Gas Detection GED

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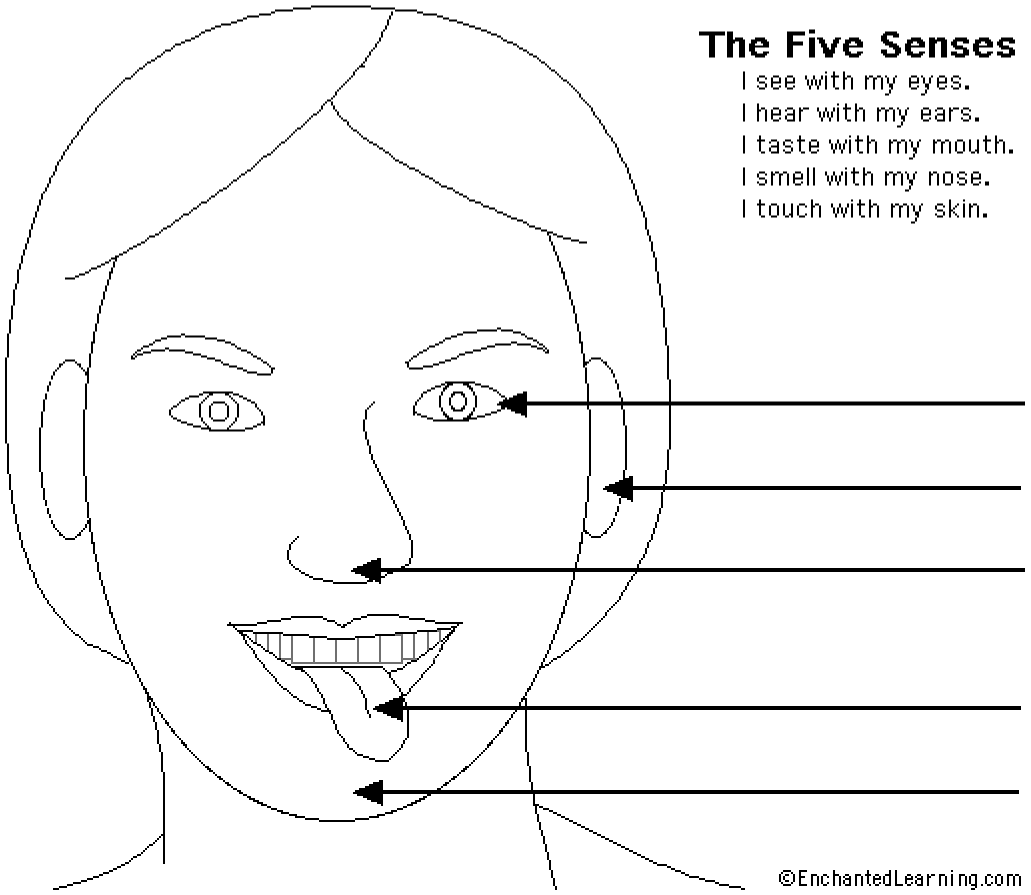
Course Agenda

- Why do we need Detection Technologies?
- Measuring Atmospheric Hazards
  - Oxygen
  - Combustible Gases & Vapors
  - Detecting Toxic Gases & Vapors
    - Understanding Exposure Limits (Alphabet Soup)
    - Electrochemical Sensors
    - PID as your basic sniffer
- Getting the Most From Your Meters
  - Caring for your detectors
  - The Importance of Calibration

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



Why is Detection Important?

We cannot rely on our 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***

Miner's Canary

- Canaries are great "biological" indicators because they are more sensitive to unsafe levels of O_2, CO and methane than humans

Photo courtesy of Museum of Cannock Chase, /www.cannockchasedc.gov.uk

- A passed out canary is an indication of an unsafe level
- Canaries were the standard of gas detection in British coal mines until 1986!

Biological Clues are Still Important Today

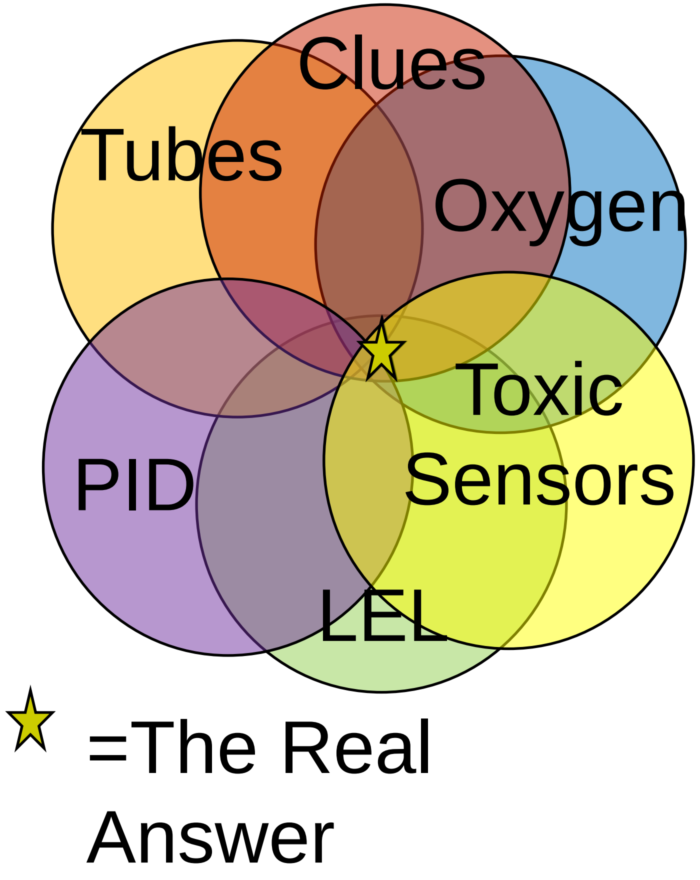
- While canaries are no longer considered valid gas detection technologies, victims, occupants and bystanders provide biological clues today
  - Symptomatic victims can help validate meter readings
  - Asymptomatic victims may be a clue that the meter is responding to some cross-sensitive gas/vapor

Flame Safety or “Davy” Lamp

- Invented by Sir Humphrey Davey in 1815
- Flame adjusted to specific height in fresh air
- Flame contained within a glass sleeve and with a flame arrestor on top
- Really it is the first two gas detector
    1. High flame means methane gas present
    2. Low flame means low oxygen

Modern instruments are easier to use, much more accurate, and far more dependable than birds or flames!

Integrating Gas Detection Techniques



- 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!

- Many detectors are essentially dumb devices that take readings and output a number
- They depend upon 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!

3 basic kinds of atmospheric hazards

- Oxygen (deficiency and enrichment)
- Flammable gases and vapors
- Toxic contaminants

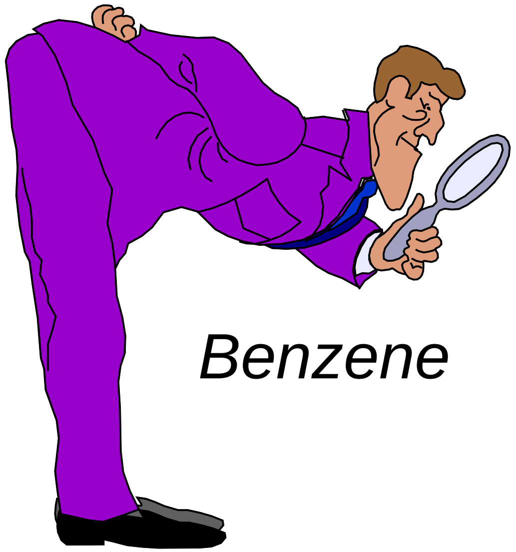
What constitutes a modern CSE detector?

- According to 29 CFR (Code of Federal Regulations) 1910.146 a confined space monitor must be able to detect the threats expected in the confined space (this is the OSHA Confined Space Entry or 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.”
- 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

Perhaps The Most Important Considerations

1. Will my detector find what is out there so that it will not harm me?
2. Does my detector work?
   - Is it calibrated

Think of yourself as a detective!



Ammonia

Carbon Disulfide

Styrene

Carbon Monoxide

Benzene

PERC

Xylene

Detectors need Detectives to come to the right conclusion

Questions?

- There are no “DUMB” questions
- Please feel free to ask questions throughout this course

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There is no Antidote for Lack of Oxygen

Understanding the oxygen sensors used in portable handheld detectors

Learning Objectives: Oxygen

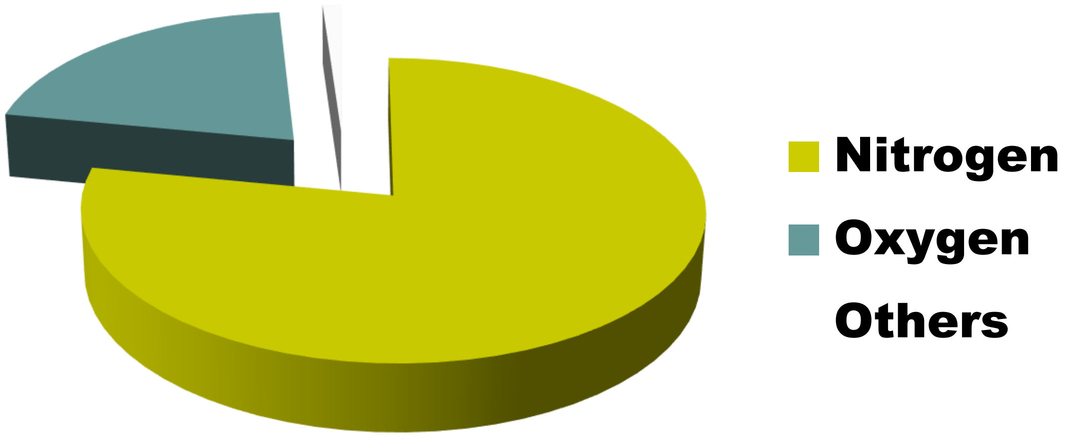
- Describe the importance of knowing the oxygen concentration in both deficient and enriched environments
- Understand how to use oxygen as a “broad-band” toxic sensor
- Describe the common types of oxygen sensors
- Describe common failure modes, and their causes, of oxygen sensors

Topics: Oxygen

- What is air?
- Oxygen levels
  - Deficiency
  - Enrichment
  - O_2 as a broadband toxic sensors
- Types of Oxygen sensors
  - Fuel cell, capillary diffusion
  - Fuel cell, membrane diffusion

Composition of “fresh air”

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



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Oxygen Deficiency

Air is oxygen deficient whenever concentration is less than 19.5%

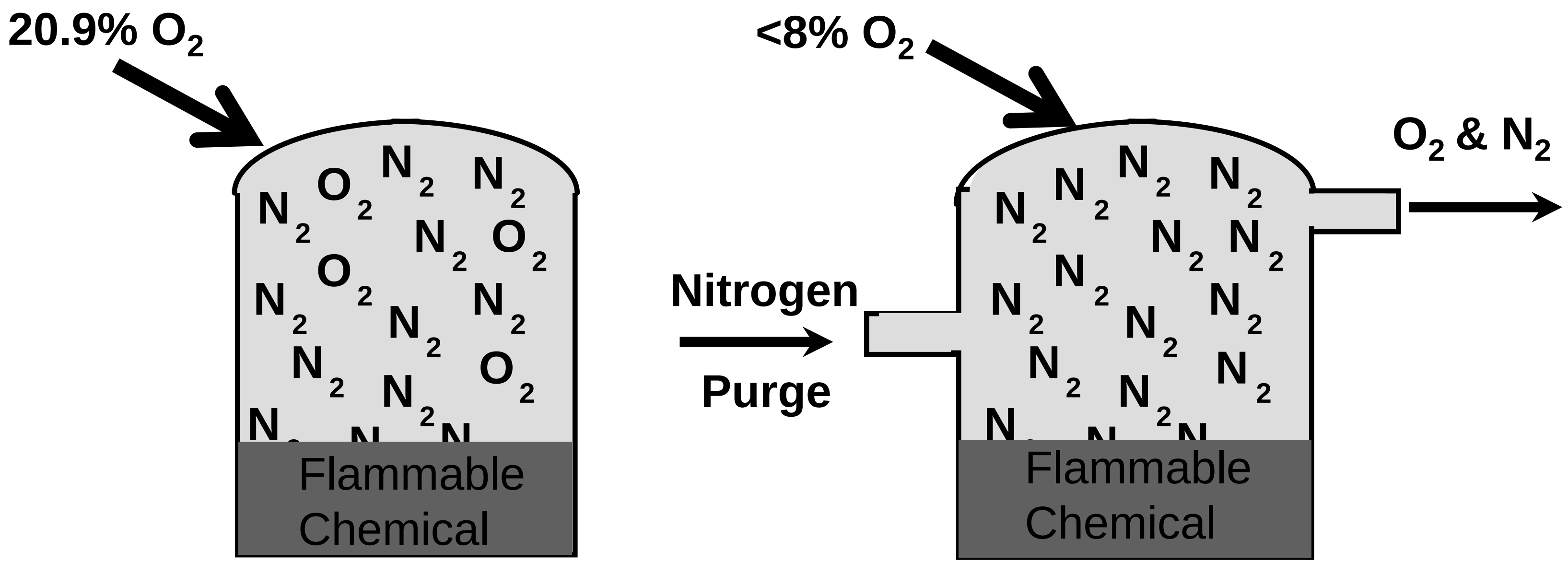
- This provides protection at sea level and higher elevations
- Oxygen transfer in the lungs isn’t dependant on concentration but really depends on partial pressure of oxygen

