEAST 7% CO_2 in the air
    - 20.9%-19.5% = 1.4 x 10 = 14 * 5000 = 70,000/10,000 = 7%
- The freezer and refrigerator was classified as a confined space until the pallet of dry ice was removed

Slow Oxygen Sensor

- 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 detectoring 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

Slow Oxygen Sensor



☆ = High CO_2 from dry ice detected by O_2 displacement

- **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 Sensors:** nothing indicated, could have used NDIR CO_2 sensor
- **LEL:** no change in reading
- **PID:** no change in reading
- **Tubes:** could have used a CO_2 tube

O_2: <19.5, LEL: 0, CO: 0, H_2S: 0, PID: 0

Agenda

- Oxygen
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Wheatstone bridge catalytic bead LEL sensors

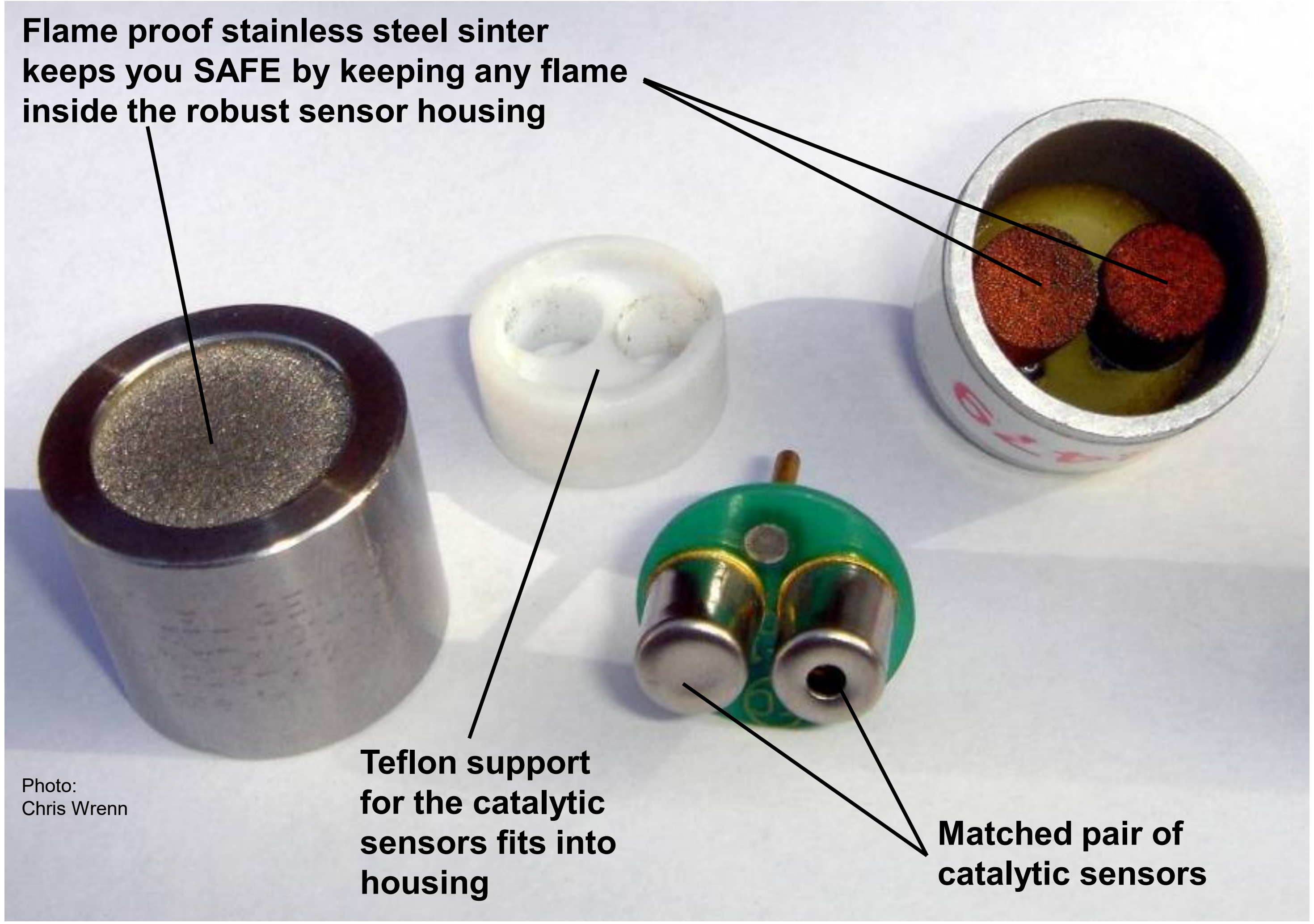
- Catalytic "Hot Bead" combustible sensors
  - Detect combustible gas by catalytic oxidation
  - When exposed to gas oxidation reaction causes bead to heat
  - Requires oxygen to detect gas!
- Developed by Dr. Oliver Johnson of Standard Oil Co. of CA (now Chevron)* in 1926-1927
- Virtually EVERY combustible gas detector today is derived from this design
- Variously called "Wheatstone Bridge" or "Catalytic Bead" sensors

* Reference and photos courtesy of RKI Instruments

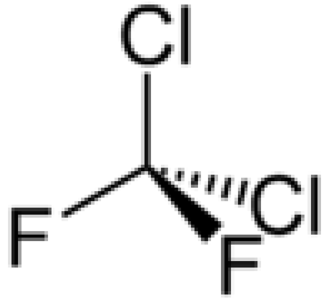
Wheatstone bridge catalytic bead sensor is like an electric stove

- One element has a catalyst and one doesn't
- Both elements are turned on low
- The element with the catalyst "burns" gas at a lower level and heats up
- As this is a combustion (or oxidation) process a minimum of 12-16% oxygen is required
- The hotter element has more resistance and the Wheatstone Bridge measures the difference in resistance between the two elements
- ***This is a primary measurement because if something burns it will burn on this sensor***

Making the Electric Stove Safe for Use in Flammable Atmospheres

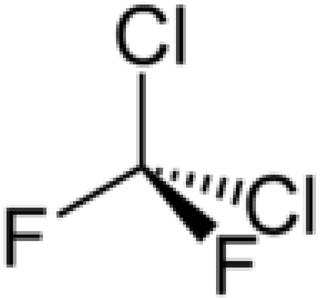


LEL Sensors Reads Freon



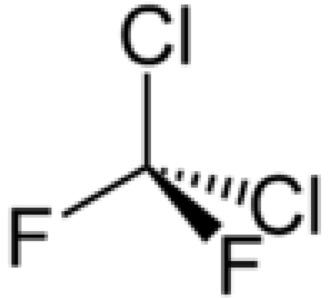
- Workers removing Freon (R-12) from a building HVAC system vented R-12 into the engineering space
- One worker succumbs another is taken to hospital
- HazMat team can see “shimmering” in the air when they make entry wearing PPE and SCBA
- Oxygen levels drop below 10%, PID reads nothing but LEL reads as high as 12%
- Once the area was ventilated and cleared of R-12 no other flammable gas was found to be present
- Responders can’t figure out the LEL sensor response because they couldn’t find any “flammable” gas/vapor

LEL Sensors Reads Freon



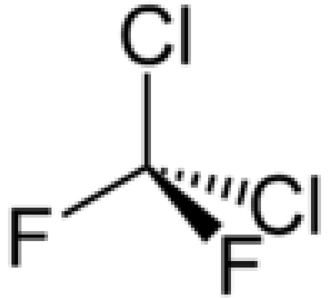
- Even though R-12 does not have an LEL value, it still can provide a reading on a catalytic sensor because the carbon at the center of the molecule will burn
- It won't read much; not all the way up to 100% LEL, but since it has carbon atoms it will burn some and cause a reading
  - Note that this "frees" the halogens which then will rot the sensor particularly if this is a chronic condition
  - This also can happen from vapors such as perchloroethylene, which also does not have an LEL and is considered non-flammable
- The fact that there was only 10% oxygen in the air shows that half of the air had been displaced by the R-12
  - Using the 5000 ppm rule for every 0.1% oxygen drop that is 20.9-10 = 10.9 or 109 X 5000 = 545,000 ppm or 54.5% of R-12 in the air

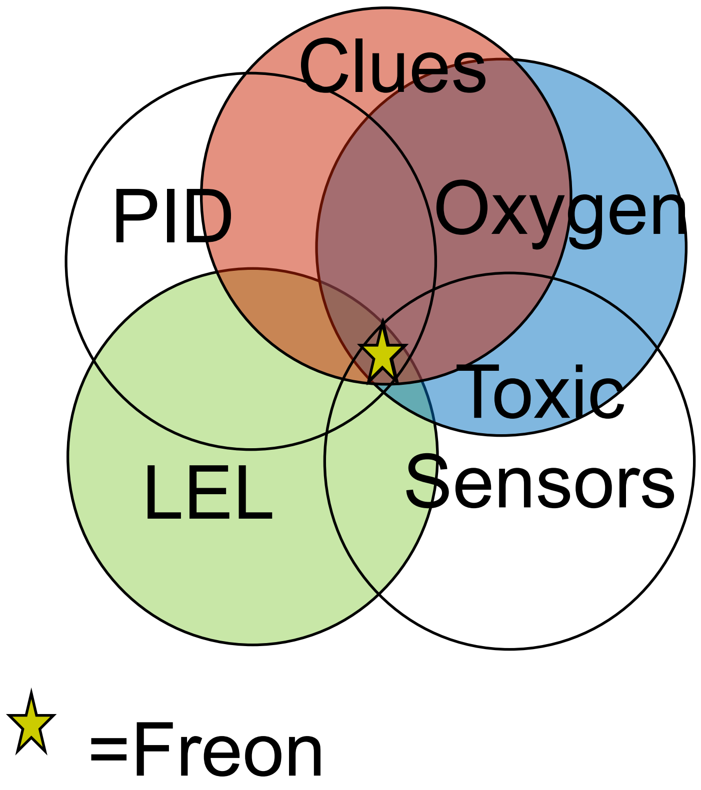
LEL Sensors Reads Freon



- A reading of 10% LEL to 12% LEL seems to be the highest reading R-12 may be able to reach
- It would need to be over 100% LEL to be flammable, but a catalytic sensor can burn it enough to cause a slight reading

