Ethanol Impacts on Handheld Gas & Vapor Detectors

Chris Wrenn

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Course Agenda

- Why do we need Detection Technologies?
- Ethanol is “Toxic” to Electrochemical Sensors
- Measuring Oxygen
- Ethanol’s impact on LEL sensors
- Ethanol’s impact on PIDs
- Wrap-up

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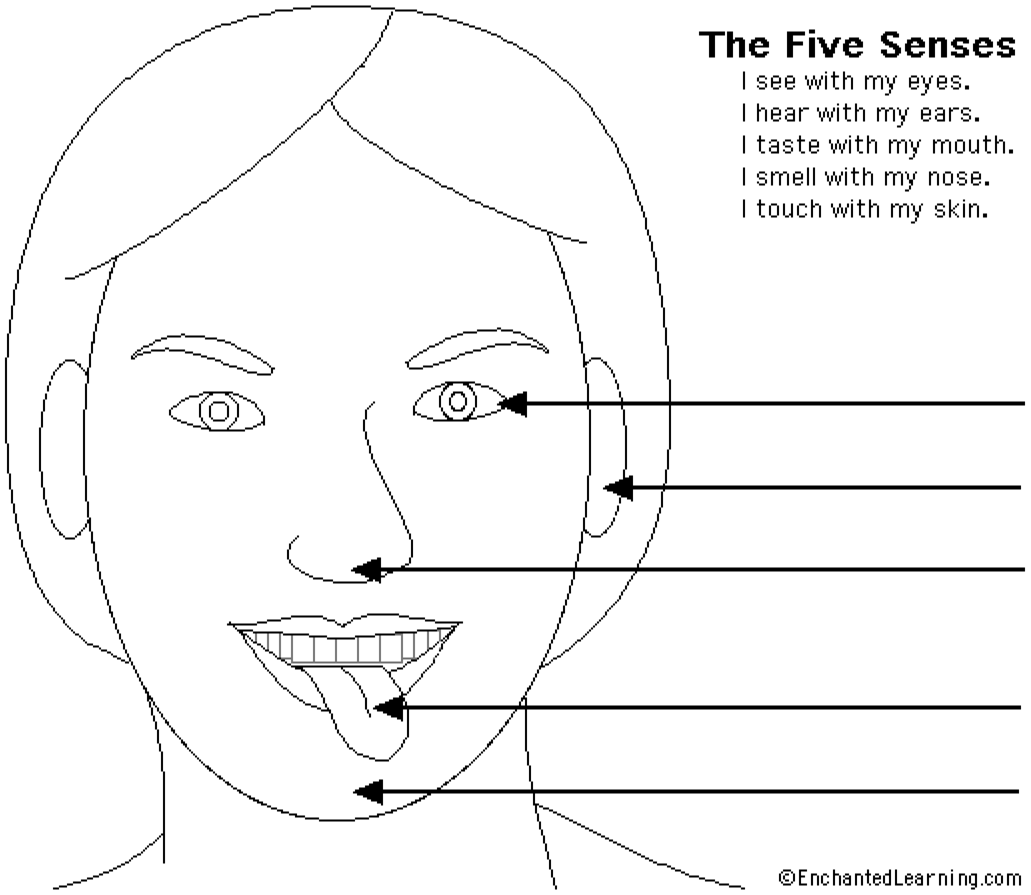
Why is Detection Important?

- Our 5 senses miss many dangerous environments
  - Too little or too much oxygen
  - Flammable levels of methane in air
  - Carbon monoxide



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Why is Detection Important?

Humans cannot rely on their senses for decision-making

- Without effectively knowing how to use detection techniques we are unable to:
  - Identify threats
  - Make Personal Protective Equipment (PPE) decisions that are appropriate to the actual hazard
- Detection technologies supplement our senses when making decisions in potentially hazardous environments: ***they become our eyes and ears!***
- ***We need to learn how to fully use and trust these detectors***

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What constitutes a modern CSE detector?