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

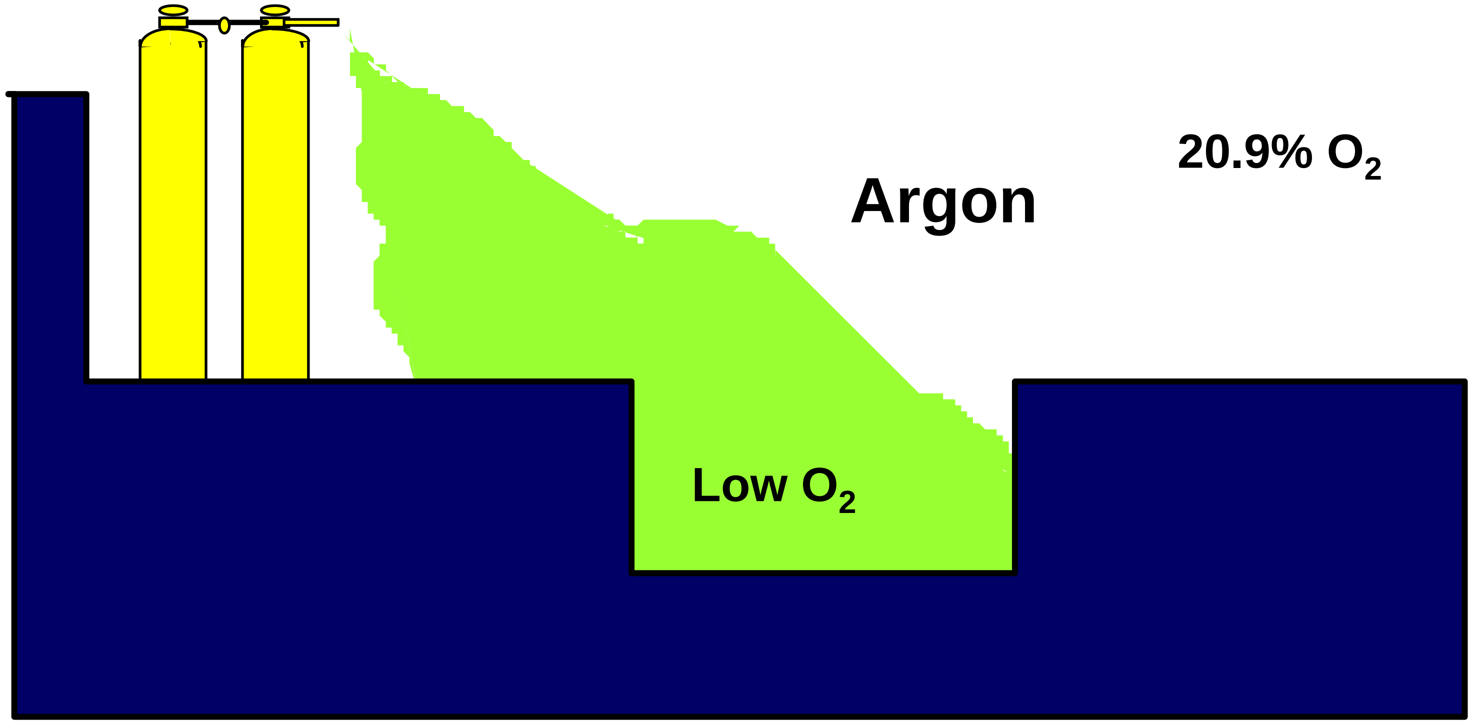
Oxygen Deficiency

Oxygen displaced by nitrogen in a process vessel to prevent explosions of flammable chemicals (called "inerting")



Oxygen Deficiency

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



Dry Ice Kills in a Meat Packing Plant

- Worker had to go into an open pit at a meat packing plant to clean out the pit
- Worker succumbed
- Investigation demonstrated that there was low oxygen in the pit because dry ice was used to help the flash freeze processing of the meat
- Dry ice sublimates to carbon dioxide which is heavier than air (MW = 44) and settled in the pit to displace air (MW = 29) and made it a low oxygen environment

Symptoms of Oxygen Deficiency

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

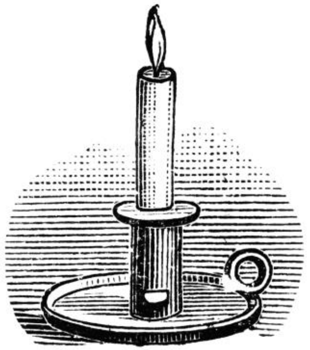
Oxygen is required to sustain life. As oxygen levels go down not only is it harder for us to breath, but it becomes increasingly difficult to make good decisions because less oxygen is going to our brain.

Oxygen Enrichment

- High levels of oxygen can increase the rate of many chemical reactions
- Can cause ordinary combustible materials to become flammable or explosive
- The Apollo 1 command module fire in 1967 was caused by Velcro becoming explosively combustible in an oxygen enriched environment

Photo courtesy NASA

Oxygen Enrichment



- "Things get strange above 30% Oxygen"
  - A candle in a pure oxygen environment burns VERY quickly
  - Mix liquid oxygen with kerosene and you have rocket fuel
    - The RD-180 main engine used on NASA's Atlas Launch vehicle uses RD-1 and LOX
- 29 CFR 1910.146 Specifies 23.5 % is oxygen enriched
  - ***Other codes are more stringent***
  - ***Most conservative approach is to use 22 % as take action point as used by Marine Chemists***
  - ***www.osha.gov***
- ***ALWAYS ask yourself "why?" if you see oxygen levels go UP!***

Oxygen Enrichment Examples

- Liquid Oxygen (LOX) spill at a hospital
  - Expect full scale readings (25 to 30%)
- LOX is increasingly being found in what were compressed oxygen applications because LOX means less deliveries
  - Home medical usage
  - Oxygen bubblers in 200 gallon live fish totes
- ***Be careful anytime you have more than 20.9% coming out of an organic substrate***

Oxygen Drops from 20.9-20.8%

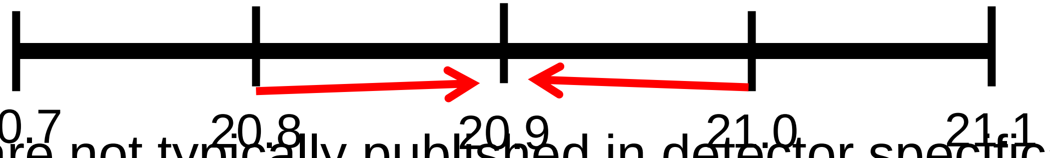
How much of “something else” has entered this room?

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

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

Oxygen sensor “Dead Band”

- Many gas 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 aerobic bacteria to people, the oxygen will be consumed
- Metabolism produces many byproducts (some may be toxic) so this is a case where the drop in oxygen may be accompanied by an increase in toxicity
  - Carbon dioxide is the chief toxic by-product of human respiration

Topics: Oxygen

- What is air?
- Oxygen levels
  - Deficiency
  - Enrichment
  - O_2 as a broadband toxic sensors
- Types of Oxygen sensors
  - Fuel cell, capillary diffusion
  - Fuel cell, membrane diffusion

Fuel Cell Oxygen Sensors

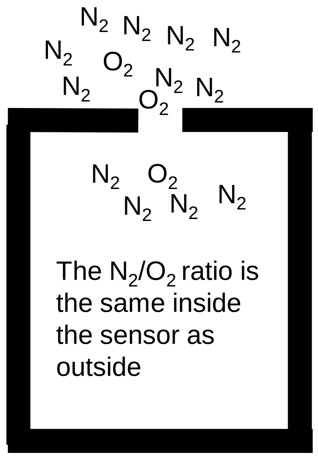
- The O_2 sensor generates electrical current proportional to the oxygen concentration
- O_2 entry into the cell must be limited or else it would be quickly used up by the 20.9% O_2 in air
- Think of the O_2 sensor as a coffee cup where the coffee is the electrolyte mixture
  - With the lid off the O_2 will get to the electrolyte and consume it quickly
  - But if you put a lid with a sip hole on the coffee cup then it limits the entry of O_2 to the coffee "electrolyte"
  - One could also put O_2 permeable "glad-wrap" over the top of the coffee cup to limit the entry of O_2

Fuel Cell Oxygen Sensors

- Sensor generates electrical current proportional to the O_2 concentration
- Sensor used up over time (usually last one to two years)
- Oxygen entry limited by one of two means
  - **Capillary limited:** a capillary hole that is about the size of a human hair limits the flow of oxygen into the most common that gives direct reading of % volume
  - **Permeation limited:** The rate at which oxygen diffuses into the sensor is limited by a membrane. It directly measure partial pressure

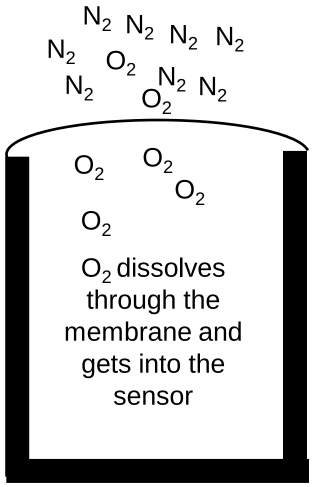
Capillary Fuel Cell Oxygen Sensors

- In a capillary fuel cell oxygen sensor oxygen entry into the cell is limited by the battle between nitrogen and oxygen molecules trying to get through the capillary
  - O_2 has a mw of 32 and N_2 has a mw of 28 so they are in relative balance in the battle to get in the capillary
  - This results in a true % volume reading
  - Most common oxygen sensor type
  - Minor fluctuations in pressure and barometric pressure will not change the sensor reading
  - At the top of Everest it will still read 20.9%



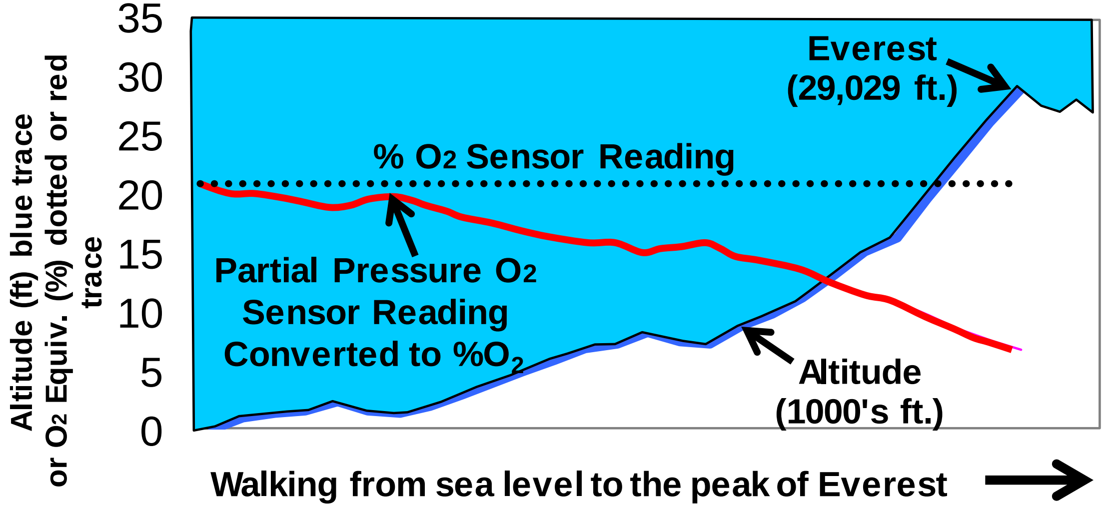
Permeation-limited Fuel Cell Oxygen Sensors

- In a permeation-limited fuel cell oxygen sensor there is a very thin, plastic membrane over the top of the sensor which is a solid barrier in which the oxygen molecules must dissolve in order to reach the sensing electrode
  - Entry into the cell is driven by the differential of oxygen partial pressure across an oxygen permeable membrane
  - This results in a partial pressure reading which is usually corrected to %Oxygen in the detector
  - Minor changes in pressure and barometric pressure can change the sensor readings unless it is corrected for pressure



% Volume vs. Partial Pressure

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



- There is more distance between oxygen molecules at altitude versus sea-level, put another way there is a lower partial pressure of oxygen at altitude, but they are still in the same ratio or concentration of 20.9%

% Volume vs. Partial Pressure

- At the top of Everest (29,029 ft., 8848m) the standard barometric pressure is 34kPa (253 mmHg), this means that there is 33% of the oxygen available at sea level
- A detector using the membrane partial pressure oxygen sensor would read only 6.9% if it had been calibrated at sea level and was not corrected for pressure changes while the % volume capillary oxygen sensor would still read 20.9%

% Volume vs. Partial Pressure

- In 2012 Hurricane Sandy hit the coast with an record low eye pressure of about 940 millibars
  - Sandy's ATM pressure was 940 millibars = 13.6 psi = 0.928 ATM
  - 20.9% of Sandy's ATM pressure = 20.9% x .928 ATM = 19.4% Partial Pressure of O_2 (PO2) corrected for Sandy's ATM Pressure
  - So, Sandy's PO2 (19.4%) was below OSHA's IDLH of 19.5%, or about the same as climbing to about 2060 feet
  - If a partial pressure oxygen sensor was not compensated or rezeroed during this record low, it would read 19.4% Oxygen and be in low oxygen alarm
  - Thanks to Kevin Johnson for this math!