LEL Sensors Reads Freon





- **Clues:** workers decommissioning an HVAC system
- **Oxygen:** as low as less than 10%
- **Toxic Sensors:** no change in readings
- **LEL:** as high as 12%, Freon has enough C in it to burn a little
- **PID:** no reading, even with natural gas and LP gas you would get a few hundred ppm from contaminants

O_2: ~10, LEL: ~12, CO: 0, H_2S: 0, PID: 0

PIDs for Combustible Vapors

- PIDs measure in ppm and we've been talking about % of LEL and % Volume
- Multiply % Volume by 10,000 to get ppm.
- LEL Gasoline is 1.2% by volume or 12,000 ppm
- 10% of LEL Gasoline is 1200 ppm

PIDs often are a better measurement tool for 10% of LEL for fuel and chemicals vapors & mists because catalytic sensors may have physical problems with these chemicals getting past their flame arrestor

Using PIDs for 10% of LEL

Gas/Vapor	LEL* (% vol)	LEL in ppm	10% of LEL in ppm	10% of LEL in Isobutylene units**	Detectable with LEL
Methane	5	50,000	5,000	Not detectable with PID	Great
Hydrogen	4	40,000	4,000	Not detectable with PID	Great
Propane	2	20,000	2,000	Not detectable with PID	Great
Gasoline	1.4	14,000	1,400	1,556	Good
Acetone	2.2	22,000	2,200	2,000	Good
Benzene	1.2	12,000	1,200	2,264	Good
n-Pentane	1.5	15,000	1,500	179	Good
MEK	1.8	18,000	1,800	1,636	Good
Toluene	1.2	12,000	1,200	2,400	Good
Diesel	0.8	8000	800	1,143	Poor

* NFPA 325 "Guide to Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids, 1994 edition
** Divide ppm by the chemical correction factor for your PID

Using PIDs for 10% of LEL

1000 ppm in Isobutylene units is a conservative measure of 10% of LEL for many common VOCs

- Always cross-reference LEL and PID for potentially flammable environments
- Always check LEL if you have a high PID reading, it could be a flammable environment, LEL may need time to catch up
- Always check PID if you have LEL, even natural gas and LP have enough contaminants (they are not pure methane or propane) that you'll see a few 100 ppm
- If neither the catalytic bead LEL and the PID read anything, most likely a potentially flammable atmosphere is not present

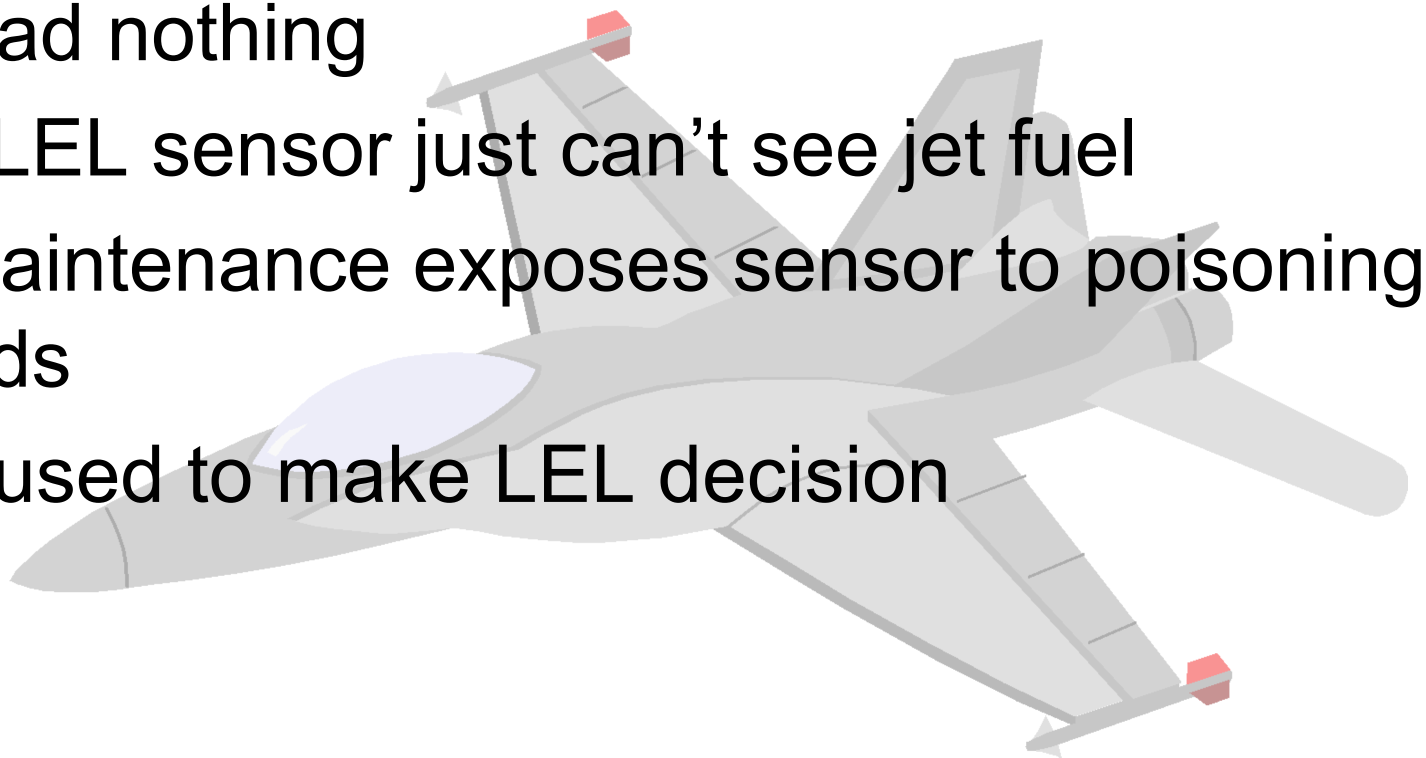
When do I use PID for 10% of LEL?

- If you can see “it” like pouring it out of a can onto the ground then the PID is probably better
- If it is a gas that you can never “see” then the wheatstone bridge catalytic bead sensor is better

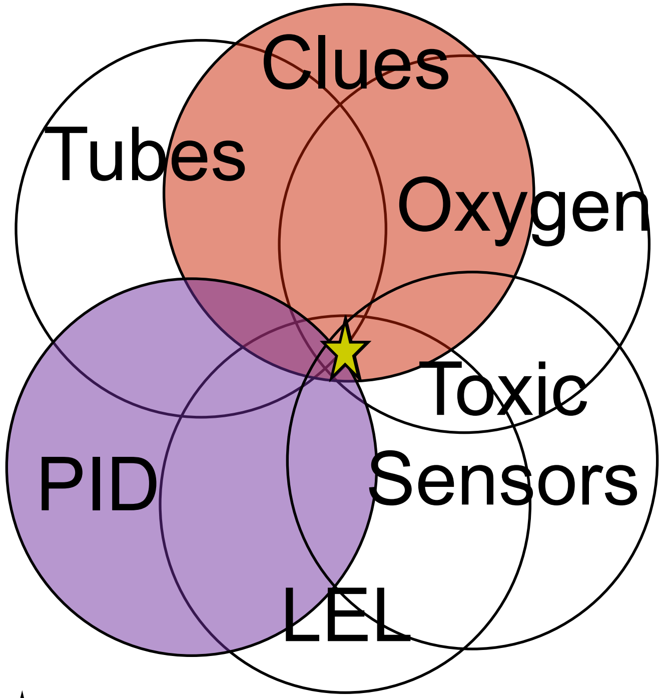
- If the ionization potential of “it” is greater than 10.6eV then the wheatstone bridge catalytic bead sensor is better

Wing tank LEL

- Entrants can see and smell jet fuel but their catalytic LEL meters read nothing
- Catalytic LEL sensor just can't see jet fuel
- Aircraft maintenance exposes sensor to poisoning silicone compounds
- PIDs are used to make LEL decision



Wing tank LEL



☆ =800 ppm of JP-8 is 10% of LEL

- **Clues:** wing tank containing jet fuel residue
- **Oxygen:** no change in reading
- **Toxic:** possible reading on an old CO sensor
- **LEL:** 10% of LEL too low to read unless scaled to jet fuel (CF ~3)
- **PID:** 800 ppm in jet fuel units is 10% of LEL (CF=0.6)
- **Tube:** none used

Agenda

- Oxygen
- Combustible Gases & Vapors
- Toxic Gases & Vapors
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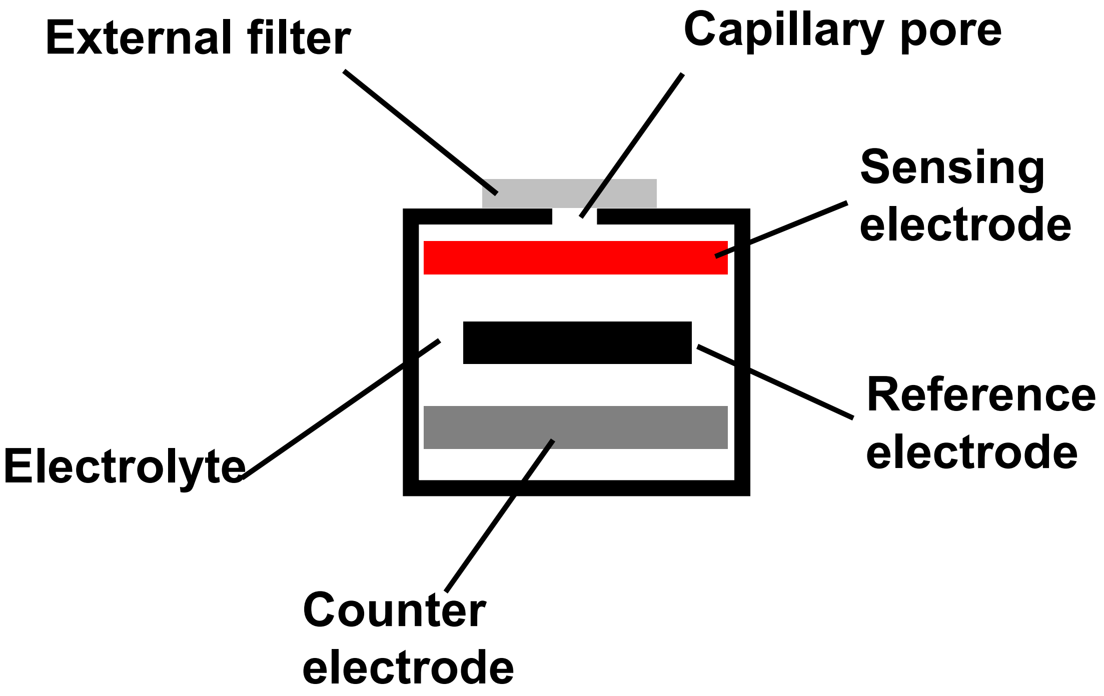
EC Toxic Gas Sensors