- According to 29 CFR (Code of Federal Regulations) 1910.146 a confined space detector must be able to detect the threats expected in the confined space
  - This is the OSHA Confined Space Entry (CSE) “standard”
  - “Before an employee enters the space, the internal atmosphere shall be tested, with a calibrated direct-reading instrument, for oxygen content, for flammable gases and vapors, and for potential toxic air contaminants, in that order.”
  - So if toxic air contaminants can be excluded, only oxygen and LEL need to be detected
- Typically in North America this is interpreted as a “4-gas” detector including O_2, LEL, CO & H_2S
- Recognizing the need to “expect the unexpected” there is a rise in adoption of “broadband” capability in the US by utilizing PIDs

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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 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”

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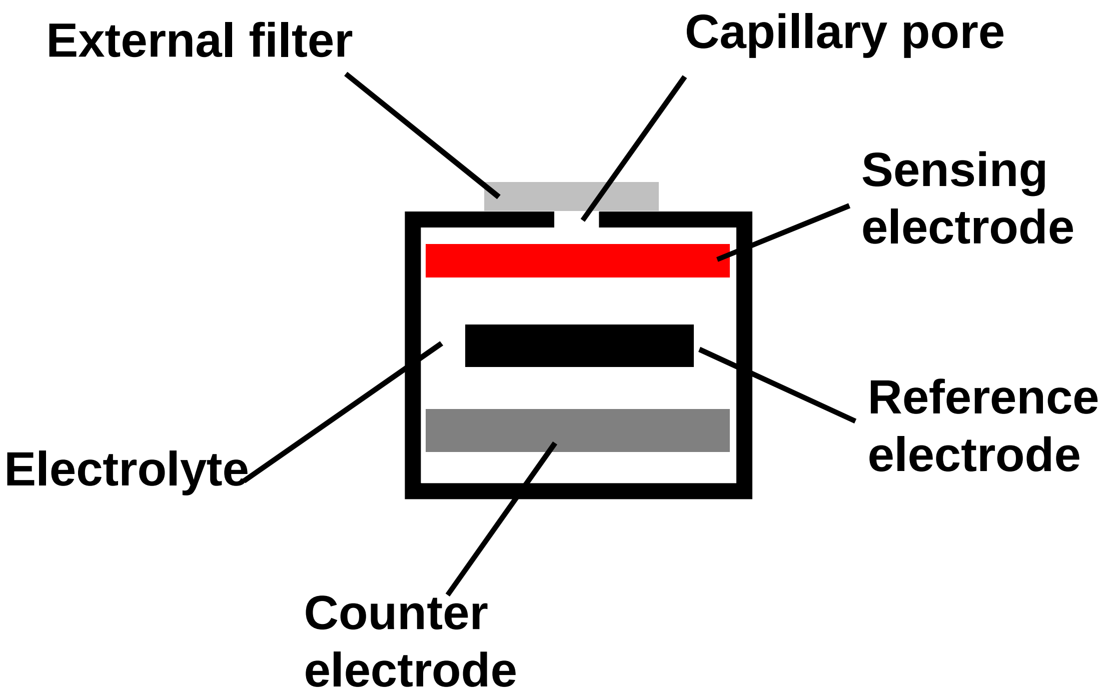
EC Toxic Gas Sensor Cross-Section



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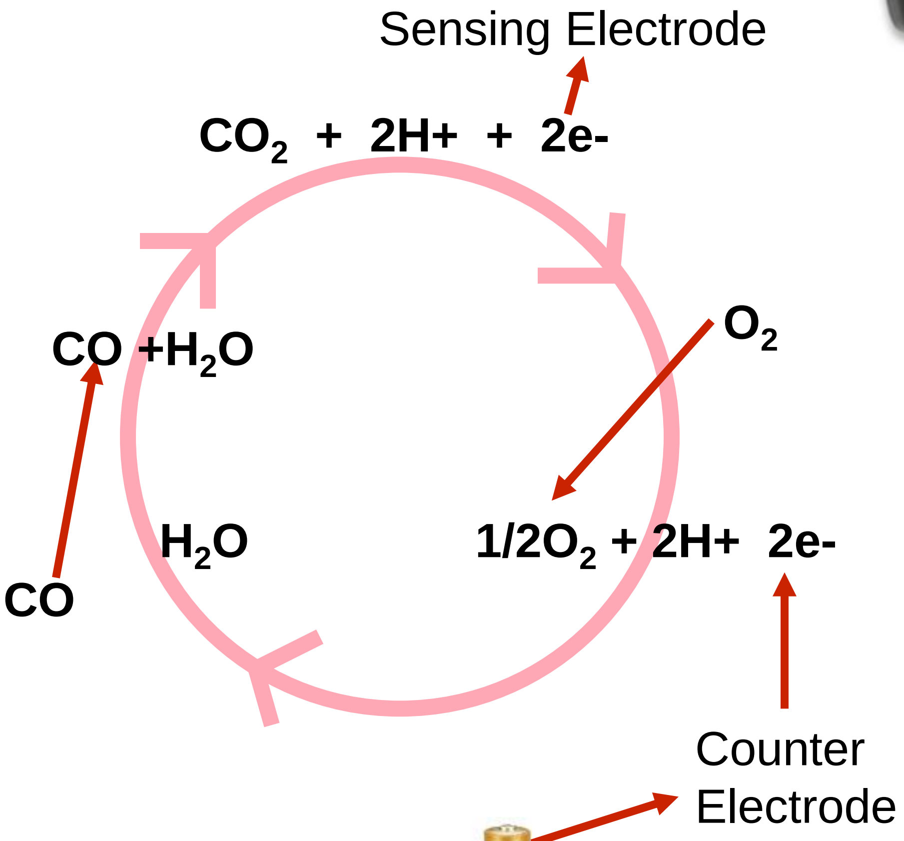
Most EC Sensors are a Regenerative or Circular Process