Fuel Cell Oxygen Sensors Compared

Capillary

- Most Common
- Reads % Volume
- \+ Reading doesn't change with pressure
- – Affected by molecular weight of matrix gases
- – Acid gases like CO_2 can get in the sensor and can affect performance
- RAE, ISC, MSA, Draeger

Membrane

- Less Common
- Read % Volume corrected from partial pressure
- \+ Unaffected by changes in matrix gases
- \+ Membrane is selective to O_2 and prevents neutralization from acid gases like CO_2
- – Reading may change with pressure
- RKI, Draeger (0-100% sensors only)

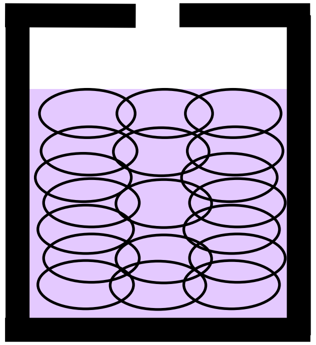
Fuel Cell O_2 Sensor Failure Modes

- When all of the available surface area of the Pb anode is converted to PbO_2 the sensor will stop working
- Electrolyte poisoned by exposure to contaminants
  - Electrolyte neutralized by exposure to high levels of Carbon Dioxide
    - CO_2 in the aqueous electrolyte (water) produces carbonic acid which neutralizes the hydroxyl ions (OH-) and shuts down the chemical reaction
    - Such levels are only found in breweries, bottlers and dry ice plants
    - Exhaling into your detector WILL NOT HURT the O_2 sensor
- Desiccation (drying out) typically due to storage in very hot dry environments
- Blockage of capillary pore/coating of the membrane by liquids or dirt, typically caused by sucking contaminants into a meter

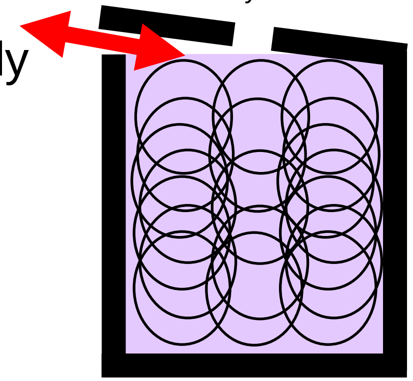
Fuel Cell O_2 Sensor Failure Modes

- As the Pb is converted to PbO_2 it will "grow" just like steel "grows" as is rusts, the sensor is designed to accommodate this change in size
  - If a new sensor is exposed to very cold weather the expanding aqueous electrolyte will expand into the room saved for the PbO_2 and the sensor may work when it thaws
  - If an older sensor is exposed to extremely cold weather, and this expansion room has already been used up by the PbO_2 the sensor envelope can be cracked by the expanding frozen electrolyte
- Electrolyte leakage
  - If the oxygen sensors reading goes high first then to zero, absent of environmental reasons this is most likely because the sensor envelope has failed
  - Caustic electrolyte can quickly ruin sensor boards

New sensor, headspace available for expansion



Old sensor, headspace filled by expanded, oxidized lead wool. When it freezes the lid can be pushed off letting oxygen in and electrolyte out



Fuel Cell Oxygen Sensors

Advantages

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

Disadvantages

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

Make a low oxygen simulator

- Take a clean 5 gallon paint bucket with a small screw off lid to sample from
- Add a handful of any steel you can find, nails, rebar, washers, bolts all work as long as they are not galvanized or coated with oil
- And/or add a handful of mulch, grass trimmings or some sort of organic material
- Add a cup or two of water to get the stuff moist but no so much as it sloshes around
- Give it at least a day or two to “fester” then sample from the screw lid of the bucket and see how even a small amount of material can oxidize/consume oxygen relatively quickly
- Sample with oxygen detector and discuss
  - What sensor(s) reading do you get?
  - Are all the sensors telling the “truth” if not what should you consider doing next?

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Blowing Up Will Ruin Your Whole Day

Understanding and using the Combustible Gas Sensors used in portable handheld detectors

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.”
    - This rules out biological indicators like canaries and mice because they can’t be calibrated

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

Learning objectives

- Understand how the most common combustible gas sensors work
- Understand the limitations of “catalytic bead” sensors
- Understand why there may be a difference between calibration gas and measurement gas
- Understand options that can be used for measuring combustible gases and vapors
- How multiple combustible gas detection technologies may be useful in reaching a decision in flammable atmospheres

Combustible gas sensor questions we'll try to answer

- Why do LEL sensors from two different companies read differently on the same gas?
- The PID reads 1000 ppm, does this impact my combustibility?
- Why doesn't my LEL sensor read all flammable vapors?
- I don't understand why my LEL sensor doesn't seem to last as long as it should

Flammability Range

- 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

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
- Meter accuracy can drastically affect your LEL readings
- Therefore, always be VERY CONSERVATIVE when making LEL decisions

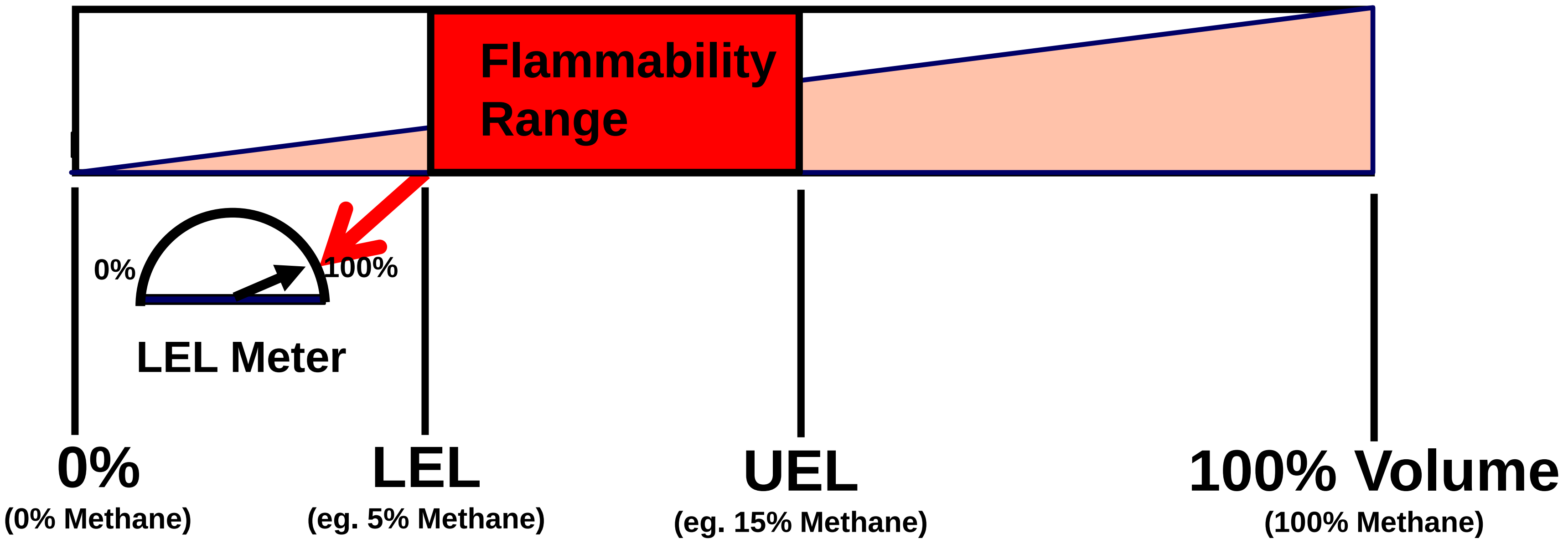
Gas/Vapor	LEL* (% vol)	UEL* (% vol)
Acetone	2.2	12.8
Benzene	1.2	7.8
Carbon Monoxide	12.5	74
Diesel	0.8	10
Ethylene Oxide	3.0	100
Gasoline	1.4	7.6
Hydrogen	4.0	75
Methane	5.0	15
MEK	1.8	11.4
n-Pentane	1.5	7.8
Propane	2.0	9.5
Toluene	1.2	7.1

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

Measuring Flammability

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

Gas Concentration



Agenda

- Wheatstone bridge catalytic bead
  - Response, calibration & correction factors
  - Poisons
- High range flammability
  - Oxygen Displacement
- Photoionization Detector (PID)
- Which technology should I trust

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 1926-1927 of Standard Oil Co. of CA (now Chevron)*
- 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

What is a Catalyst?

- According to Miriam Webster:
  - “a substance that enables a chemical reaction to proceed at a usually faster rate or under different conditions (as at a lower temperature) than otherwise possible
- Platinum or palladium are two catalysts commonly used in the catalytic bead to facilitate the oxidation (burning) of flammable gases and vapors at lower (safer) temperatures (~250^{o}F, ~120^{o}C)

Catalytic “Hot Bead” Structure

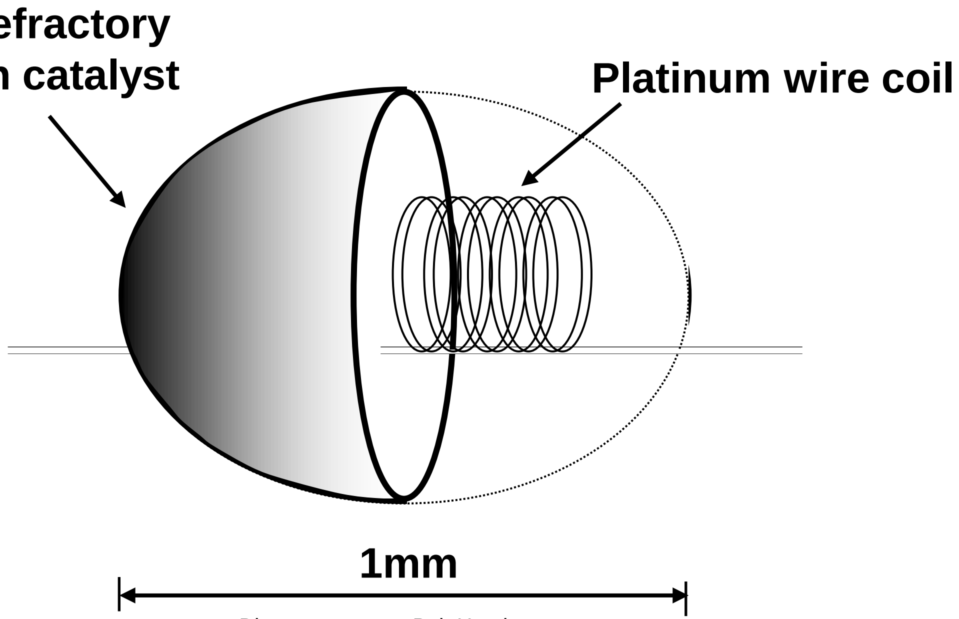
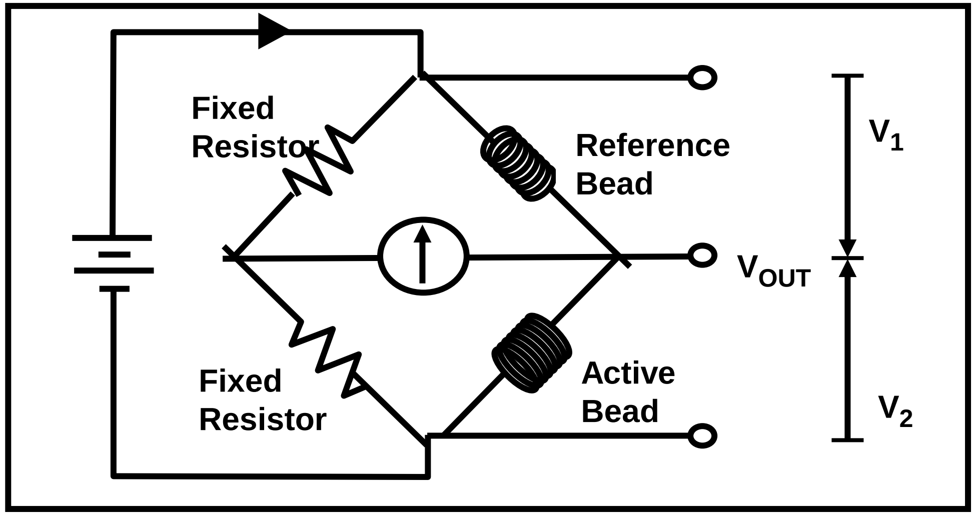


Diagram courtesy Bob Henderson

- A coiled wire is used to maximize the surface area of catalyst
- The catalyst is put into a porous ceramic bead to keep it from flexing like a “Slinky” and shorting out on itself
- This adds to the durability of the sensor

Balanced Wheatstone Bridge



- As a gas/vapor burns on the active bead that bead heats up and has greater resistance than the reference bead
- The “Wheatstone Bridge” circuit measures the difference in resistance from the active bead to the reference bead
- The reference bead reflects any atmospheric effects
- Active bead – Reference Bead = Flammability

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***

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
- Oxygen must also be measured first because the cat bead sensor produces the same amount of heat at a point below LEL where it is “fuel starved” or “too lean” as it does at a point above UEL where it is “oxygen starved” or “too rich”
- The cat bead sensor only measures heat so it can’t know if it’s below LEL or above UEL
- OSHA requires that oxygen is measured 1^{st} because the regulation was written in a time when one might have an oxygen meter and a LEL meter 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

Making the Electric Stove Safe for Use in Flammable Atmospheres

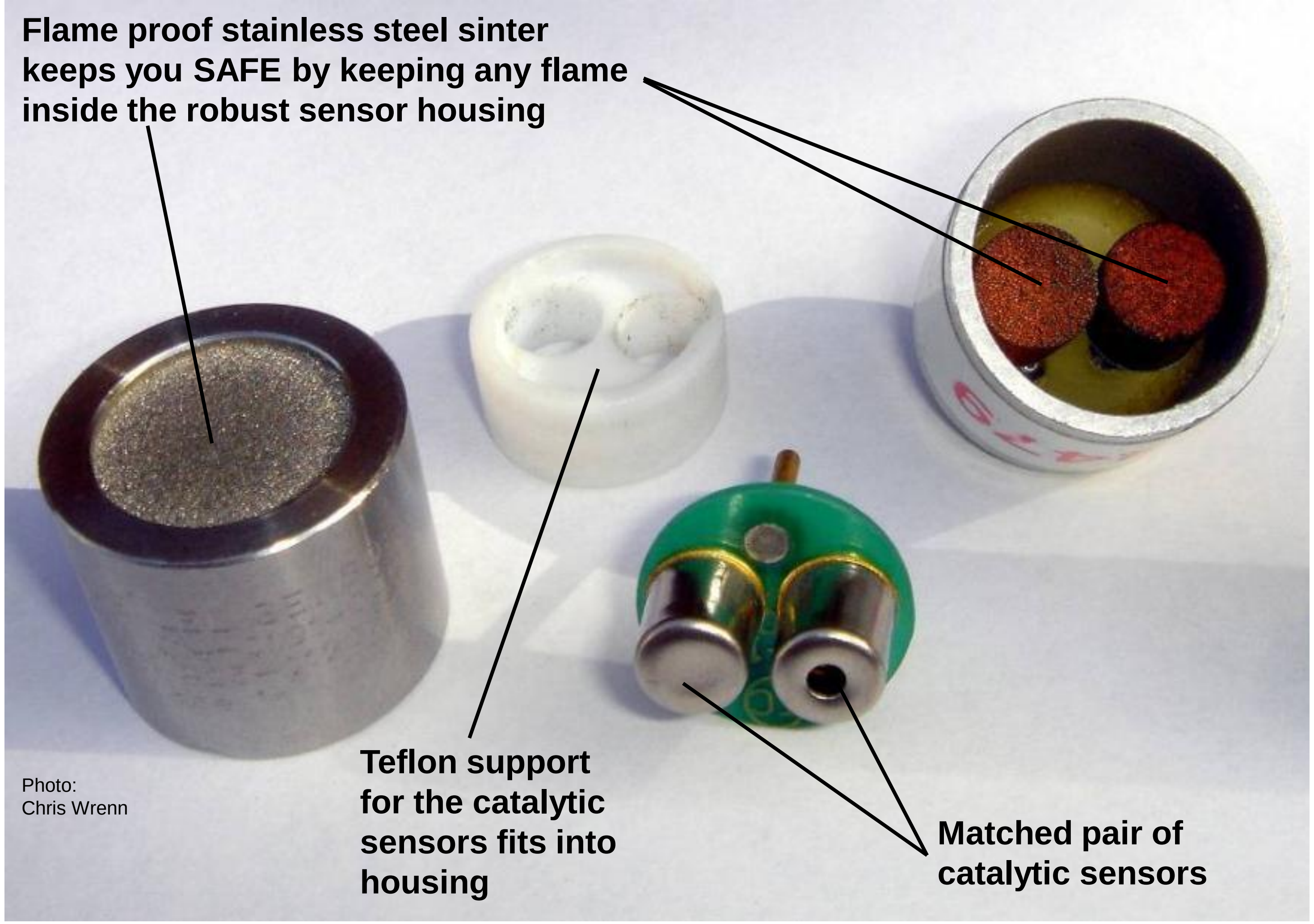


Photo:
Chris Wrenn

Explosion-Proof LEL Sensors

- Due to elevated operating temperatures these sensors are typically “explosion-proof” subsets of the intrinsically safe detector so that the “tiny electric stove” is contained in an explosion proof housing to prevent any ignition in the sensor from igniting potentially flammable environments