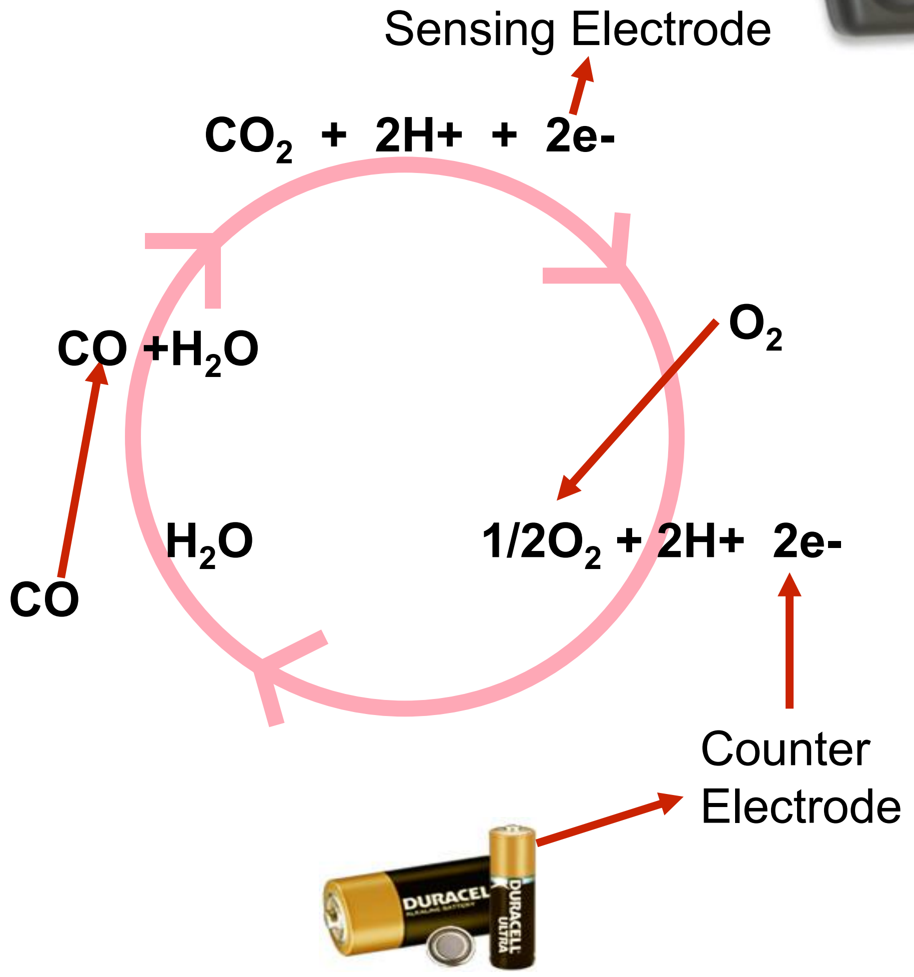
- Basically the EC sensor is a battery that turns concentrations of the gas of interest into a current output in proportion to the concentration of the gas
- EC sensors are similar to dry cell batteries in construction
- Gas diffusing into sensor reacts at the surface of the sensing electrode
- The sensing is electrode made to catalyze 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
- Unlike "fuel-cell" oxygen sensors EC sensors are not a "one-way trip"

EC Toxic Gas Sensor Cross-Section



EC Sensors are a Regenerative or Circular 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
- Really a regenerative or circular process as long as you stay within the operating parameters (specs) of the sensor

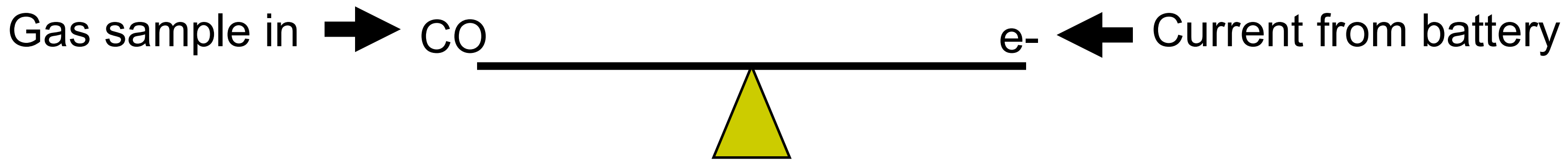


Consuming EC Sensors

- Two EC sensors consume key components and therefore are not "self-replenishing" like the more common EC sensors
  - Ammonia (NH_3)
  - Hydrogen Cyanide (HCN)
- This is the reason these sensors have significantly less life and users seem to experience more reliability issues with them

Stay within the operating parameters and you stay in balance

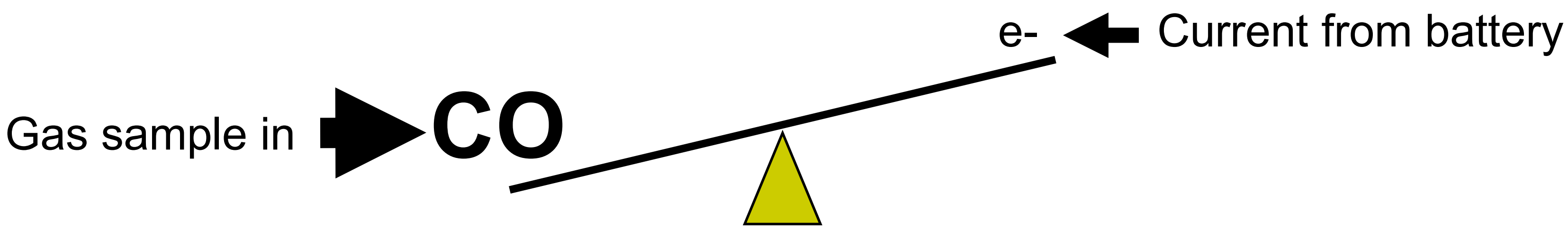
- Another way to look at EC sensors is that they are like a “see-saw”



- Under normal operation the amount of toxic gas in can be balanced by the electrical current added back in at the counter electrode

Exceed the operating parameters & you destroy the balance (& 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.

EC Sensor Cross-Sensitivity

- Virtually 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 gas can either decrease the signal (negative cross-sensitivity) or increase the signal (positive cross-sensitivity)
  - The actual values may vary between batches because the cross sensitivity is not typically controlled during the manufacturing process

Understanding EC Sensor Cross-sensitivities

- "When you hear stampeding hooves think horses not zebras"
- But sometimes when you can't find the horses 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
- Expect cross-sensitive responses ***anytime*** oxygen reads <20.9%

Methanol Tank Truck Rollover

- Customer calls because CO & H_2S sensors are "acting funny"
- Multigas meter was exposed to a high level of methanol the day before due to a spill
- Both sensors were giving "Neg" or negative alarms
- Reading the sensor spec sheet
  - **Note**: High levels of polar organic compounds including alcohols, ketones, and amines give a negative response.

Photo by Abby Taylor, Houmatoday.com

CO sensor cross-sensitivity*

Gas	Concentration	Response#
H_2S	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	$\geq$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

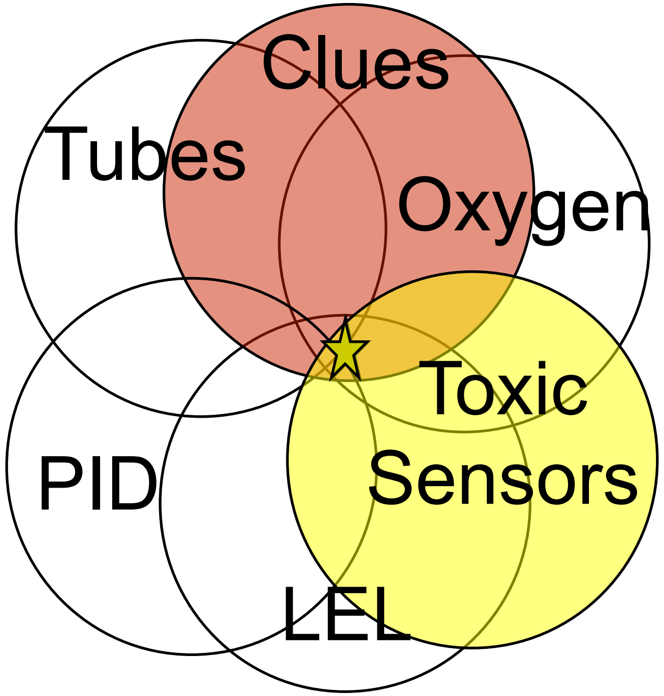
Note: High levels of polar organic compounds including alcohols, ketones, and amines give a negative response.