- Unlike “fuel cell” oxygen sensors which have a one-way trip from lead to lead oxide, most 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



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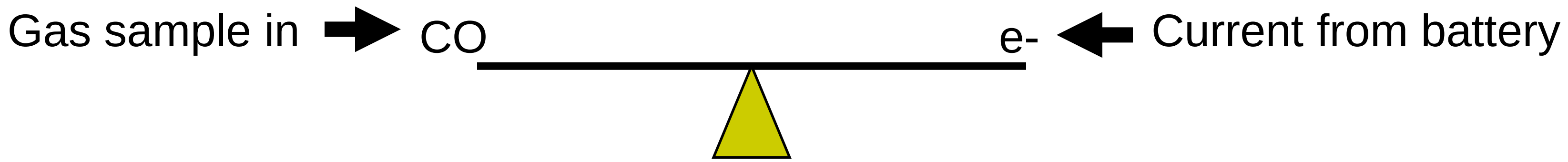
Stay within the operating parameters and you stay in balance

- 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

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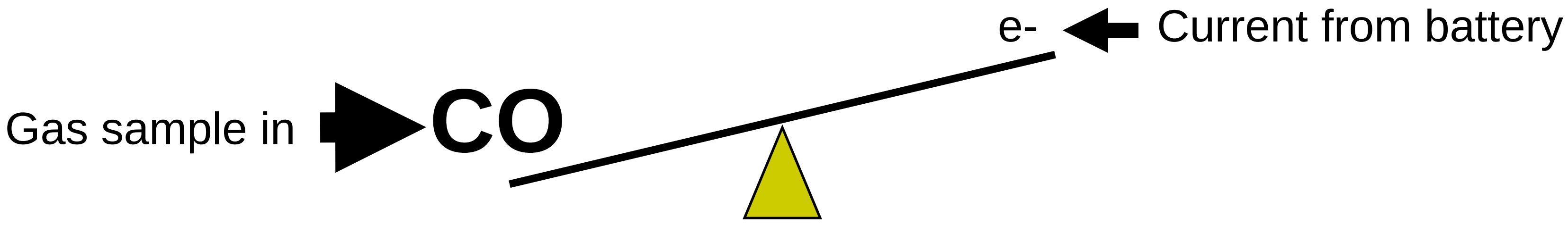
Exceed the operating parameters & you destroy the balance (& the cell)

- 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

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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)

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EC Sensor Cross-Sensitivity

- EC sensors are primarily designed for the industrial TWA detection market. When exposed to large concentrations of other gases/vapors (above IDLH levels or when oxygen measurements are below 20.9%) then 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**
- **Ethanol drives CO and H_2S sensors negative**

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CO sensor cross-sensitivity*

This is another way of saying that alcohols are potentially "Toxic" to CO (and H_2S) sensors

Alcohols make EC sensors read negative

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

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

Used sensors show increasing response to VOCs

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Methanol Tank Truck Rollover

- Customer calls because CO & H_2S sensors are "acting funny"
- Multigas detector 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

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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 detector 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

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Custom Kits Cause Strange CO & H_2S Sensor Readings

- Custom kits containing a Multigas meter with PID, calibration gas, spares and lamp cleaning kit (anhydrous methanol) were shipped out to many federal response entities in sealed “Pelican” cases
- Upon receiving them the responders reported “weird” CO & H_2S sensor response, which was eventually diagnosed as negative readings
- At first we thought that this was due to the foam used in the cases