Agenda

- Wheatstone bridge catalytic bead
  - Response, calibration & correction factors
  - Poisons
- High range flammability
  - Oxygen Displacement
- Photoionization Detector (PID)
- Which technology should I trust

Questions we'll answer

- A fire department finds that their LEL sensors calibrate correctly but don't "see" natural gas
- A fire department arrives at a confined space rescue and finds that their meter doesn't agree with the contractor's meter

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

Gases/Vapors burn with different heat outputs at their LELs

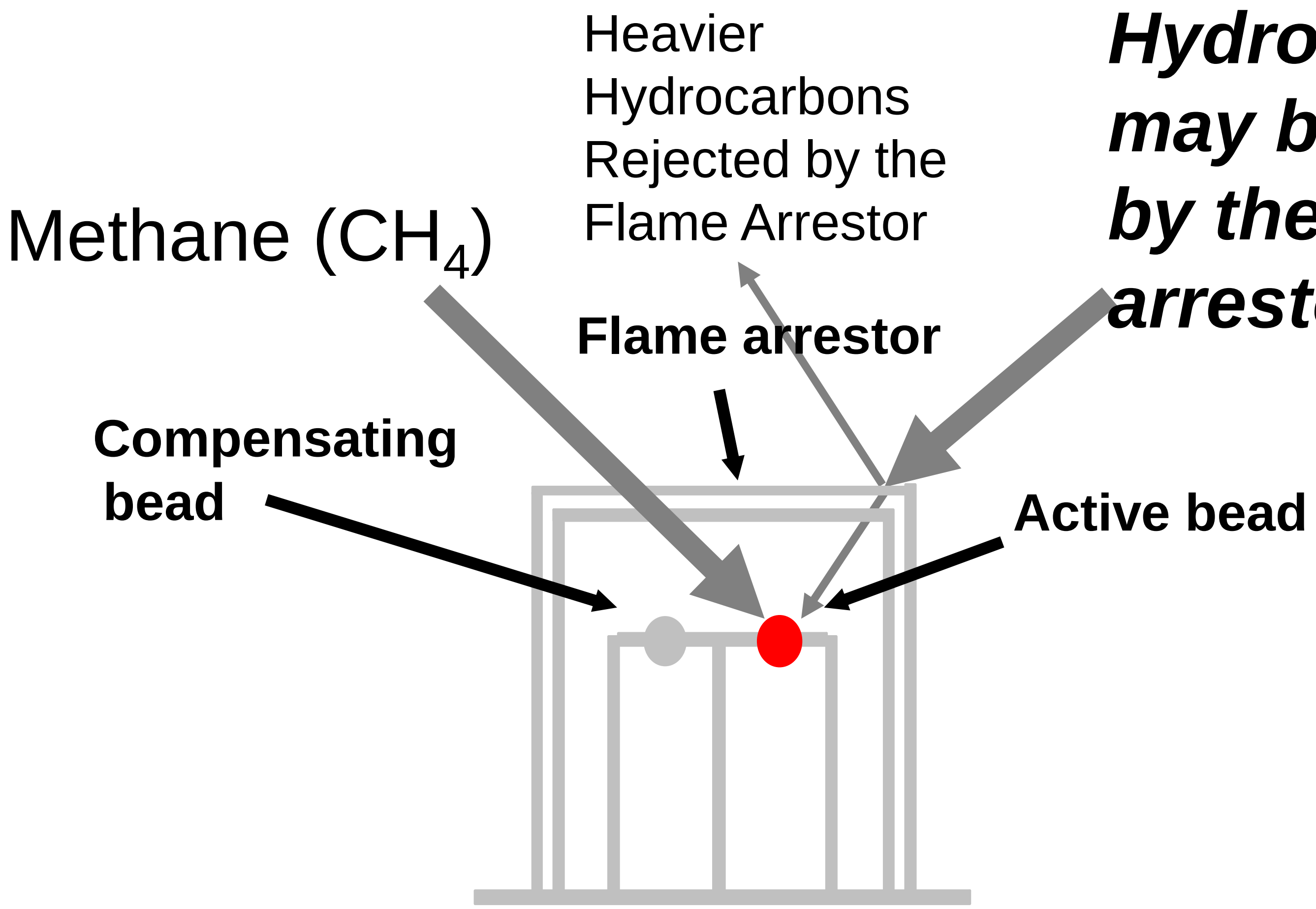
- Most “gas” stoves are setup for Natural Gas when they ship
- When used on “LP” or “Propane” gas these stoves need to be recalibrated with new jets and new regulator pressure
- LP/Propane burns with ~1/2 the heat of Natural Gas
- This is an example of why LEL sensors will respond differently to different gases

Heavier Hydrocarbons have difficulty getting into the sensor

- Imagine a pitcher
  - Fill it with methane and pour it out on the floor, how much hits the floor?
    - Methane has a vapor pressure of +760mm/Hg so it won't even stay in the pitcher
  - Fill it with ethyl ether and pour it out
    - Most evaporates on the way to the floor because ether has a vapor pressure of 440 mm/Hg
  - Fill it with diesel and pour it out
    - It all hits the floor, it's all there an hour later, a week later and even a year later because it has a vapor pressure of 0.4 mm/Hg

Catalytic LEL Sensor Cut-Away

Heavier Hydrocarbons may be rejected by the flame arrestor



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

- The combination of different heats of combustion and varying vapor pressures means that different gases and vapors will have differing responses on the cat bead sensors
- The LEL sensor doesn't know one gas/vapor from another
- It only knows ONE thing, how much heat is produced when that gas/vapor "burns" in the LEL sensor due to catalytic oxidation
- Some gases like methane produce a lot of heat on this sensor
- Some vapors like diesel produce a lot less heat on this sensor
- So the cat bead sensor doesn't know that the "lot less" heat is 10% of LEL diesel OR 3.3% of LEL methane unless the user knows what the detector is detecting because the same amount of heat is produced on the sensor by these two gases/vapors at two different concentrations

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

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)

Catalytic LEL Sensor Response

LEL Sensors were designed to measure Methane

Gas/Vapor	LEL (% vol)	Sensitivity (%)*	Ignition Temp. F°(C°)**
Methane	**5**	**100**	**999 (537)**
Hydrogen	4	91	932 (500)
Propane	2	63	842 (450)
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

* 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

Catalytic LEL Sensor Response

- By looking at the “Sensitivity” column in the next chart, gasoline produces less than half of the heat of methane on a Wheatstone bridge sensor
- When a LEL detector is calibrated to and reading in methane units but it is exposed to 1.2% by volume or 100% of LEL gasoline vapors, the detector will only display 48% (less than half) of the true % of LEL
- If this same LEL sensor displays 48% of LEL in a mixture of gasoline and air, the actual LEL is approximately 100% because gasoline produces just 48% of the sensor output versus methane
- This is dangerous because one might think that 48% of LEL (while above the 10% allowed for confined space entry) is safe enough, but in this case it really represents a flammable environment

Catalytic LEL Sensor Response

Gas/Vapor	LEL (% vol)	Sensitivity (%)*	Ignition Temp. F°(C°)**
Methane	**5**	**100**	**999 (537)**
Hydrogen	4	91	932 (500)
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Catalytic LEL Sensor Response

- A more conservative means of setting the scale on a LEL detector is to choose a calibration gas/scale whose response is closer (or even lower) than the gases that are commonly being encountered
- The next chart shows that the LEL response of n-pentane (45% response) is much closer to common VOCs like acetone (45%), gasoline (48%) and toluene (38%) than methane is
- It would seem that n-pentane would be a safer calibration/scaling alternative than methane
- A number of LEL detector manufacturers calibrate their LEL sensors to a n-pentane scale so that the LEL sensor response is corrected to a more appropriate scale for most common gases and vapors

Catalytic LEL Sensor Response

Gas/Vapor	LEL (% vol)	Sensitivity (%)*	Ignition Temp. F°(C°)**
Methane	**5**	**100**	**999 (537)**
Hydrogen	4	91	932 (500)
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Gasoline	1.4	48	536 (280)
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Catalytic LEL Sensor Response

- The problem with calibrating directly to n-pentane is that it ignites at 50% of the temperature of methane
- In the next chart one can see that the ignition temperature of n-pentane is just 500^0F (260^0C) compared with the ignition temperature of methane which is 999^0F (537^0C)
- As the catalyst in the LEL sensor wears out over time, it loses its ability to impart energy into a gas to cause it to oxidize
- A LEL sensor will lose the ability to oxidize methane long before it loses the ability to oxidize n-pentane because methane’s ignition temperature is significantly higher
- It is quite possible that a weakened LEL sensor that has been properly calibrated to n-pentane gas may not respond in an environment containing methane

Catalytic LEL Sensor Response

- This is of critical importance because methane is one of the most common flammable gases encountered due to its prevalence not only in sewers but also because it is the dominant component of natural gas
- For this reason, a number of manufacturers insist on a methane calibration for their LEL sensors because it is the best and most rigorous test of the LEL sensor to make sure that it remains viable in the widest variety of environments

Catalytic LEL Sensor Response

Gas/Vapor	LEL (% vol)	Sensitivity (%)*	Ignition Temp. F°(C°)**
Methane	**5**	**100**	**999 (537)**
Hydrogen	4	91	932 (500)
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Catalytic LEL Sensor Response

Setting the scale is not dependent on the calibration gas

- One does not have to calibrate on n-pentane to set the LEL sensor to an n-pentane scale. Correction Factors (CFs, a.k.a: response factors) can be used during calibration or electronically applied by the gas detector to correct the reading to the intended target gas while still calibrating on methane
- This is known as a “simulant” or “surrogate” calibration

What is a Correction Factor?

- A Correction Factor (CF) is a measure of the sensitivity of the LEL sensor to a particular gas or vapor
- Manufacturers challenge their sensors with a known concentration of a flammable gas and measure the sensors response to create correction factors
- A low CF means that the LEL sensor is very sensitive to a gas or vapor
- A high CF means that the LEL sensor does not have as good sensitivity to a gas or vapors
- Corrections factors are scaling factors, they do not make a LEL sensor specific to a chemical, they only correct the scale to that chemical.

CF Example: Diesel

- LEL reads 10% of LEL in methane units in a Diesel atmosphere
- Then the actual concentration is 30% LEL Diesel units

$$3.0_{CF*} \times 10\%LEL_{methane} = 30\%LEL_{diesel}$$

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

Ammonia

- LEL reads 10% of LEL in methane units in an Ammonia atmosphere
- Then the actual concentration is 8% LEL Ammonia units

$$0.8_{CF*} \times 10\%LEL_{methane} = 8\%LEL_{ammonia}$$

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

Correction Factors

- CFs are scaling factors
- Imagine that your LEL detector is a car radio
  - You need to turn the volume up 3 times to accurately “hear” or measure in diesel LEL units if you were first measuring in methane units
  - You need to turn the volume down by 20% (multiply by 0.8) to accurately “hear” or measure in ammonia LEL units if you were first measuring in methane units

Photo courtesy
www.crutchfield.com

Applying Correction Factors (CFs)

- Applying CFs during calibration
  - One manufacturer's LEL gas concentration reads "58% Pentane" but a closer read of the calibration gas cylinder shows that there isn't pentane in the cylinder but "methane equivalent." This means that the concentration of methane in the cylinder (in this case 38% by volume balance air) produces the same LEL sensor response as 58% by volume pentane balanced with air

Applying Correction Factors (CFs)

- Applying CFs manually
  - Calibrate to a known concentration of gas (such as 50% of LEL or 2.5% by volume methane)
  - Some manufacturers provide a chart of Correction Factors in their manuals or in whitepapers. Typically the user multiplies the meter reading by the correction to get the actual reading for the gas being detected
- Applying CFs electronically
  - Calibrate to a known concentration of gas (such as 50% of LEL or 2.5% by volume methane)
  - Libraries in the firmware of the detector allow users to select a the gas being detected and the meter will automatically do the math to correct the meter reading to the correct scale

Making LEL Decisions

- It is difficult to make a decision with an LEL detector unless you know the scale in which you are measuring
- Measurement scale is usually the calibration gas
- Correction factors allow you to change scale without changing calibration gas

Know your LEL detector measurement scale

Fire Dept. Changes Cal. Gas

- Used an LEL sensor calibrated with n-pentane gas
- Found that their older LEL sensors sometimes didn't detect natural gas
- Switched from n-pentane in the cylinder to methane with a calibration factor on the side of the cylinder

Photo courtesy of Oxford Classic Motor Club, www.oxcmc.org.uk

- n-pentane has an ignition temperature of just 500ºF (260ºC) compared with an ignition temperature of 999ºF (537ºC) for methane. As the catalyst aged, it was still able to catalyze the oxidation of n-pentane but it had lost the ability to catalyze the oxidation of methane.