Used sensors show increasing response to VOCs

Methanol Tank Truck Rollover

- ***This situation is dangerous because a negative alarm means that if CO or H_2S were present, the sensors would go into alarm LATE because of the negative condition of the sensors***
- Recommended putting meter into calibration mode to silence the sensor alarms
- Run 24 hours on charger to clear the poison from the sensor
- If after 24 hours the sensors calibrate go ahead and continue to use them
- Calibrate more often for a while to make sure they are all right
- They probably will have greater cross-sensitivities
- If they don’t calibrate or if they remain unstable you should replace the sensors

Methanol Tank Truck Rollover

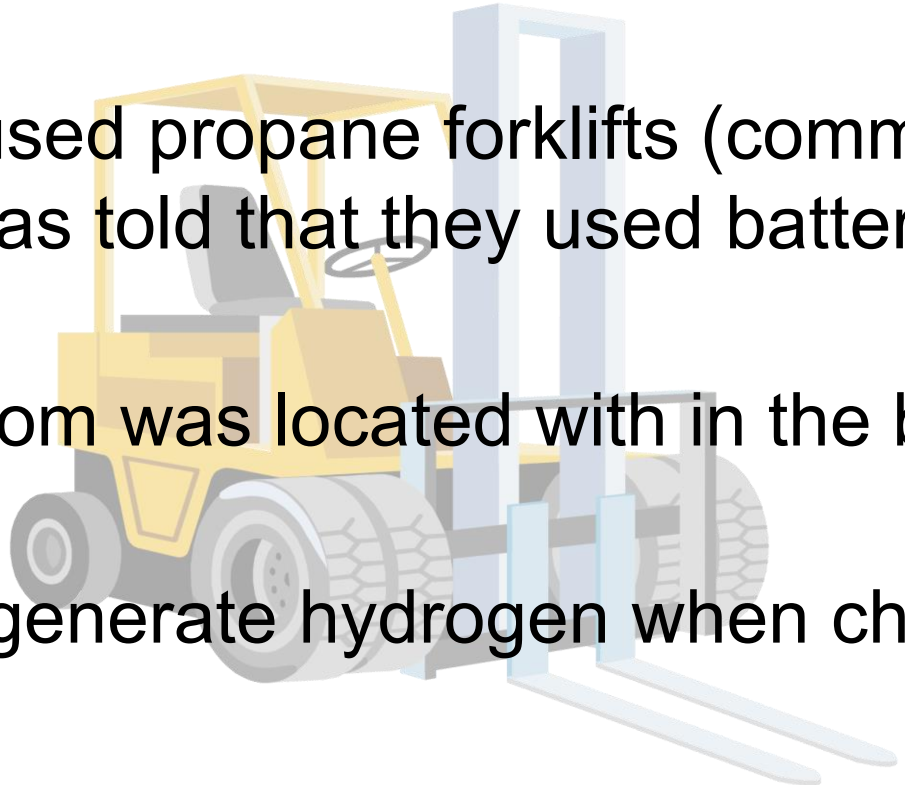


☆ =Toxic sensors poisoned by methanol

- **Clues:** methanol tank truck rollover the day before
- **Oxygen:** no change in reading
- **Toxic sensors:** NEG alarm from both CO and H_2S 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

Food Warehouse CO

- In food warehouse maintenance room had 80 ppm CO indicated
- Asked them if they used propane forklifts (common source of CO) but was told that they used battery powered forklifts
- The maintenance room was located with in the battery charging area
- Lead acid batteries generate hydrogen when charging



CO sensor cross-sensitivity*

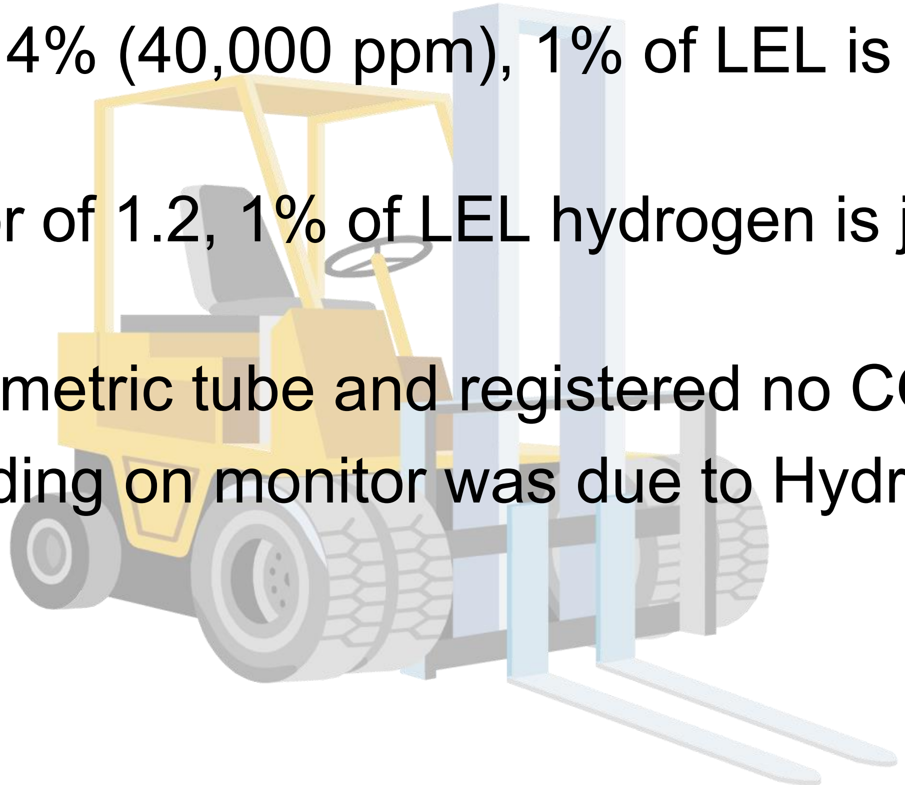
Gas	Concentration	Response#
H_2S	24 ppm	0 ppm
SO_2	5 ppm	0 ppm
Cl_2	10 ppm	0-1 ppm
NO	25 ppm	0 ppm
NO_2	5 ppm	0 ppm
NH_3	50 ppm	0 ppm
PH_3	5 ppm	0-1 ppm
H_2	100 ppm	40 ppm
Ethylene	100 ppm	16 ppm
Acetylene	250 ppm	250 ppm
Ethanol	200 ppm	1 ppm
Ethylene Oxide	125 ppm	≥40 ppm
Propane	100 ppm	0 ppm
Isobutylene	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

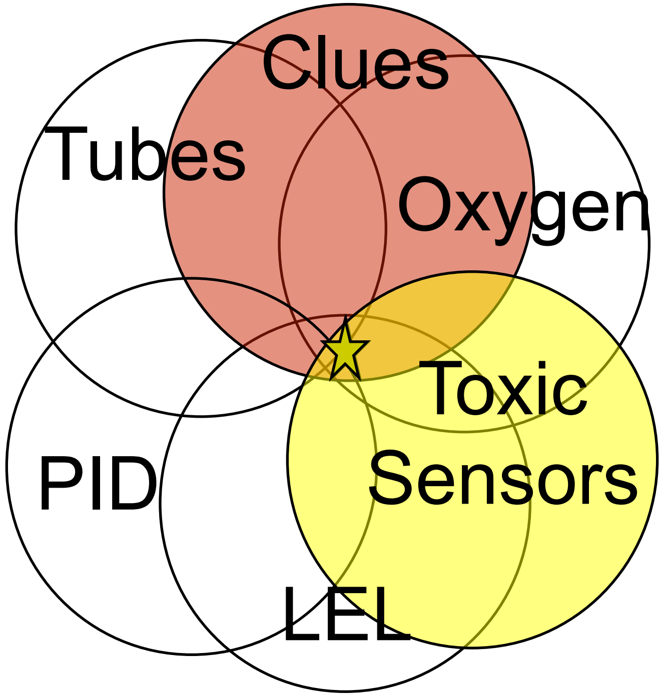
The CO sensor is about a 40% hydrogen sensor

Food Warehouse CO

- 80 ppm indicated CO translates to 200 ppm hydrogen or about 0.5% of LEL
- No LEL reading, LEL is 4% (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
- Checked with CO colorimetric tube and registered no CO reading
- Concluded that CO reading on monitor was due to Hydrogen cross-sensitivity



Food Warehouse: CO Cross-Sensitivity



☆ = Probably Hydrogen gas from forklift batteries

- **Clues:** Warehouse w/ battery powered forklifts
- **Oxygen:** no change in reading
- **Toxic Sensors:** 80 ppm reading on CO if H_2 it's approximately 200 ppm,
- **PID:** no reading on PID
- **LEL:** no reading on LEL (CF = 1.1)
- **Tubes:** no reading on CO tube

O_2: 20.9, LEL: 0, CO: 80, H_2S: 0, PID: 0

“CO” in House Renovation

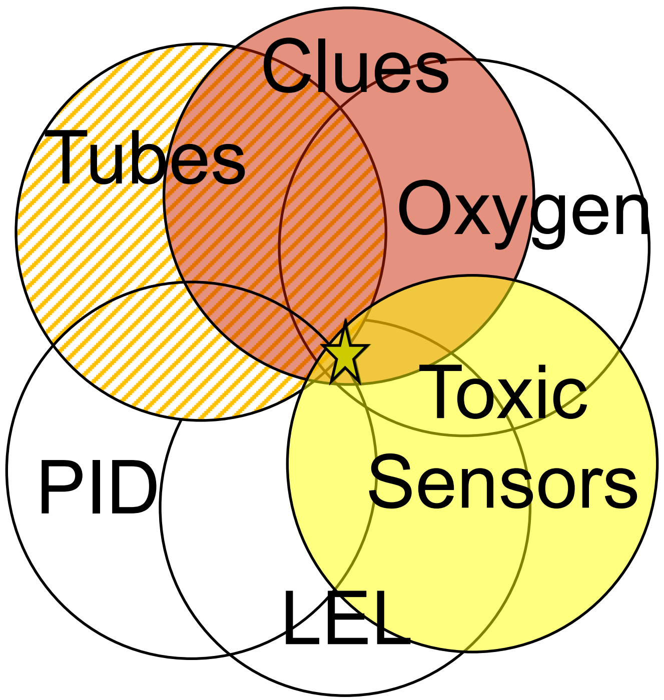
- CO monitors installed because a natural gas furnace was being added to house
- CO monitors alarmed even when the furnace was not hooked up to gas
- Multiple CO manufacturers where used but all gave the same high readings
- Occupants were not symptomatic of CO toxicity
- Draeger tubes gave low CO reading (about 10% of CO sensors
- PID gave no reading
- Sample tubes driven into the ground around house gave CO & FID reading

“CO” in House Renovation*

Gas	Concentration	Response#
H_2S	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

CO in House Renovation



 =More testing required?