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Custom Kits Cause Strange CO & H_2S Sensor Readings

- We replaced the foam and still periodically had the same problem
- We studied the problem for nearly a year
- Traveling from one HazMat conference to another the director of sales was carrying a kit with 6 Multigas detectors with PIDs in them and brought along a vial of methanol for PID lamp cleaning

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Custom Kits Cause Strange CO & H_2S Sensor Readings

- Upon getting to the next hotel he opened the case to a strong alcohol smell and found that all of the Multigas meters CO and H_2S sensors were negative when powered up
- It was found that when the cases were in an airplane the lower pressure in the hold lowered the pressure in the case
- The low case pressure relative to the "normal" pressure in the methanol vial caused the methanol to leak into the sealed foam case

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Custom Kits Cause Strange CO & H_2S Sensor Readings

- As the case was sealed there was no chance to allow the methanol to outgas which saturated the sensors with alcohol
- Running the meters overnight removed the methanol and allowed the sensors to return to normal
- In general the EC sensors won't die after being exposed to high concentrations of alcohol
- EC sensors mainly use platinum for electrodes and sulfuric acid for electrolytes
- Both platinum and sulfuric acid are sensitive to alcohol

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Gases & Vapors are like Ketchup

- Let's think of gases and vapors like 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)

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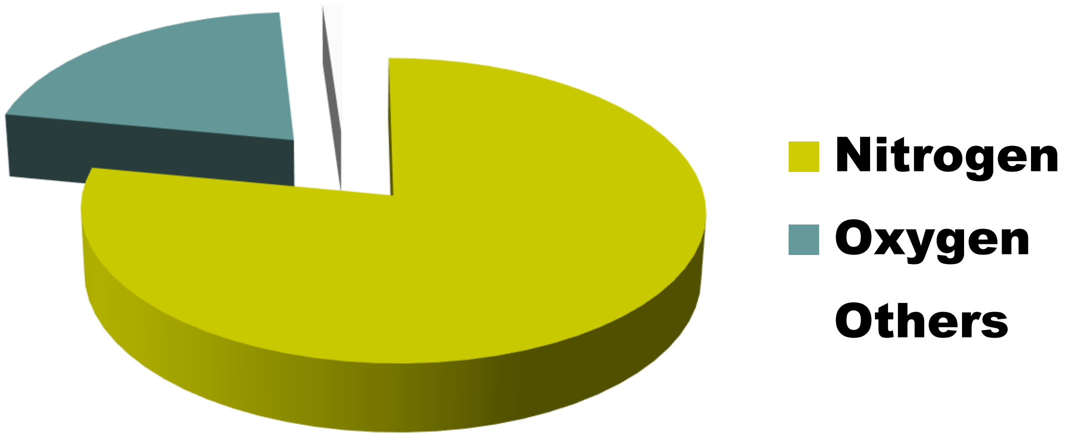
Composition of “fresh air”

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



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Oxygen Deficiency

According to 1910.146, air is oxygen deficient whenever concentration is less than 19.5%

- This provides protection at sea level and inhabited higher elevations

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Oxygen Deficiency

- Lack of oxygen is more acutely fatal than even the most toxic gases and vapors, like CWAs
- There is no antidote for lack of oxygen!
- Causes:
  - **Displacement:** another gas/vapor replaces air reducing oxygen content
  - **Metabolic activity:** oxygen is consumed by living organisms
  - **Oxidation:** the combination of a chemical substance with oxygen to form another chemical
  - **Combustion:** oxygen consumed by fire
  - **Absorption/Adsorption:** oxygen dissolves into a substance or bonds to the surface of a substance