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.”

Correction Factors Solve a Confined Space LEL Argument

- Tank cleaning contractor had a slip/trip/fall injury in a chemical tank containing toluene
- HazMat team responded as part of the extrication team
- HazMat team argued that the contractor shouldn’t have been in the tank due to +10% of LEL reading from their confined space meter
- Contractor argued that they had a -10% of LEL reading on their meter and they were OK

Confined Space LEL Argument

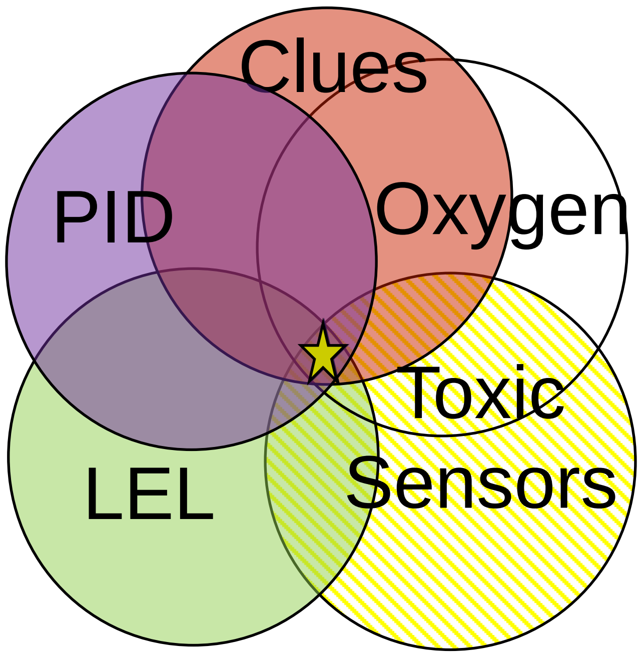
- HazMat team used meter measuring in n-pentane which read 11% of LEL
- Contractor used meter measuring in methane with a reading of 6% of LEL (this meter also had a PID)
- Tank contained Toluene
- HazMat Team: O_2: 20.9, LEL: 11, CO: ~20, H_2S: 0
- Contractor: O_2: 20.9, LEL: 6, CO: ~20, H_2S: 0, PID: 2640

Confined Space LEL Argument

- HazMat Team:
  - $11\%LEL_{pentane}$ x $1.06_{CF^*Toluene}$ = $11.7\%LEL_{Toluene}$
- Contractor:
  - 6% $LEL_{methane}$ x $1.9_{CF^*Toluene}$ = $11.4\%LEL_{Toluene}$
- References:
  - 2640 ppm_{iso} x $0.5_{CF^*Toluene}$ = 1320 $ppm_{Toluene}$ or 11% of LEL
  - 100% $LEL_{Toluene}$ = 1.2% or 12,000 $ppm_{Toluene}$
  - 10% of $LEL_{Toluene}$= 1,200 $ppm_{Toluene}$
- Who Was Right?

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

Confined Space LEL Argument



=~11% of LEL Toluene

- **Clues:** tank cleaning with Toluene present
- **Oxygen:** 20.9%
- **Toxic Sensors:** Given the high concentration of toluene in this space the CO reading is most likely due to the electrochemical CO sensors cross-sensitivity to toluene
- **LEL:** both sensors were wrong and right until properly corrected
- **PID:** 2640 ppm isobutylene units exceeds 1000 ppm 10% of LEL guideline and is 11% LEL corrected

Confined Space LEL Argument

- So in this case the fire department and contractor meters were not set to the same "volume" or measurement scales
- When the two meters were corrected to the same "volume" they both "heard" the vapors at the correct level
- Later we will talk about using Photoionization Detectors (PIDs) for LEL and we'll see that in this case the contractor has exceeded the PID 10% of LEL guideline number of 1000 ppm
  - But to be fair to the contractor this happened before the creation of the PID 10% of LEL guideline.

Agenda

- Wheatstone bridge catalytic bead
  - Response, calibration & correction factors
  - Poisons
- High range flammability
  - Oxygen Displacement
- Photoionization Detector (PID)
- Which technology should I trust

Catalytic LEL Sensor Poisons

- Common chemicals can degrade and destroy LEL sensor performance
- Acute Poisons act very quickly, these include compounds containing:
  - Silicone (firefighting foams, waxes)
  - Lead (old gasoline)
  - Phosphates and phosphorous
  - High concentrations of combustible gas

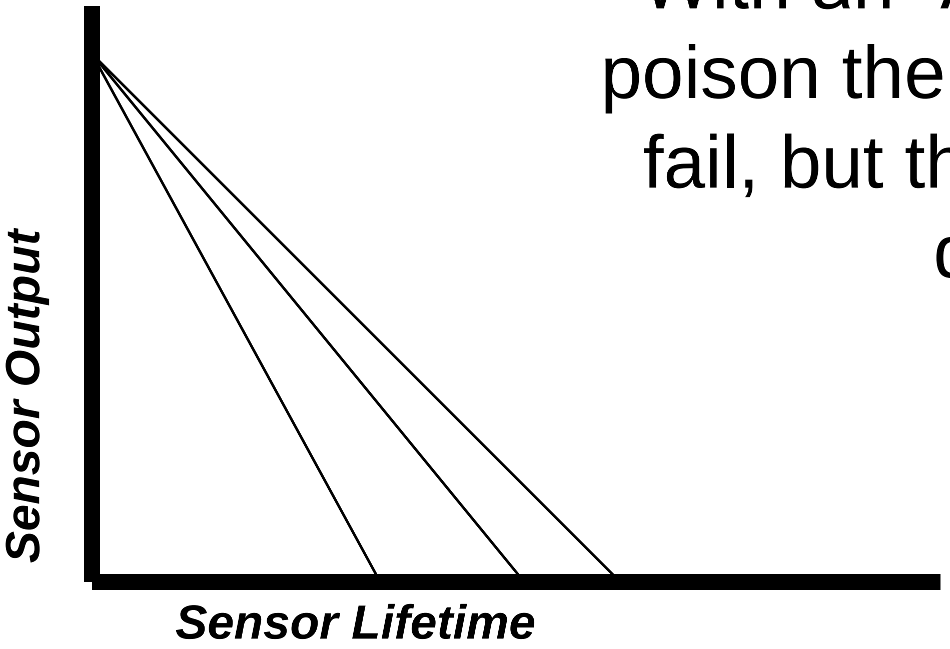
Armor-All is not the Catalytic Bead Sensor's Friend

- A fire department complained about routine catalytic bead sensor failures
- Investigation showed that the 4-gas detector was stored on a clip next to a jump seat that was Armor-All'ed weekly
- Armor-All doesn't only coat the seat, but it also coated the catalytic bead in the LEL sensor so that gas couldn't get to the catalyst wire and it finally failed to work
- Consider **BANNING** the use of Armor-All anywhere near where detectors are stored or routinely used

The case of the killer case

- 4 gas detector customer put their detector in a custom heavy duty, waterproof storage case
- The customer made a custom foam insert to store everything neatly
- The LEL sensor in the detector was not lasting long
- Investigation determined that the custom foam was glued into the case with silicone caulk that was killing the LEL sensor in the tightly sealed case

Catalytic LEL Sensor Poisons



With an “Acute” LEL sensor poison the sensor is going to fail, but the time to failure is dosage dependant

Catalytic LEL Sensor Poisons

- Chronic Poisons are often called “inhibitors” and act over time
  - Often exposure to clean air will allow the sensor to “burn-off” these compounds
  - Chronic exposures to high concentrations (above human health and safety levels) can degrade LEL sensors
- Examples include:
  - Sulfur compounds: H_2S, CS_2
  - Hydride gases: like phosphine (PH_3)
  - Halogenated Hydrocarbons: Refrigerants (“Freon”), trichloroethylene, methylene chloride
  - Styrene

Catalytic LEL Sensor Poisons

- Chronic Poisons
  - Carbonization: caused by the build-up of carbon on the surface of the catalyst when the concentration of combustible gas is allowed to remain high for too long
    - Basically it puts the catalyst in a “rich” environment and it carbons up
    - Virtually all current LEL detectors automatically turn the sensor off when concentrations exceed 100% of LEL, although the meter remains in alarm

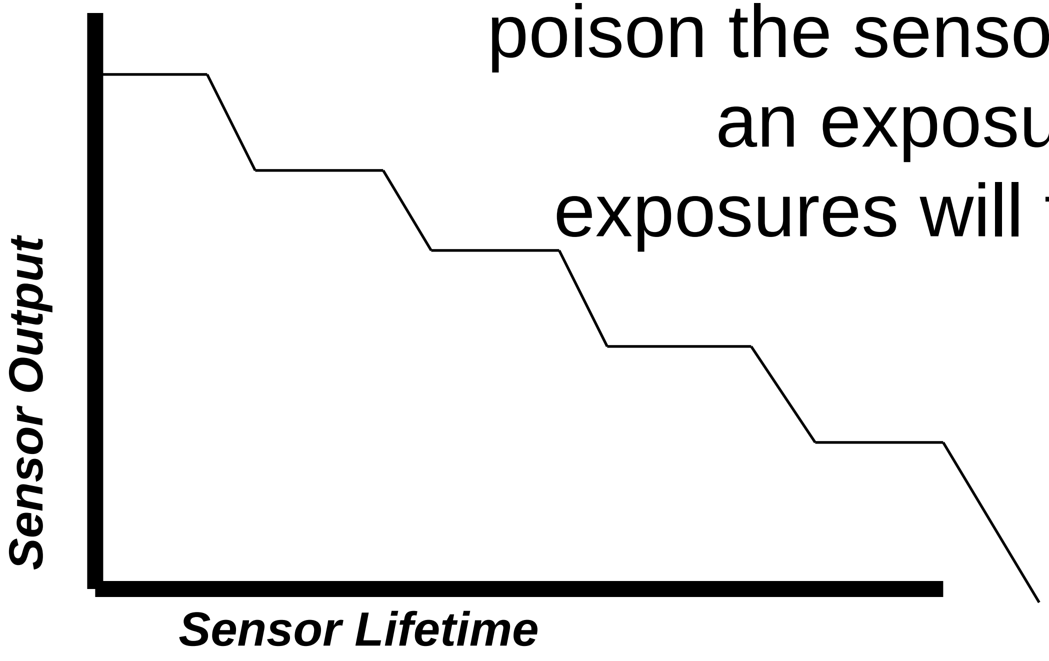
Pulp Mill Stink Kills LEL Sensors

- Pulp plant customer complains of getting short life out of their LEL sensors
- The plant stinks with H_2S and mercaptans which are chronic LEL sensor toxins
- PIDs are best for the turpentine areas but methane is present
- Could use NDIR and PID

Photo courtesy Millwatch (www.rfu.org)

Catalytic LEL Sensor Poisons

With a “Chronic” LEL sensor poison the sensor recovers after an exposure, subsequent exposures will further degrade sensor output



Wheatstone bridge catalytic bead LEL sensors

<u>Advantages</u>

+ Proven technology
+ Direct measurement of flammability

<u>Disadvantages</u>

– Can be poisoned
– Cannot measure above 100% of LEL
– Needs at least 12-16% oxygen for measurements
– Difficulty measuring diesel, jet fuel, kerosene and similar vapors
– Not sensitive enough for toxicity measurements

Agenda

- Wheatstone bridge catalytic bead
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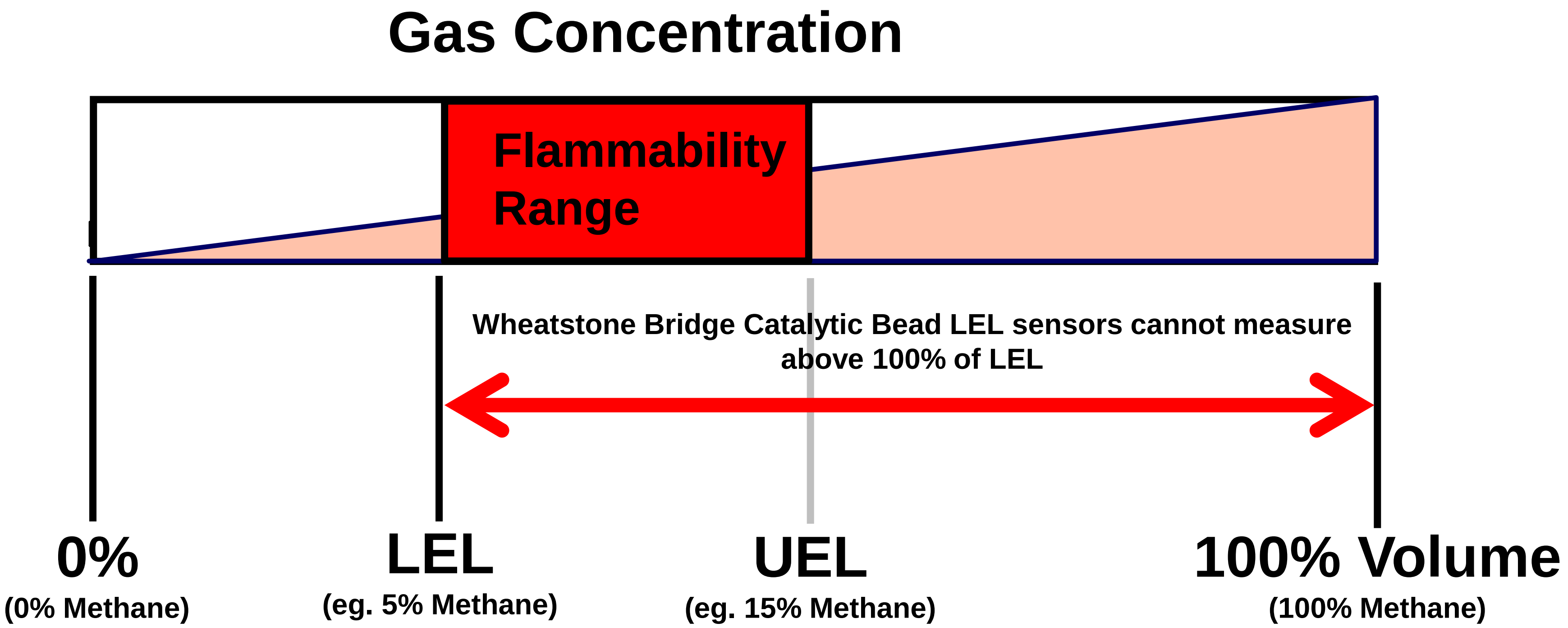
High Range Combustible Sensor Limitations