- **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 alarm
- **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 required

O_2: 20.9, LEL: 0, CO: 100, H_2S: 0, PID: 0

Firehouse CO detectors

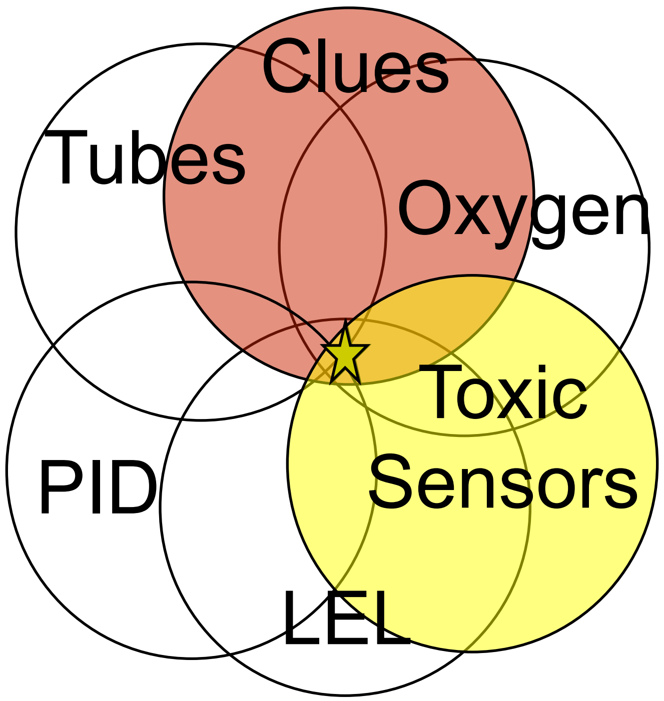
- All the fixed AND personal CO detectors carried by officers in a firehouse all went into alarm
- Went to the heater room but it was fine
- Looked to see if the batteries from the vehicles in the equipment bay were cooking off but they were fine
- Removed all of the vehicles from the equipment bay and the alarms went away
- Brought the equipment in until they had alarms again
- Found that the acetylene tank in one truck was leaking

Firehouse CO detectors*

Gas	Concentration	Response#
H_2S	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	$\geq$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

Firehouse CO detectors



☆ =CO sensors are also acetylene sensors

- **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

O_2: 20.9, LEL: 0, CO: 60, H_2S: 0, PID: 0

CO_2 in Corn Silo

- 2 men down in silo with water in it
- User thought that high CO "must be CO_2 cross-sensitivity because the grain was fermenting"
- CO sensors are NOT cross-sensitive to CO_2 at all
- Let's look at fermentation by-products:
  - Common: ethanol, lactic acid, hydrogen
  - Less common: butyric acid & acetone
  - Silage "greens" in corn can lead to NO/NO_2

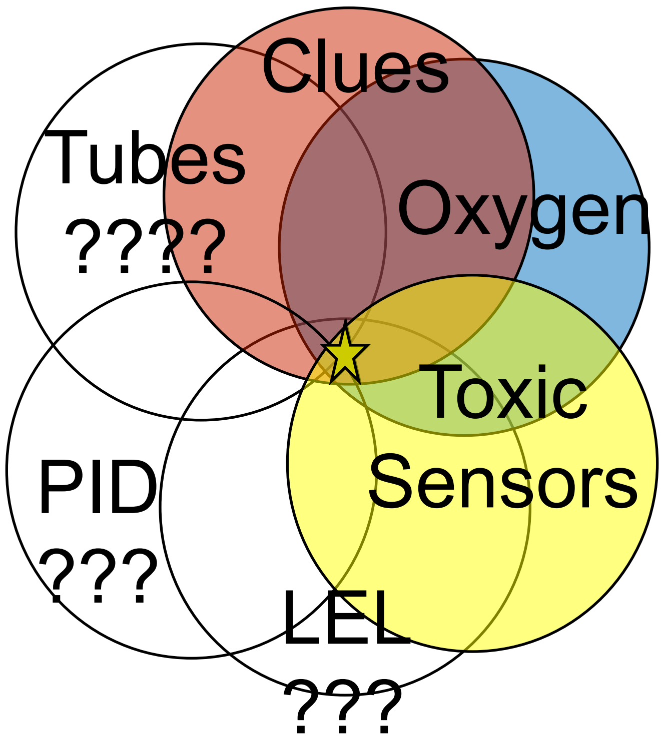
CO_2 in Corn Silo*

Gas	Concentration	Response#
H_2S	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

Possibly oxides of nitrogen, hydrogen or ethanol or other organics with an old CO sensor

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

CO_2 in Corn Silo



★ =possibly H_2, NOx, ETOH

- **Clues:** Corn silo with two victims
- **Oxygen:** in alarm (<19.5%) meaning that 70,000 (14 x 5000) or 7% of something else is there
- **Toxic Sensors:** high reading on CO, could be from cross-sensitive to oxides of nitrogen NOx), hydrogen, ethanol or other organics with an old CO sensor
- **PID:** no data, if zero strongly suspect hydrogen. Hydrocarbons and a little of NOx will show here
- **LEL:** no data, but could pick up ethanol (CF = 1.7) or H_2 (CF = 1.1)
- **Tubes:** would have been nice to run a CO tube to rule it out

O_2: <19.5, LEL: ?, CO: >50, H_2S: 0, PID: ?

"TWA Meter" Confused by IDLH Atmosphere

- Well before dawn on a hot summer morning, a HazMat team reports to a dwelling with multiple un-responsive occupants that were taken to hospital
- Meter readings:
  - Oxygen: 20.6% (meaning 15,000 ppm of "something else" is there)
  - CO: more than 750+ ppm
  - H_2S: ~24 ppm
  - ppb PID: 1500-2000
- Recon:
  - In addition to the multiple victims, the house is well sealed with multiple window mounted AC units set to recirculate
  - No obvious source of a lot CO identified, although there is a gas stove and hot water heater in the dwelling

“TWA Meter” Confused by IDLH Atmosphere

- Recon (cont.):
  - It appears that rat poison has been spread in the basement/crawl space and these areas are wet from rain water leakage
- Because of the rat poison, phosphine (PH_3) is suspected because when it gets wet it may produce PH_3
  - PH_3 has a very distinctive “dead fish” odor at extremely low (ppb) levels and while responders were fully masked throughout the response there was no reported odors
  - A PH_3 sensor was used and readings were as high a 8 ppm
- Victim blood gas confirms high CO and many were put in hyperbaric chambers
- What was happening?

"TWA Meter" Confused by IDLH Atmosphere

- CO Exposure Limits:
  - TWA: 50 ppm (OSHA)
  - IDLH: 1200 ppm
- If not an IDLH environment it certainly was over the TWA for CO and near IDLH for CO
- There may be something else there 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 meters and especially electrochemical (EC) sensors are designed for the industrial environment in which staying at or below TWA values (the "speed limit") is the primary concern

"TWA detector" Confused by IDLH Atmosphere

- 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 read so there was at least IDLH levels of CO in the foyer
- There may have been even more CO 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

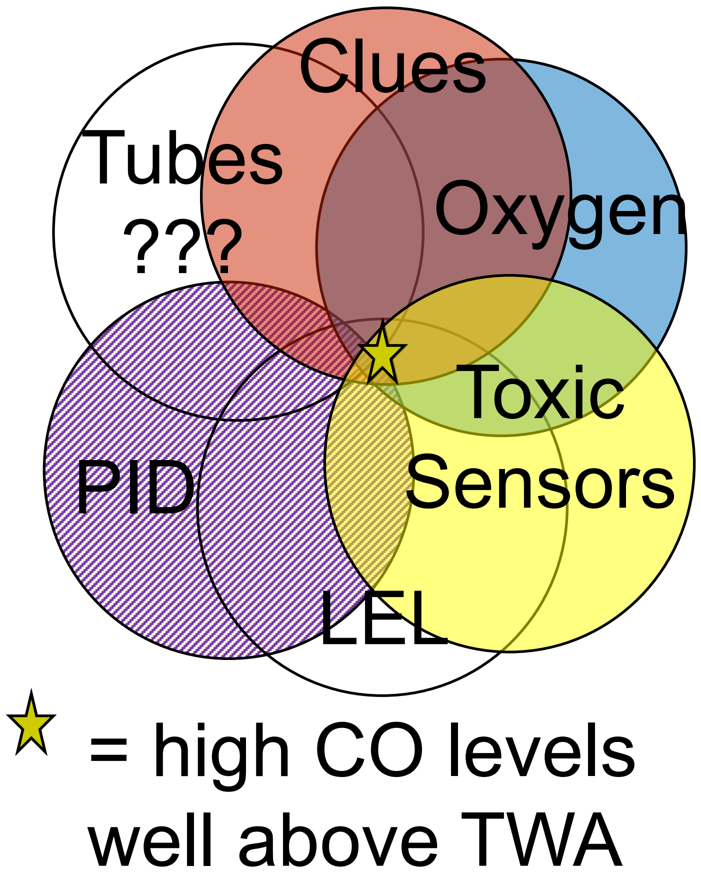
"TWA detector" Confused by IDLH Atmosphere

- When exposed to concentrations near or above IDLH levels these "TWA" detectors can get "stressed" leading to some "crazy" sensor readings
- Checking the cross-sensitivity charts for the H_2S and PH_3 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 H_2S or PH_3 present.
- The next detection technology to think of in this call should have been colorimetric tubes, they can handle higher ranges or CO (when reduced volume is pumped through it) than the EC sensors that are best at TWA levels. And they could have been used to rule out the presence of H_2S and PH_3.

“TWA detector” Confused by IDLH Atmosphere

- When detectors are stressed like they were in this call, calibration should be certainly be performed done 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 TWA environment beyond their design parameters

TWA detector Confused by IDLH Atmosphere



- **Clues:** multiple victims in hyperbaric chambers
- **Oxygen:** 20.6% indicates 15,000 (3 x 5000) of something else is there
- **Toxic Sensors:** more than 750 reading on CO, 24 on H_2S and 8 on PH_3. Checking cross-sensitivity charts we find that the H_2S and PH_3 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

Gases & Vapors are like Ketchup

- Let's think of gases and vapors to ketchup
- If one were to have a hamburger and fries with ketchup, they might leave a puddle of ketchup on their plate
- It is easy to rinse the ketchup off the plate if done quickly, but if one leaves the plate sitting out in air for some period of time, the ketchup will harden and one must soak and scrap to get the ketchup off of the plate
- For our detectors gases and vapors can be like this ketchup. If we rinse it off by scrubbing with clean air after the exposure, the residual chemical is easily "rinsed" off.
- If one lets the chemicals "harden" on the sensors then they may be permanently damaged!