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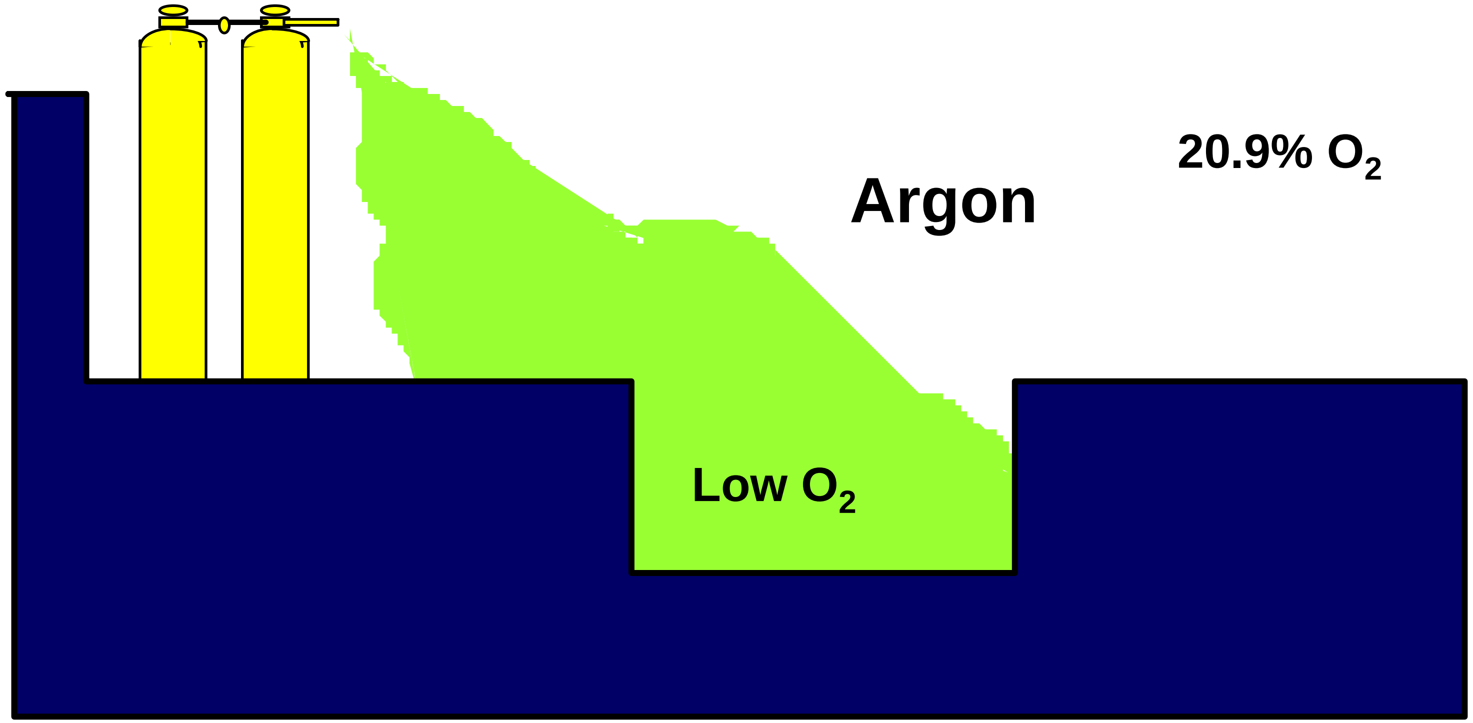
Oxygen Deficiency

Air (MW = 29) displaced by Argon (MW = 40) in an open topped confined space



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Oxygen Drops from 20.9-20.8%

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

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

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

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

- 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***

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Oxygen consumption

- Now that we'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.

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Flammability is the 2nd most important atmospheric parameter

- After oxygen, the detection of combustible gases and vapors is the next most important atmospheric parameter to measure
- According to the OSHA (US Occupational Safety and Health Administration) rule contained in 29CFR1910.146 or “the Confined Space Standard:”
  - “Before an employee enters the space, the internal atmosphere shall be tested, with a calibrated direct-reading instrument, for oxygen content, for flammable gases and vapors, and for potential toxic air contaminants, in that order.”

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Human's can't measure flammability

- While in some cases humans can smell and even taste some flammable gases and vapors, we are not calibrated to know when we have reached a concentration that is potential flammable
- When we smell gasoline we can't tell if there is a flammable concentration or not
- Because we can't measure flammability we need to use and understand detection technologies that will provide us with the information we need to make decisions

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Flammability Range: LEL/UEL

- The flammable range of a chemical is the concentration of gas that lies between its lower explosive limit (LEL) and upper explosive limit (UEL)
- Below the LEL the gas or vapor is too “lean” to burn or it is full starved
- Above the UEL the gas or vapor is too “rich” to burn or it is oxygen deprived
- Concentrations within the flammable range will burn or explode if a source of ignition is present

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Common Flammability Ranges

- Note that LELs and UELs can vary between reference sources
- CO and EtO have very wide flammability ranges because they carry their own oxygen
- detector accuracy can drastically affect your LEL readings
- Therefore, always be VERY CONSERVATIVE when making LEL decisions