- Traditionally, even with protective circuitry which protects bead at concentrations above 100% LEL, catalytic bead sensors cannot read above 100% of LEL to 100% by volume



Oxygen Sensors for LEL Decisions

- LEL of methane is 5% by volume or 50,000 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 methane (or 5% by volume) the oxygen level will only drop by 1% from 20.9% to 19.9% and the oxygen sensor will NOT be in alarm
- 10% of LEL methane is just 5000 ppm, this will theoretically cause a drop in oxygen of 0.1% but due to detector dead-band users probably will not see this drop
- At UEL of Methane (or 15% by volume) the oxygen level will be 17.9%
- So oxygen measurements are a crude LEL sensor but sometimes they are all we have
- ***Remember that once oxygen levels drop below 12-16% cat bead LEL sensors may be unreliable***

Oxygen sensors as a LEL sensor

- ***The oxygen sensor will not be in alarm at LEL levels of common gases and 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
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

Agenda

- Wheatstone bridge catalytic bead
  - Response, calibration & correction factors
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  - Oxygen Displacement
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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”

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**
Methane	5	50,000	5,000	Not detectable with PID
Hydrogen	4	40,000	4,000	Not detectable with PID
Propane	2	20,000	2,000	Not detectable with PID
Gasoline	1.4	14,000	1,400	1,556
Acetone	2.2	22,000	2,200	2,000
Benzene	1.2	12,000	1,200	2,264
n-Pentane	1.5	15,000	1,500	179
MEK	1.8	18,000	1,800	1,636
Toluene	1.2	12,000	1,200	2,400
Diesel	0.8	8000	800	1,143

* 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

PIDs for combustible vapors

Advantages

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

Disadvantages

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

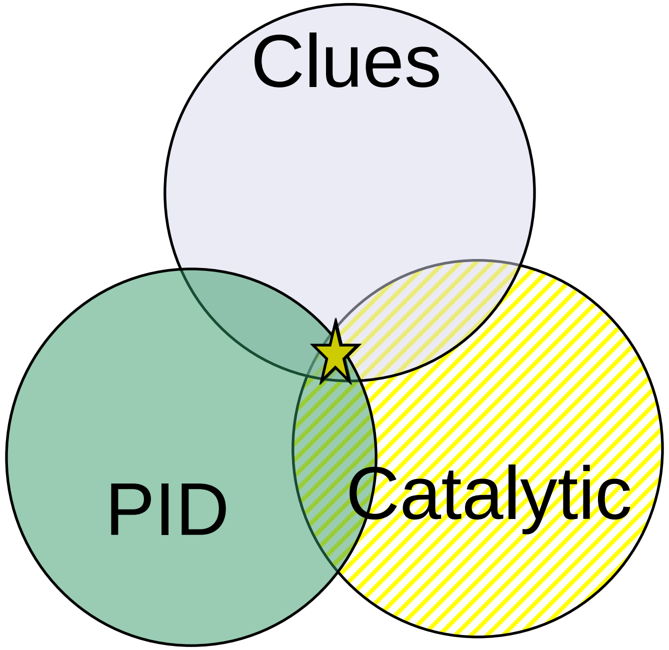
Agenda

- Wheatstone bridge catalytic bead
  - Response, calibration & correction factors
  - Poisons
- High range flammability
  - Oxygen Displacement
- Photoionization Detector (PID)
- Which technology should I trust

Fuel Oil in the Basement

- In the spring of 2010 a fuel oil delivery truck mistakenly delivered to the wrong address in northern VA
- The wrong house had a disconnected oil fill tube because the house had been converted to natural gas
- The driver “delivered” nearly 700 gallons before realizing that the house was only supposed to have a 250 gallon tank
- The oil filled the basement and flowed into the sewers via a floor drain
- Responders found pools of fuel oil in the basement with readings of about 250 ppm on their PID and nothing on LEL

Fuel Oil in the Basement



- **Clues:** pools of heating oil
- **Catalytic:** little to no reading for fuel oil (but house had natural gas)
- **PID:** 250 ppm fuel oil units or 2.5% of LEL

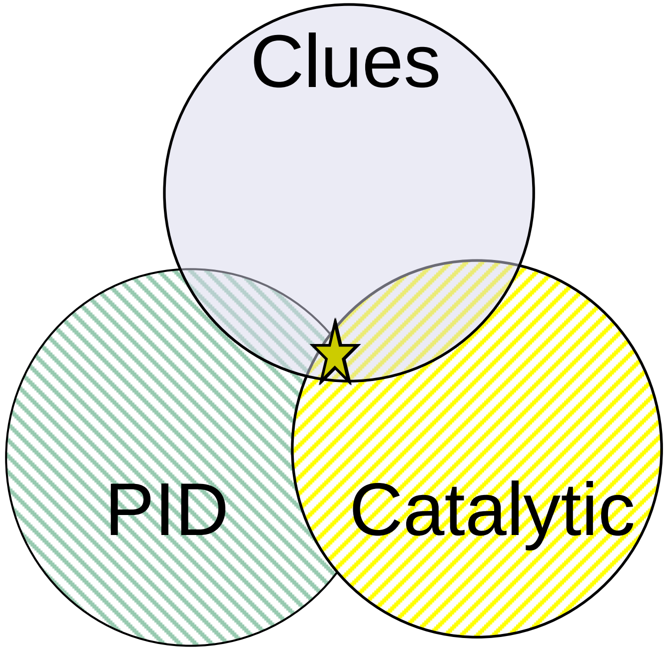
☆ = 250 ppm of fuel oil on the PID is ~2.5% of LEL

O_2: 20.9, LEL: 0, CO: 0, H_2S: 0, PID: 278

Sewer Investigation

- A sewer authority need to track down people dumping industrial chemicals in their sewer because the organic solvents were harming the digester at their treatment facility
- This required entering the sewer to “sniff out” where the chemical was coming from
- Investigators used a multi-sensor confined space detector with catalytic bead sensor for the methane in the sewer and a PID to track or “sniff out” the organics

Sewer investigation



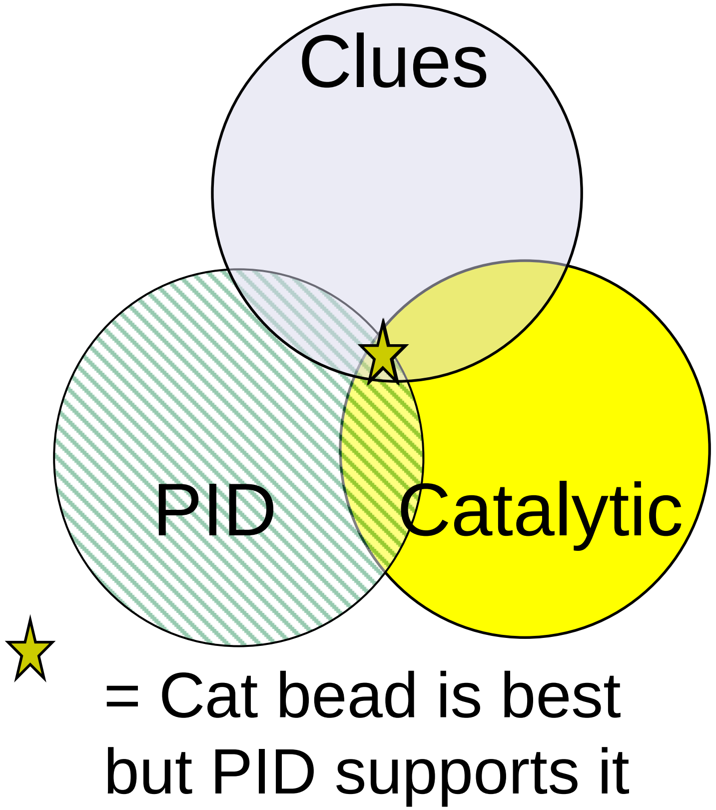
- **Clues:** sewer investigation
- **Catalytic:** strong reading for methane no reading for the organics
- **PID:** strong reading for organics

★ = PID for sniffing and LEL for methane flammability

Natural Gas Leak

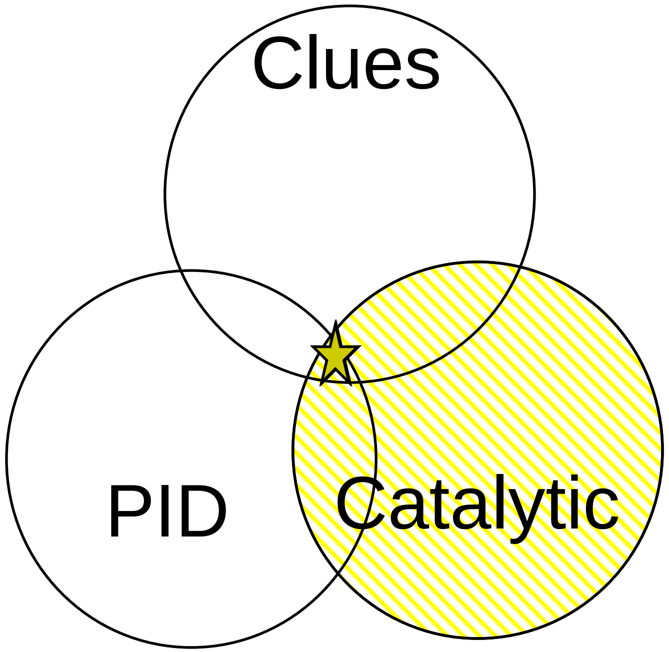
- Large natural gas leak “filled” a basement with natural gas
- LEL read above 20% on a methane scale
- PID read above 400 ppm

Natural Gas Leak



- **Clues:** natural gas leak with strong smell
- **Catalytic:** strong reading
- **PID:** reading represents contaminants in natural gas as well as the mercaptan odorants

Combustible Gas Sensors



- Only catalytic bead sensors are a primary measurement technology, that's why it is at least hatched for every proceeding story
- Know your measurement gas scale
- Watch out for catalytic bead sensor poisons
- All other combustible gas sensors will have "blind spots" to some classes of combustible gases
- Catalytic bead and PID sensors are a great pairing for LEL measurements because they have complimentary "blind spots"
- ***When possible, multiple sensors can help your decision-making***

Make a LEL simulator

- Take a clean 5 gallon paint bucket with a small screw off lid to sample from
- Add about 10 cc (0.3-0.5 once) of a volatile liquid
    1. Start with a relatively high vapor pressure liquid like acetone or lacquer thinner
    2. Clean out the bucket and let air out for at least 15 minutes outside (or make a second one). Then compare response to a low vapor pressure combustible liquid like mineral spirits or diesel
- Swish or agitate the bucket to get the liquid to vaporize as much as possible
    - It is recommended to “burp” the screw off lid so that the vapors don’t overpressure the bucket
- Sample with LEL sensor and PID and compare

Course Agenda

- Why do we need Detection Technologies?
- Measuring Atmospheric Hazards
  - Oxygen
  - Combustible Gases & Vapors
  - Detecting Toxic Gases & Vapors
    - Understanding Exposure Limits (Alphabet Soup)
    - Electrochemical Sensors
    - PID as your basic sniffer
- Getting the Most From Your Meters
  - Caring for your detectors
  - The Importance of Calibration

Alphabet Soup

Understanding exposure limits
and how to use them

Agenda

- What are Exposure Limits
- Occupational Exposure Limits
- Some Exposure Limit Examples

Everything is Toxic

- Even benign substances like water are toxic in quantity
  - On January 12, 2007, Jennifer Strange, 28, died of water intoxication after taking part in the "Hold Your Wee for a Wii" contest on KDND radio in Sacramento, CA
- Toxicity is a concept to help one judge if enough chemical is present to cause humans negative effects
  - Acute = immediate effect
  - Chronic = effects come later
- A newscast that says “a cloud of toxic chemicals blanketed the town” is wrong because they have no way of knowing the concentration of the potential toxins
- The newscast would be correct in saying “a cloud of potentially toxic chemicals blanketed the town”

What are Exposure Limits?

- Exposure limits are line in the sand that help us make informed decisions about human exposures to chemicals in the form of gases, vapors and mist
- Exposure limits protect workers against the health effects of exposure to hazardous substances
- As "the dose makes the medicine" (1^{st} said in the 16^{th} century by Paracelsus) exposure limits are given in some unit of measure
- Exposure limits only cover a small number of the 10’s of 1000’s of chemicals used in the world today

What are Exposure Limits?

- Exposure Limits apply to the "average" worker and may not be applicable to smaller or larger workers
  - Much of the epidemiological data is based upon white men because they have historically made up the working population
- Exposure limits are determined by:
  - Epidemiology: the study of factors affecting the health and illness of populations, and serves as the foundation and logic of interventions made in the interest of public health and preventative medicine
  - Toxicological studies of workers, cohort mortality studies
  - Laboratory bio-assays
  - Animal studies

What are Exposure Limits?