Best practice is to run detectors for at least 30 minutes after high exposures (plugged into the wall overnight won't hurt them)

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:
  - Hydrogen (your 1st and 2nd stop after CO has been ruled out):
    - Charging lead-acid batteries in cars, golf carts or tractors
    - Nuclear power plant containment buildings
    - Self-heating meals (like MREs)
    - Inactive hot water heaters (H_2 generated by hydrolysis)
  - Some manufacturers offer special CO sensors that are not cross-sensitive to hydrogen but they are more expensive, ***consider this sensor for your one of your detectors if your manufacturer offers it***
  - Acetylene: CO sensors ARE acetylene sensors
  - Hydrocarbons: this is less of a problem because some manufacturers supply charcoal filters to fit above the CO sensor to help prevent this
    - Acetone: 1 gallon of acetone spilled on a carpet set off the household CO detectors AND the fire department CO detectors

Clan Lab: Using Cross-Sensitivity

- In the clan lab application it is common to see ammonia (NH_3) and phosphine (PH_3) 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

Clan Lab: Using Cross-Sensitivity

- Sometimes the only way to measure something is to use the cross-sensitivity of an EC sensor
- Even when it is possible to purchase a specific phosphine sensor (PH_3) an H_2S sensor may do in a pinch
- As it is much less expensive to own a H_2S sensor for detecting PH_3 than a dedicated PH_3 sensor, for some it may be a better choice=
  - H_2S sensor: 2 year sensor for $195 + $295 for 4 gas mix calibration gas good for 2 years = $240/year
  - PH_3 sensor: 1 year sensor for $295 + $280 for PH_3 cal. gas good for 4-6 months = $855/year

A clan lab scene encountered by the AMCOS Clan Lab Team.

Clan Lab: Using 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*

The H_2S sensor is 80% cross-sensitive to PH_3 but has poor NH_3 cross-sensitivity

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

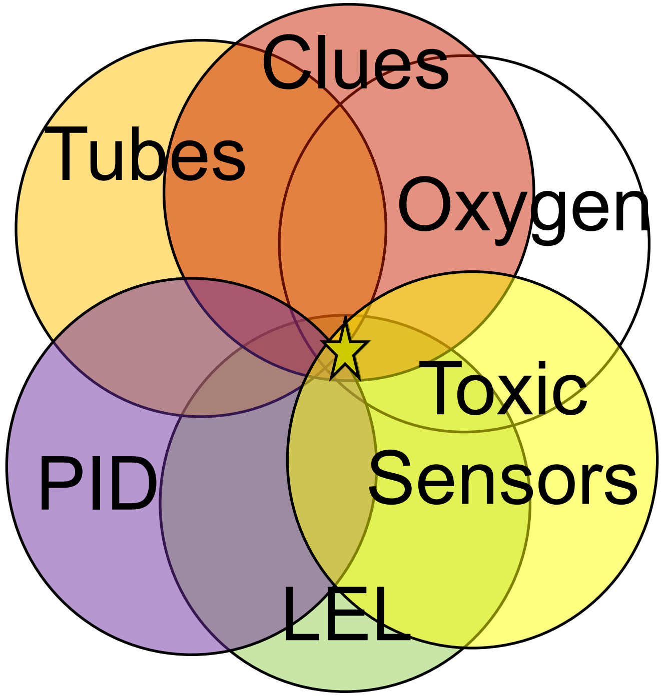
Clan Lab: Using Cross-Sensitivity*

Gas	Concentration	Response#
H_2S	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
NH3	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

The CO sensor has some PH_3 cross-sensitivity but poor NH_3 cross-sensitivity

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

Clan Lab: Using Cross-Sensitivity



☆ = H_2S sensors are a big help

- **Clues:** clan lab
- **Oxygen:** no change in reading
- **Toxic Sensors:** H_2S sensor will read for PH_3 so 10 ppm of PH_3 will read 8 ppm on the H_2S sensor.   CO helps a little because 10 ppm PH_3 will read ~1-2 ppm
- **LEL:** will pick up high levels of PH_3 but it will permanently ruin the sensor
- **PID:** with a CF of 3.9 the PID isn't sensitive enough for PH_3 which has a low TWA of 0.3 ppm, and long term PH_3 exposure will develop a coating on the lamp
- **Tubes:** PH_3 and NH_3 tubes are just two that could be used

O_2: 20.9, LEL: 0, CO: 1, H_2S: 8, PID: 0

Other places to find Phosphine

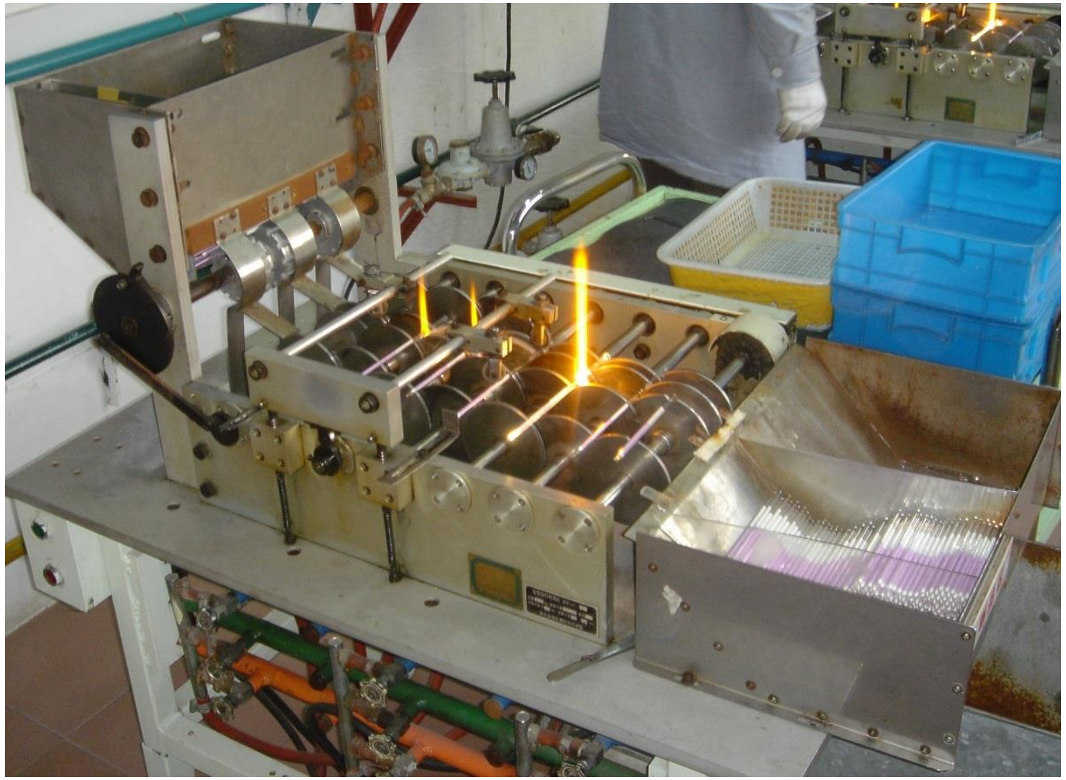
- Grain fumigation in both rail cars and silos
- Shipping container fumigations
- When some “rat” poisons get wet they may off gas phosphine
- When some rat poisons are ingested for chemical suicide the vomit can off-gas phosphine and in the case of death the body bag may be found to contain phosphine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

Colorimetric Gas Detection Tubes

- In an era of “cool gizmos” sometimes people forget that the “basic” colorimetric tube is a great tool to get another angle on the problem
- Colorimetric gas detection tubes (also known as “Draeger” tubes) produce a color change in proportion to the amount of the gas/vapor of interest present
- First developed in the US in the early 1900’s they have developed to measure a wide range of gases and vapors
  - One manufacturer claims to measure approximately 500 different substances
- The concept is similar to other colorimetric methods like pH paper for measuring acids and bases

Colorimetric Gas Detection Tubes

- The tube is filled with a substrate (typically silica) coated with reagent that will produce a color change when exposed to the chemical of interest
- The tube ends are flame sealed so that they are stable for storage over a period of time (usually 2 years)



Automatic Tube Flame-sealing machine

Colorimetric Gas Detection Tubes

- Prior to use the user breaks the ends off of the tubes to allow gas to flow through it
- Then the user draws a predetermined sample through the tube and reads the scale like reading an old glass thermometer
- Tube is calibrated at the factory and this calibration is printed on the side of the tube as a scale

EC Sensors vs. Colorimetric Tubes

- Electrochemical (EC) sensors range in price from $125-$500+
- Calibration gases range in price from $50-$300+
- Calibration gases have shelf-lives of 6-24 months
- Use EC sensors if the threat is always present and real
  - Water treatment plant using chlorine
  - Metal plating plant using HCN

EC Sensors vs. Colorimetric Tubes

- **Tubes are your “friends” when concentrations are IDLH and above**
  - Electrochemical (EC) sensors are designed for the average industrial environment where the goal is to stay below TWAs and high concentrations (above IDLH) are not normally to be expected
  - Tubes are your “friends” for high concentrations of gases and vapors because they are “ruined” every time you use them and they can provide high range reading by decreasing the volume of the gas sample
  - If oxygen levels have dropped at all and you are confused it’s time to start thinking about tubes because you probably have A LOT of something else in the air

EC Sensors vs. Colorimetric Tubes

- Use tubes if you think you might someday have a threat
  - Price is much more affordable
  - Use expired tubes for training
- Use tubes to compare and contrast with EC sensors and PIDs
  - ***Tubes are your next step ANYTIME you think you are running into cross-sensitivities***

Agenda

- Oxygen
- Combustible Gases & Vapors
- Toxic Gases & Vapors
- PIDs
- Putting it all together

Why are Survey Sensors Important?

- After oxygen, flammability and your basic electrochemical toxic sensors, survey sensors are one of your best tools to quickly identify if something is out there
- On their own, survey sensors will not tell you what that “something” is, but they can often quickly tell you where it is coming from and give you a quick idea of how much is there
- Coupled with clues (like placards, waybills, etc.) that provide identification of a chemical some survey sensors (PIDs & FIDs) can quickly tell you how much is there (quantification)

Why are Survey Sensors Important?