Gas/Vapor	LEL* (% vol)	UEL* (% vol)
Acetone	2.2	12.8
Benzene	1.2	7.8
Carbon Monoxide	12.5	74
Diesel	0.8	10
Ethanol	3.3	19
Gasoline	1.4	7.6
Hydrogen	4.0	75
Methane	5.0	15
MEK	1.8	11.4
n-Pentane	1.5	7.8
Propane	2.0	9.5
Toluene	1.2	7.1

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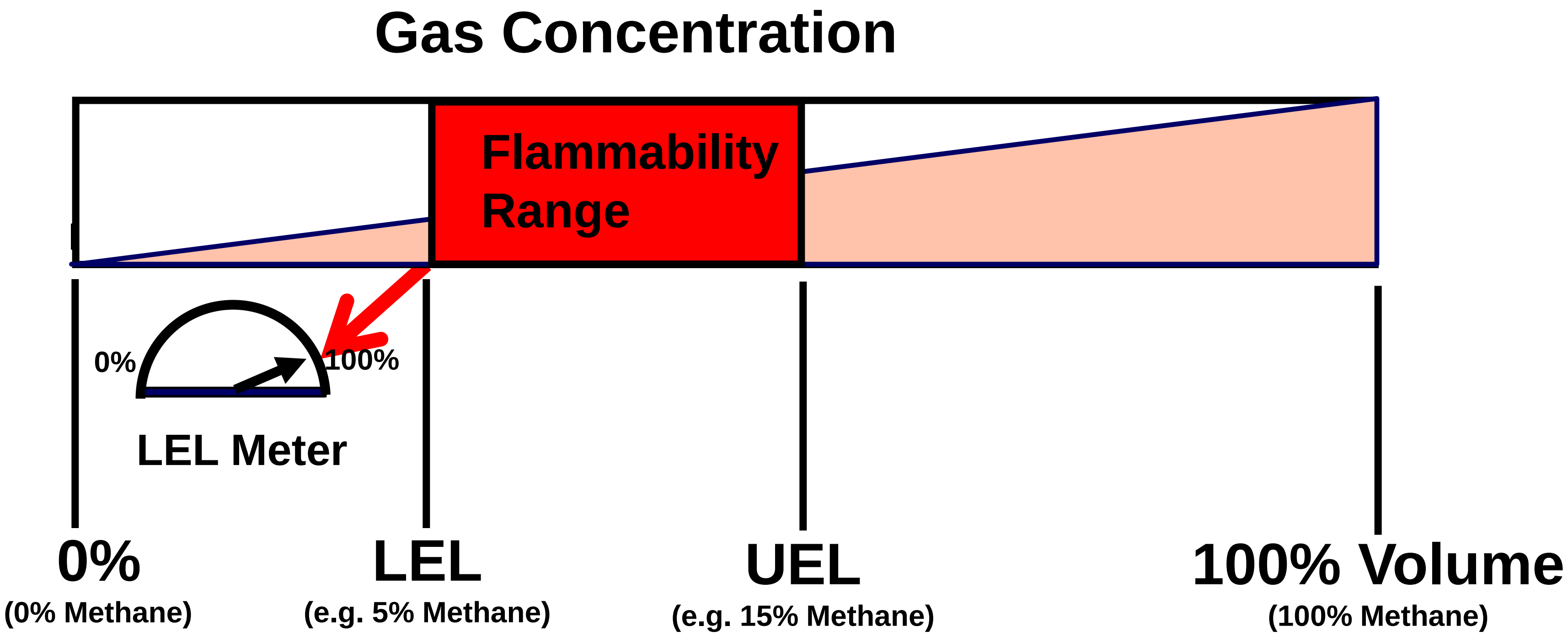
* NFPA 325 “Guide to Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids, 1994 edition

Measuring Flammability

Combustible Gas/Vapor detectors typically read in “% LEL” not “%Volume”



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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

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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***

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Oxidation Requires Oxygen

- The Wheatstone bridge catalytic bead sensor oxidizes or “burns” flammable gases and vapors so oxygen is a requirement for this sensor to operate
- OSHA requires that oxygen is measured 1st because the regulation was written in a time when one might have an oxygen detector and a LEL detector rather than a multigas product
- If one measures more than 19.5% oxygen then the LEL sensor is definitely measuring below LEL not above UEL

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Wheatstone bridge catalytic bead LEL Sensor Shortcomings