- Exposure Limits are expressed as a concentration in air because the primary mechanism for chemical exposure is absorption through the lungs
  - Lungs: gas permeable organ with $70m^2$ ($750ft^2$) of surface area or approximately the same amount of area of one side of a tennis court
  - Skin: gas and liquid resistant organ with 1.5-$2m^2$ (16-$20ft^2$) of surface area
- Exposure Limits can be expressed in the following scales
  - parts per million (ppm)
  - parts per billion (ppb)
  - milligrams per cubic meter (mg/m^3)

Parts Per Million (ppm)

- 1 ppm is the same as 1 inch in 16 miles
- 1 ppm is the same as 1 oz in 10,000 gallons
- ppm (and ppb or parts per billion) are commonly used to express concentrations of gases and vapors

  - 1 pbb is the same as 7 people out if the entire earths population

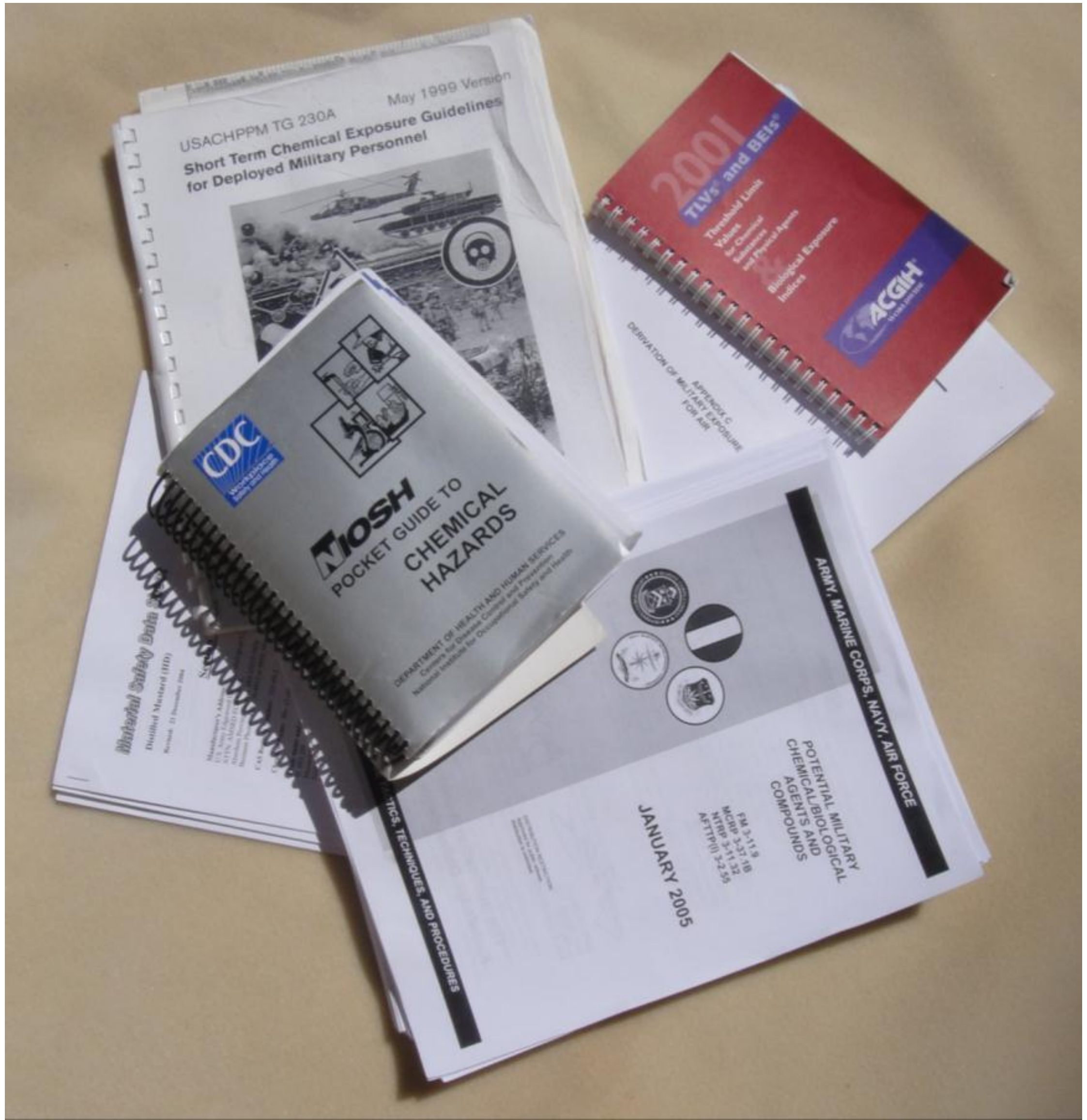
Who sets Exposure Limits?

- Government Agencies
  - OSHA: US Occupational Health and Safety Administration
  - NIOSH: US National Institute for Occupational Safety and Health
  - CHPPM: US Army Center for Health Promotion and Preventive Medicine
  - EPA: US Environmental Protection Agency
  - EU: European Union members create OELs (Occupational Exposure Limits)
- Non-Government Agencies
  - ACGIH: American Conference of Industrial Hygienists

Where Can One Find Exposure Limits?

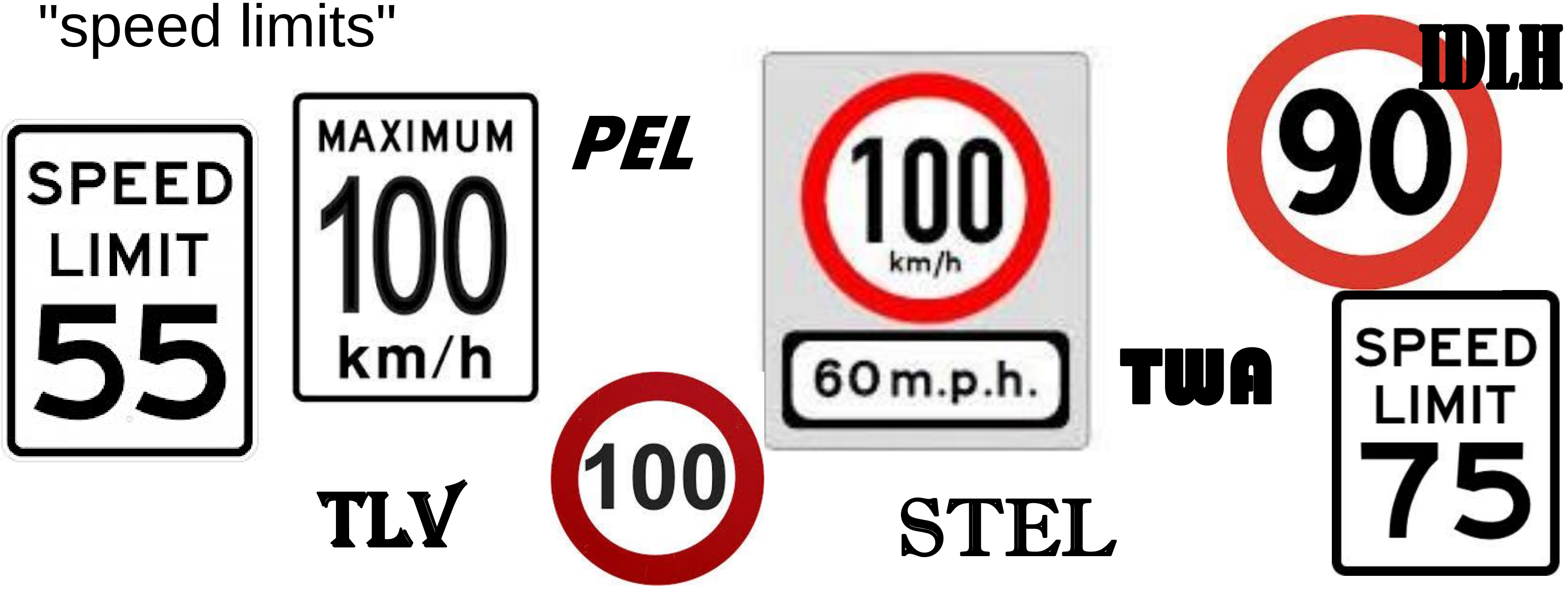
- NIOSH “Pocket Guide”
  - NIOSH RELs
  - OSHA PELs
- ACGIH “Threshold Limit Values for Chemical Substances and Physical Agents” (TLVs)
- Safety Data Sheets (SDS)
- Various government publications

Who sets Exposure Limits?



Exposure Limits are the “Speed Limits” for gases and vapors

- Exceeding the speed limit can get you into trouble
- We are "enforcing" the “speed limit” with gas/vapor detectors
- If you don't understand exposure limits and where they are coming from you can't properly obey and enforce the "speed limits"



Agenda

- What are Exposure Limits
- Occupational Exposure Limits
- Some Exposure Limit Examples

Permissible Exposure Limit (PEL)

- The PEL is the legal limit in the US for exposure of an unprotected worker to a chemical
- PELs are regulatory limits on the amount or concentration of a substance in the air
- PELs protect workers against the health effects of exposure to hazardous substances
- PELs are also found as the “Z tables” (29 CFR 1910.1000) listing ~450 chemicals
  - Largely based on the 1968 ACGIH TLV list adopted as law in 1971 (so they represent really old data)

Permissible Exposure Limit (PEL)

- PELs are created by OSHA and carry the force of law!
  - Even “Non-OSHA states” must at least follow OSHA but they typically adopt the more conservative TLVs (ex: CA)
- PELs are usually expressed in parts per million (ppm) or sometimes in milligrams per cubic meter (mg/m^3)

PELs

- OSHA Permissible Exposure Limits can be defined in three ways:
  - Time Weighted Average (TWA) is the most typical expression
  - Ceiling, used for quick acting irritants
  - Short Term Exposure Limit (STEL)

Threshold Limit Value (TLV)

- Determined by ACGIH
  - Peer reviewed
  - Consensus based process using a volunteer committee
- The TLV list "is the most popular source of alternative, more modern limits"
  - The OSHA PEL for trichloroethylene (TCE), based upon the 1961 TLV, is 100 ppm while the current TLV (2007) is 10 ppm
- Guidelines for control of potential health hazards
  - OSHA recognizes that many of their exposure limits are dated and while to seek to update them soon they currently provide a comparison of TLVs to RELs & CA TLVs at: https://www.osha.gov/dsg/annotated-pels/index.html

Threshold Limit Value (TLV)

- TLVs take into account recent research and change much quicker than PELs or even RELs
- Intended as recommendation
- Some states and other organizations like US Military adopt TLVs as their standards

What is a TWA?

- If the instantaneous reading on a gas detector is like how many miles per hour we are traveling
- TWA is like an odometer alarm that says that if we keep traveling at this rate after 8 (or 10) hours we will have traveled too far for that day (too much dose)
- A further simplification is that TWA is like the average “speed limit.” If you keep at or below the speed limit you won’t get into trouble

TWA is the “Speed Limit”

- In industrial settings TWA can be looked upon as the “speed limit”
- Staying at or around the speed limit is the goal in industrial settings
- Most detectors are designed around the speed limit (TWA) and may have issues when exposed to concentrations that are well above the “speed limit” such as IDLH
- Therefore, concentrations significantly above TWA values can lead to cross-sensitivities and other “crazy” readings on the target sensor or other sensors used in the high concentration environment

What is a STEL?

- STEL: Short Term Exposure Limit
- If TWA is an 8-10 hour "dosage" alarm STEL is a 15 minute dosage alarm
- Some gases and vapors have an allowable maximum STEL which is higher than the 8 hour TWA
- STELs are a 15-minute, time-weighted average exposure which should not be exceeded at any time
- STEL exposures should not be repeated more than four times daily with a 60-min. rest period required between each STEL exposure

$$\frac{\text{(the sum of all max logged values in last 15 min)}}{\text{values in last 15 min}}$$

What is a Ceiling Limit?

- Ceiling is the maximum concentration to which an unprotected worker may be exposed
- Ceiling concentration “must not be exceeded during any part of the workday”
- If no Ceiling value is given for a chemical then the IDLH becomes the Ceiling value

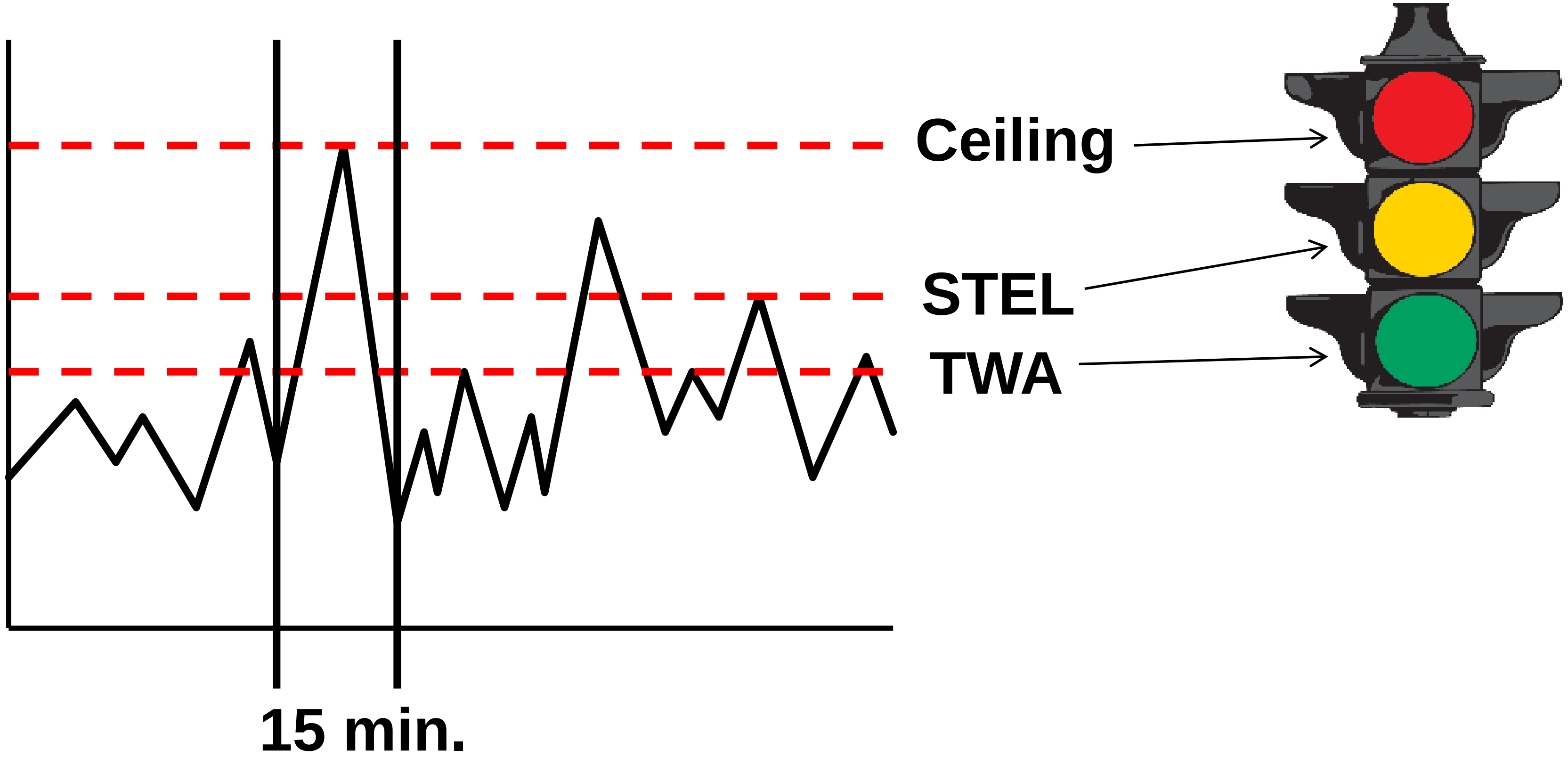
What is IDLH?