- If you can’t see “it” you can’t find “it”
- If you can’t find “it” you can never clean “it” up
- If you can’t see “it” you can’t fix the problem
- Survey sensors are our best “Sniffers”

What is a PID?

- **PID** = Photo-Ionization Detector
- Detects VOCs (volatile organic compounds) and Toxic gases from <10 ppb to as high as 10,000 ppm
- Fuel products are easily measured with a PID
- A PID is a very sensitive broad spectrum monitor, like a “low-level LEL”

What does a PID Measure?

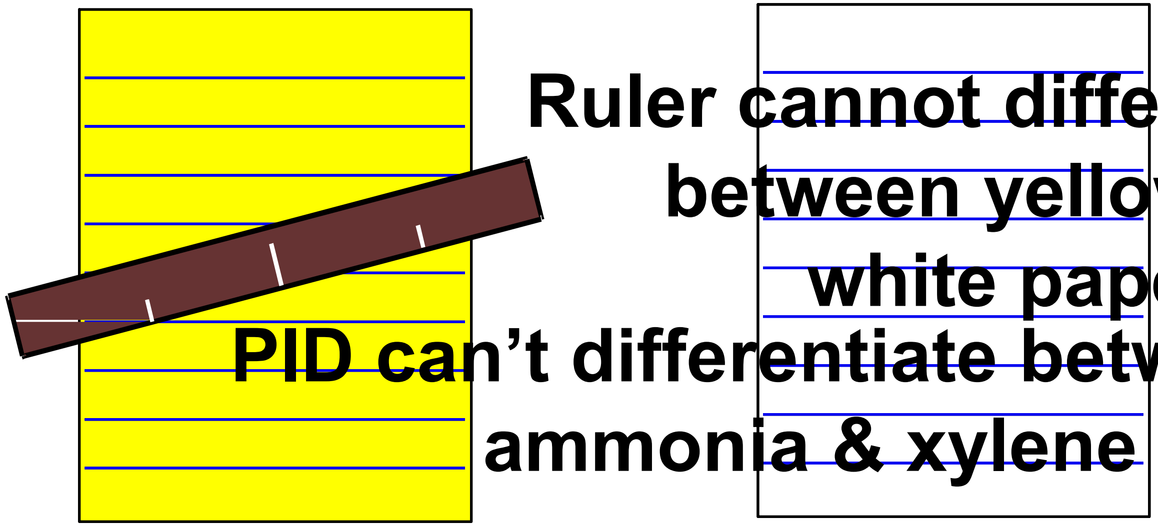
- Organics: Compounds Containing Carbon (C)
  - **Aromatics** - compounds containing a benzene ring
    - BETX: benzene, ethyl benzene, toluene, xylene
  - **Ketones & Aldehydes** - compounds with a C=O bond
    - acetone, MEK, acetaldehyde
  - **Amines & Amides** - Carbon compounds containing Nitrogen
    - diethyl amine
  - **Chlorinated hydrocarbons -** trichloroethylene (TCE)
  - **Sulfur compounds –** mercaptans, carbon disulfide
  - **Unsaturated hydrocarbons** - C=C & C C compounds
    - butadiene, isobutylene
  - **Alcohol’s**
    - Ethanol, IPA
  - **Saturated hydrocarbons**
    - butane, octane
- Inorganics: Compounds without Carbon
    - Hydride Gases
      - Ammonia. Phosphine, Arsine

What PIDs Do Not Measure

- Radiation
- Air
  - N_2
  - O_2
  - CO_2
  - H_2O
- Toxics
  - CO
  - HCN
  - SO_2
  - Cl_2
- Non-volatiles:
  - PCBs
  - Greases
- **Pure** Short Chain Saturated Hydrocarbons
  - Pure Methane (CH_4)
  - Pure Ethane (C_2H_6)
  - Pure Propane (C_3H_8)
- Acids Gases
  - HCl
  - HF
  - HNO_3
- Others
  - "Freons"
  - Ozone O_3
  - Hydrogen Peroxide

Selectivity Vs Sensitivity

- PID is very sensitive and accurate
- PID is not very selective



Ruler cannot differentiate between yellow and white paper

PID can't differentiate between ammonia & xylene

Selectivity Vs Sensitivity

Use your head for Selectivity and the PID for Sensitivity

- PID is sensitive to chemicals not specific
- Correction Factors set correct PID scale
- PID should stay on Isobutylene (Calibration gas) until unknown is identified

A PID is a Gas Chromatograph where the column is between your ears!

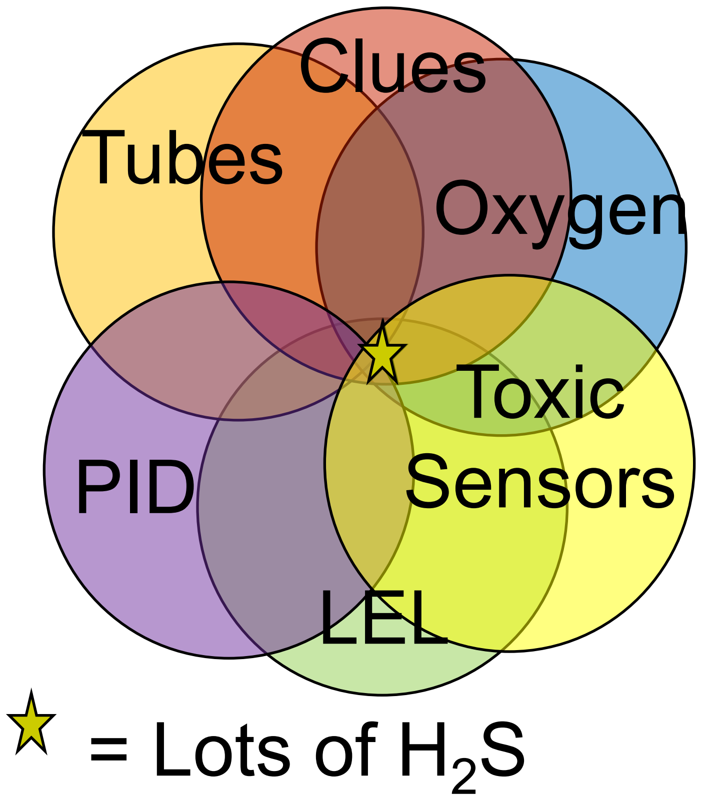
Agenda

- Oxygen
- Combustible Gases & Vapors
- Toxic Gases & Vapors
- PIDs
- Putting it all together

H_2S Car Suicide

- Dead body found in car with note on the window advising of high levels of H_2S
- Concentrations of H_2S can go into the percent by volume levels (1-10%=10,000-100,000 ppm)

H_2S Car Suicide



- **Clues:** Body in car with note on the window
- **Oxygen:** ~15.9-20.7%
- **Toxic Sensors:** H_2S EC sensor going to over-range at 100-500 ppm
- **LEL:** could get some reading at high levels (~4 CF) but can kill sensor
- **PID:** up to 15,000 ppm (~3.3 CF)
- **Tubes:** good bet for high readings of H_2S

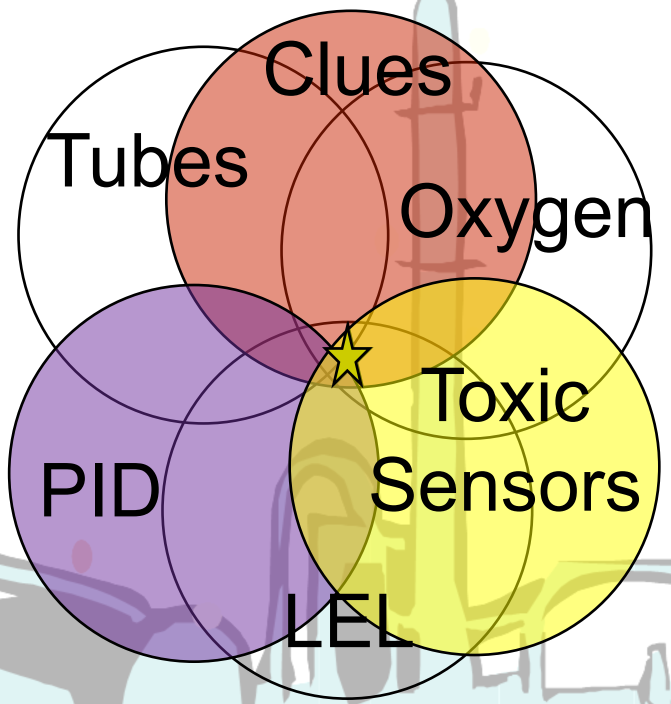
Oil Refinery Remediation H_2S

- Datalogging meter showed H_2S of straight 199 ppm indicating they had maxed out the H_2S circuit on the meter (meter & sensor only rated to 100 ppm H_2S)
- This data is questionable but we certainly have more than 100 ppm and may have more than 200 ppm H_2S
- PID data from the same meter showed 240 ppm in Isobutylene units
- No LEL reading and H_2S is a LEL inhibitor

Oil Refinery Remediation H_2S

- Using PID correction factor for H_2S of 3.3, the concentration if it were just H_2S is 792
  - (240 x 3.3 = 792)
- PID measures total VOCs including H_2S so part of the signal could be VOCs
- We can be pretty sure that we had a lot of H_2S and it could be 100-790 ppm (IDLH =100 ppm)
- Further testing via sampling and lab testing was recommended
- H_2S colorimetric tubes could also be used

Oil Refinery Remediation H_2S



★ = a lot of H_2S is present

- **Clues:** Refinery clean-up with strong H_2S smell
- **Oxygen:** no change in reading
- **Toxic Sensors:** 199 ppm reading on H_2S sensor
- **LEL:** no reading (LEL = 4% or 40,000 ppm) possible clue that there are low or no VOCs
- **PID:** 240 ppm in iso units or 792 in H_2S units (CF = 3.3)
- **Tubes:** not used but would have been helpful

Leaking Refrigeration System

- An old apartment building was being renovated
- 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
- Typically Freon wouldn't sicken people

Leaking Refrigeration System

- The initial gas detectors showed high levels of H_2S at upper levels of the building where the refrigerator was found
- No sewer openings were around to produce the gas
- Upon searching the building HazMat found an SO_2 tank in the basement of the building
- This tank was plumbed to a building wide refrigeration system