Two mechanisms affect the performance of Wheatstone bridge LEL sensors and reduce their effectiveness when applied to all but methane:

- Gases burn with different heat outputs at their LEL
- "Heavier" (low vapor pressure) hydrocarbon vapors have difficulty diffusing into the LEL sensor and reduce its output

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LEL Sensor Response can vary with the Gas/Vapor at its LEL

Methane

Propane Hydrogen

Gasoline

Acetone Benzene N-Pentane

MEK Toluene

Diesel

Some flammable gases/vapors are "louder" than others at their LEL on the cat bead sensor

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LEL Sensor Response can vary with the Gas/Vapor at its LEL

- Gases/vapors may be louder or quieter than the calibration gas
- Loud means that they get more response on the LEL sensor and they will go into alarm early (safe state)
- Quiet means that they get less response on the LEL sensor and they will go into alarm late (unsafe state)

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Catalytic LEL Sensor Response

LEL Sensors were designed to measure Methane

Louder

Quieter

Gas/Vapor	LEL (% vol)	Sensitivity (%)*	Ignition Temp. F°(C°)**
Methane	**5**	**100**	**999 (537)**
Hydrogen	4	91	932 (500)
Propane	2	63	842 (450)
Ethanol	3.3	59	793 (423)
Gasoline	1.4	48	536 (280)
Acetone	2.2	45	869 (465)
Benzene	1.2	45	928 (498)
n-Pentane	1.5	45	500 (260)
MEK	1.8	38	759 (404)
Toluene	1.2	38	896 (480)
Diesel	0.8	30	NA

LEL sensor sensitivity varies with the gas/vapor

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* Relative sensitivities are for example only, please consult your detector manufacturer for sensitivities specific to your product

** NFPA 325 "Guide to Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids, 1994 edition

Pentane calibrated units don't respond to Methane

- A detector manufacturer calibration recommendation is a 4 gas mixture composed of **pentane (25%LEL)**, O_2 (19%), CO (100 ppm) and H_2S (25 ppm)
- A fire department used bump gas canisters with **methane (25% LEL)**, O_2 (15%), H_2S (75 ppm) and CO (200 ppm).
- "A detector successfully passed calibration with pentane…but when the same unit was bumped, it barely registered 3% LEL whereas it should have been going into alarm with much higher readings"
- This is because methane gas should provide about twice the response on a pentane calibrated LEL sensor, so 25% of LEL methane should give a response of approximately 50% of LEL on a pentane calibrated detector
- "…once the LEL sensor was changed, it not only easily passed calibration with a very high span reserve (176%), but also passed the bump test, i.e. detector went into alarm when exposed to the (methane) bump gas."
- "The apparent conclusion is that if the detectors are not exposed to methane on a regular basis, while consistently being calibrated with pentane, the LEL sensor becomes almost "blind" to methane. The detectors would pass calibration, but would essentially fail bumping."

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Wheatstone bridge catalytic bead LEL sensors

Advantages

- ✚ Proven technology
- ✚ Direct measurement of flammability

Disadvantages

- − Can be poisoned
- − Cannot measure above 100% of LEL
- − Needs at least 12-16% oxygen for measurements
- − Difficulty measuring low vapor pressure combustibles like diesel, jet fuel and kerosene
- − Not sensitive enough for toxicity measurements (wakes up ~300-500 ppm)

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Oxygen Sensors for LEL Decisions

- LEL of Ethanol is 3.3% by volume or 33,000 ppm
- Every 5000 ppm of something else will drop oxygen by 0.1% so 50,000 ppm will drop oxygen by 1%
- At 100% of LEL Ethanol (or 3.3% by volume) the oxygen level will only drop by 1% from 20.9% to 20.2% and the oxygen sensor will NOT be in alarm
- 10% of LEL Ethanol is just 3300 ppm, this will not cause a perceivable drop in oxygen concentration
- At UEL of Ethanol (or 19% by volume) the oxygen level will be 17.1%
- So oxygen measurements are a crude LEL sensor but sometimes they are all we have
- ***Remember that once oxygen levels drop below 12-16% catalytic bead LEL sensors may be unreliable***

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Oxygen Sensors as a LEL sensor

- ***The oxygen sensor will not be in alarm at LEL levels of common gases and vapors and is NOT an effective alarm for LEL levels of gases & vapors***
- Even at UEL levels the oxygen sensor is just going into alarm for the vapors highlighted in orange
- If the detector is in low oxygen alarm it's more likely to be in a UEL state than a LEL state