Leaking Refrigeration System

- SO_2 is an early refrigerant that is also found in old "monitor style" refrigerators
- H_2S sensors are cross-sensitive to SO_2 at a 5-1 ratio
- The correction factor to change the scale from H_2S to SO_2 is 5, multiply the H_2S sensor value by 5 to get the value in units of SO_2
- 10 ppm on an H_2S sensor means 50 SO_2, the TWA of SO_2 is 2 ppm and IDLH is 100 ppm
- PIDs cannot "see" SO_2 so cannot be used to sniff for the source

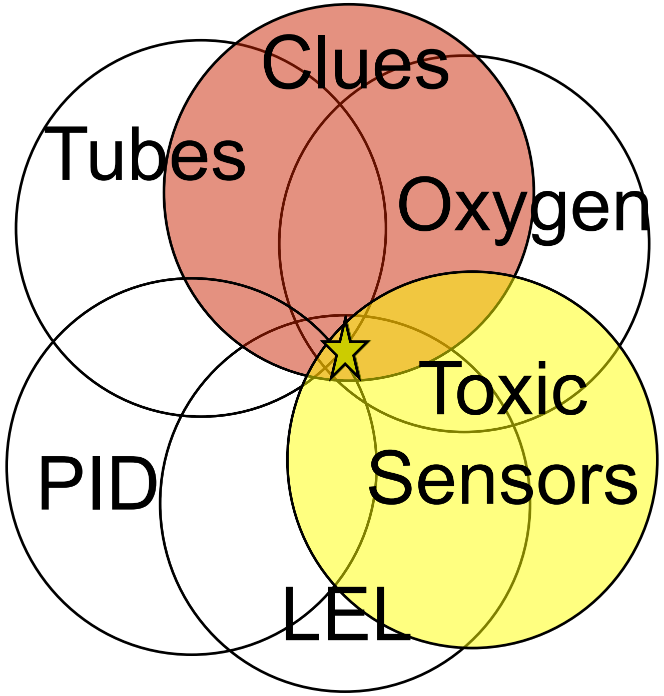
Leaking Refrigeration System*

Gas	Concentration	Response	Equation	CF
CO	300 ppm	≤1.5 ppm	300/1.5	200
SO_2	5 ppm	about 1 ppm	5/1	5
NO	35 ppm	<0.7 ppm	35/0.7	50
NO_2	5 ppm	about -1 ppm	5/-1	-5
H_2	100 ppm	0 ppm	101/1	101
HCN	10 ppm	0 ppm	11/1	11
NH_3	50 ppm	0 ppm	51/1	51
PH_3	5 ppm	about 4 ppm	5/4	1.25
CS_2	100 ppm	0 ppm	101/1	101
Methyl sulfide	100 ppm	9 ppm	100/9	11
Ethyl sulfide	100 ppm	10 ppm*	100/10	10
Methyl mercaptan	5 ppm	about 2 ppm	5/2	2.5
Ethylene	100 ppm	≤ 0.2 ppm	100/0.2	500
Isobutylene	100 ppm	0 ppm	101/1	101
Toluene	10000 ppm	0 ppm*	10000/1	10000
Turpentine	3000 ppm	about 70 ppm*	3000/70	42

The H_2S signal probably is SO_2.

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

Leaking Refrigeration System



☆ $=H_2S$ signal was SO_2 from the cut line

- **Clues:** Renovation causes a leak, HazMat finds an SO_2 cylinder
- **Oxygen:** no change in reading
- **Toxic Sensors:** H_2S sensors are cross-sensitive to SO_2 at a 5-1 ratio,10 ppm on an H_2S sensor means 50 SO_2, the TWA of SO_2 is 2 ppm and IDLH is 100 ppm
- **LEL:** no reading
- **PID:** can't read SO_2
- **Tubes:** none used, but an SO_2 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 SO_2 produced 1 ppm of response on the H_2S sensor
- So the H2S sensor is 20% cross-sensitive to SO_2
  - $1_{H2S}/5_{SO2}$ = 0.20 or 20%
- To get the reading in units of SO_2 divide by the H_2S reading by 0.20
- So 10/0.20 = 50 ppm
- 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!
  - You could always confirm with tubes

Gas Delivery Truck

- Driver hears cylinders/bottles fall as he his 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 or Hydrogen

Gas Delivery Truck

- Driver hears cylinders/bottles fall as he his 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 or Hydrogen
- CO sensor will detect both EtO (~40% response), H_2 (~40% response), and even Cl_2 (~10% response)

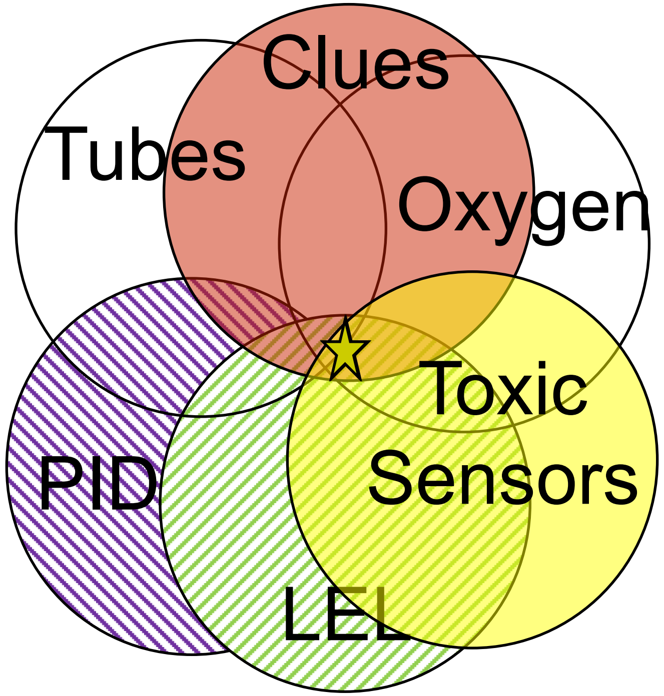
Gas Delivery Truck*

Gas	Concentration	Response#
H_2S	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	[illegible] 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

CO Chart: The CO sensor can help out on H_2, EtO and even a little on Cl_2

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

Gas Delivery Truck



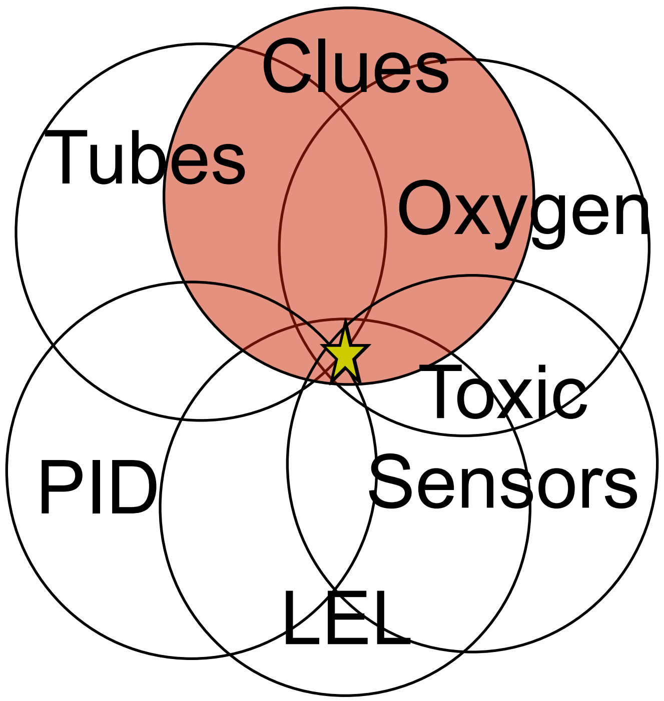
☆ =5 gas detector should be able to find the leak

- **Clues:** Driver tells HazMat he thinks something's leaking
- **Oxygen:** no change in reading
- **Toxic Sensors:** Cl_2 sensor will work on Cl_2, but CO sensor will detect both EtO (~40%), H_2 (~40%), and even Cl_2 (~10%), H_2S doesn't help
- **LEL:** won't see Cl_2 but may see EtO and H_2 in high concentrations
- **PID:** with 10.6ev lamp may see EtO at high levels but won't pick up Cl_2 or H_2
- **Tubes:** Specific tubes would work

Wal-Mart Delivery Truck

- Workers unloading a trailer got sick from fumes in the trailers
- Local HazMat was called and they moved the closed trailer away from the loading dock

Wal-Mart Delivery Truck



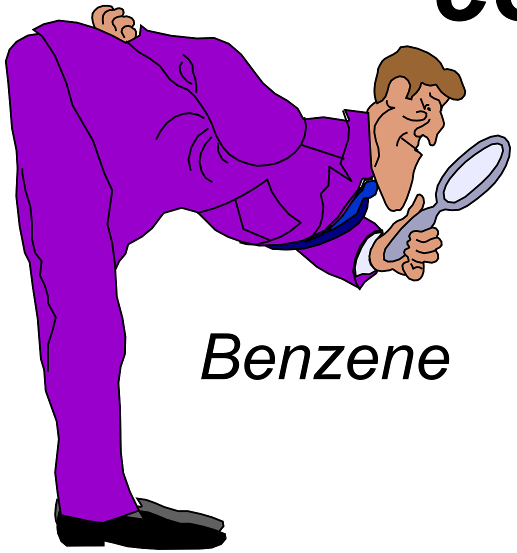
=Used ChemPro on trend line can see high IP chemicals

- Clues: Workers get sick from unloading a trailer
- Oxygen: no change in reading
- Toxic Sensors: neither CO nor H_2S sensors on four gas got a reading
- LEL: no change in reading
- PID with 10.6ev lamp didn't get any reading
- Tubes: none used
- ***Sometimes you have to think out of the box and add another circle!***

Solving Cross-Sensitivity Issues

1. **Detective work:** what's 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 possible 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.

Gas Detectors need Gas Detectives to come to the right conclusion



Ammonia

Carbon Disulfide

Styrene

Carbon Monoxide

Benzene

PERC

Xylene

Questions?

chriswrenn@att.net

"Still confused but at a higher level"

If you are ever challenged with a gas detection problem, call, text or email me and we'll work through it

610-659-4507

Check out www.DetectionGeek.com for downloads of slides and whitepapers