Gas/Vapor	LEL (% vol)	UEL (% vol)	Oxygen Reading at LEL	Oxygen Reading at UEL
Methane	5	15	19.9	17.9
Hydrogen	4	75	20.1	5.9
Propane	2	9.5	20.5	19
Gasoline	1.4	7.6	20.62	19.38
Ethanol	3.3	19	20.24	17.1
Acetone	2.2	12.8	20.46	18.34
Benzene	1.2	7.8	20.66	19.34
n-Pentane	1.5	7.8	20.6	19.34
MEK	1.8	11.4	20.54	18.62
Toluene	1.2	7.1	20.66	19.48
Diesel	0.8	10	20.74	18.9

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What is a PID?

- **PID** = Photo-Ionization Detector
- Detects VOCs (volatile organic compounds) in ppm or parts per million
- Liquid hydrocarbon fuel products are easily measured with a PID
- A PID is a very sensitive broad spectrum detector, like a “low-level LEL”

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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 1.4% by volume or 14,000 ppm
- 10% of LEL Gasoline is 1,400 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

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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
Ethanol	3.3	33,000	3,300	330	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

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Using PIDs for 10% of LEL

330 ppm in Isobutylene units is 10% of LEL Ethanol

- 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
- If neither the catalytic bead LEL and the PID read anything, most likely a potentially flammable atmosphere is not present
- Note: in most “normal” situations 1000 ppm in isobultylene units is 10% of LEL
- PIDs are not particularly sensitive to Ethanol

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PIDs for Combustible Gases/Vapors

Advantages

+ Easily measures "heavier" chemical and fuel vapors
+ Resist poisons

Disadvantages

- Secondary measurement
- Misses common flammable gases like pure methane, propane, ethane and hydrogen
- More expensive

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CF Example: Ethanol

- Ethanol's CF with 10.6eV lamp is 12 so a PID isn't very sensitive to Ethanol
- If PID reads 100 ppm of isobutylene units in a Ethanol atmosphere then the actual concentration is 1000 ppm Ethanol units (TWA of Ethanol is 1000 ppm)

$$12_{CF} \times 100\ ppm_{iso} = 1200\ ppm_{Ethanol}$$

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Correction Factors

- CFs are scaling factors
- Imagine that your PID is a car radio
  - You need to turn the volume up 12 times to accurately “hear” ppm of Ethanol relative to isobutylene units

Photo courtesy
www.crutchfield.com

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Ethanol Toxicity

- Ethanol has a TWA of 1000 ppm so essentially 1000 ppm is the "speed limit" for ethanol exposure
- One can set the PID scale to "Ethanol"
- If one keeps their PID measuring on Isobutylene they need to set their alarm to 83 ppm for TWA of Ethanol

Chemical Name	10.6eV CF*	EL Chemical	EL Isobutylene
Ethanol	12	1000	83.33

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Course Agenda

- Why do we need Detection Technologies?
- Ethanol is “Toxic” to Electrochemical Sensors
- Measuring Oxygen
- Ethanol’s impact on LEL sensors
- Ethanol’s impact on PIDs
- Wrap-up

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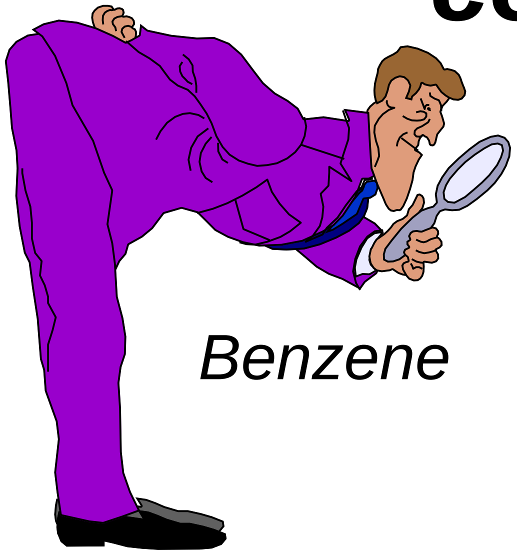
Gas Detectors need Gas Detectives to come to the right conclusion



Ammonia

Carbon Disulfide

Styrene

Carbon Monoxide

Benzene

PERC

Xylene

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Questions?

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"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

Please fill out your course evaluation and hand it in before you leave

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

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