- IDLH: Immediately Dangerous to Life and Health
- “The IDLH was considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection was permitted”
- “the ability of a worker to escape without loss of life or irreversible health affects”
- Critical symptoms that could retard escape are:
  - Blindness
  - Unconsciousness
  - Impaired judgment

What is IDLH?

- “As a safety margin…IDLH values were based on the effects that might occur as a consequence of a 30-minute exposure”
- However every effort should be made to exit the area immediately when IDLH levels are present
- Four basic IDLH environments
  - Toxicity above IDLH defined levels
  - Oxygen deficient below 19.5%
  - Oxygen enriched above 23.5%
  - Anything above 10% of LEL (once you are above this you are well past most toxic levels)

STEL vs. TWA and Ceiling



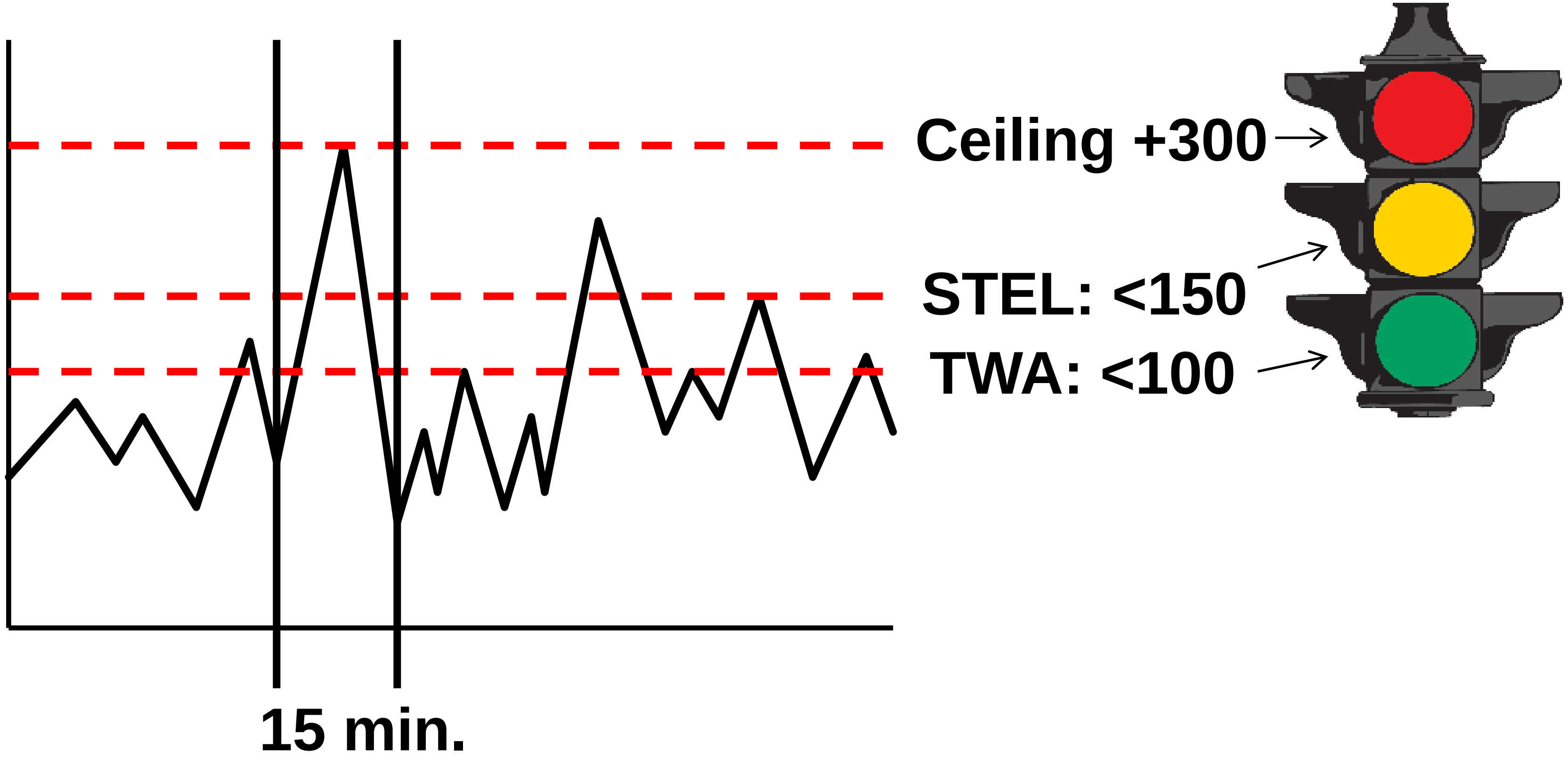
Ceiling, STELs & IDLHs work together to keep people honest

- Toluene has a NIOSH TWA of 100 ppm (OSHA 200 ppm), so an unscrupulous employer could have someone work in 800 ppm of Toluene for one hour and then send him out to rake leaves for the other seven hours of work and still be legally under the TWA

Ceiling, STELs & IDLHs work together to keep people honest

- But Toluene has a NIOSH STEL of 150 and an OSHA ceiling of 300 ppm that prevents this from occurring
- The IDLH and the OSHA 5 minute maximum peak is 500 ppm which also prevents this kind of abuse

Ceiling, STELs & IDLHs work together to keep people honest



Agenda

- What are Exposure Limits
- Occupational Exposure Limits
- Some Exposure Limit Examples

Industrial Users

- Conservative seems to be the best way to protect ones company
- The OSHA “General Duty Clause” states:
  - Each employer…shall furnish to each of his employees employment and a place of employment which are free from recognized hazards that are causing or are likely to cause death or serious physical harm to his employees

Industrial Users

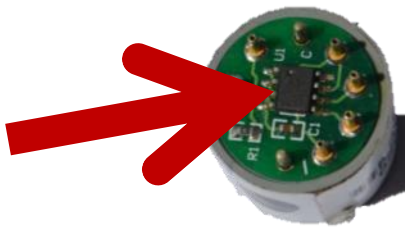
- Some think that PELs provide complete legal protection from the General Duty Clause
- But the courts have found that PELs **DO NOT** provide complete protection from the general duty clause
- To provide the best protection from liability from the general duty clause due to exposures to chemicals many companies adopt the most conservative limits which often are represented by the TLVs

What exposure limit(s) should a responder use?

- Conservative is always best because there is less second guessing
- For most “normal” responses of less than 12 hours staying under the TWA as a not to exceed limit is a VERY conservative set point
  - Examples include toluene, acetone, ammonia
- Chemicals with higher toxicity and very low exposure limits mean greater usage of STELs and IDLHs
  - Examples include benzene, phenol, TDI, ETO, Cl_2

Gas Detector Manufacturers Can Help

- Specific toxic gas sensors usually automatically set alarm levels for the chemical that they were designed for when they are plugged into a detector
  - The chip on the sensor carries the appropriate exposure limit information
  - CO, H_2S, Cl_2, NH_3, PH_3, SO_2
- Some broadband detectors (PIDs) will automatically set alarm levels when the correction factor is set but only for low (ascending), high (ascending), TWA (sometimes running average or “AVG”) and STEL alarms



Course Agenda

- Why do we need Detection Technologies?
- Measuring Atmospheric Hazards
  - Oxygen
  - Combustible Gases & Vapors
  - Detecting Toxic Gases & Vapors
    - Understanding Exposure Limits (Alphabet Soup)
    - Electrochemical Sensors
    - PID as your basic sniffer
- Getting the Most From Your Meters
  - Caring for your detectors
  - The Importance of Calibration

Getting the most from toxic gas sensors

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

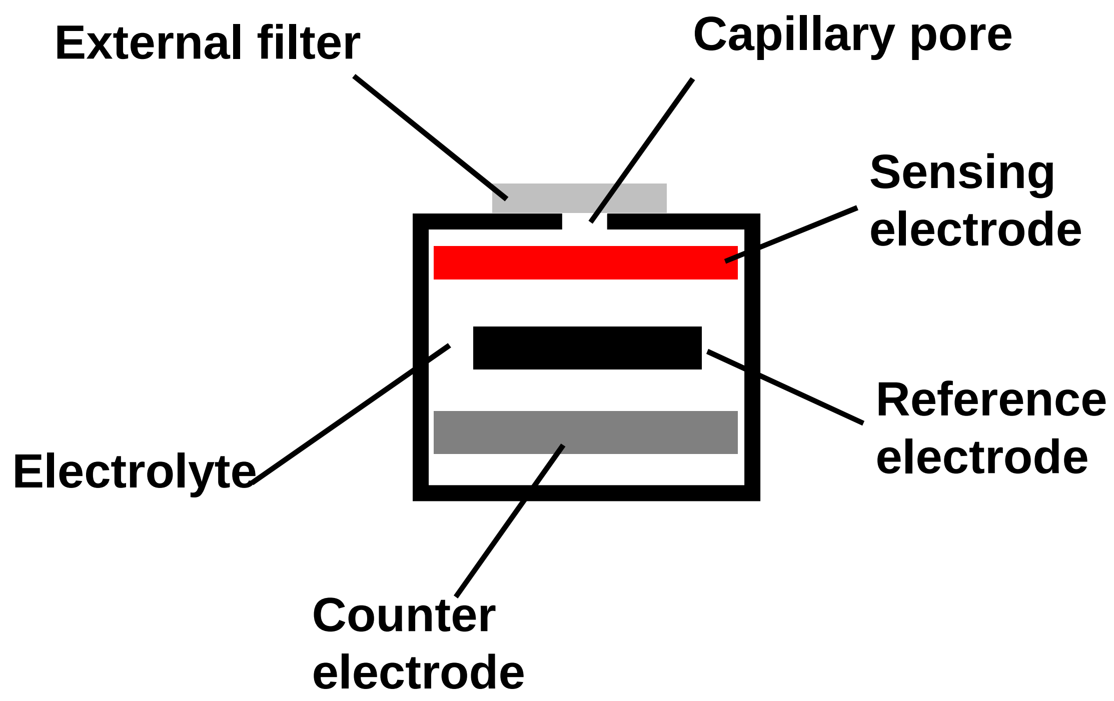
Topics: EC Sensors

- How Electrochemical (EC) toxic gas sensors work
- Understand basic sensor specifications and how they might impact decision-making

EC Toxic Gas Sensors

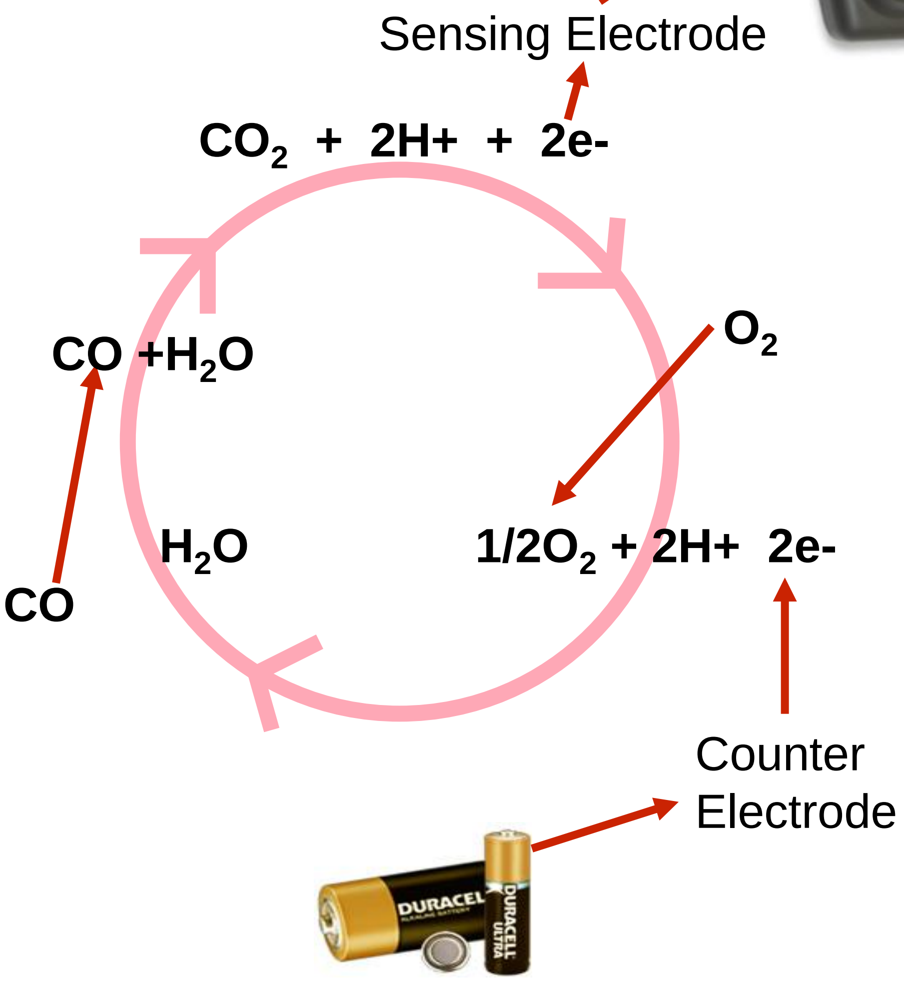
- Basically the EC sensor is a battery that turns concentrations of the gas of interest into a current output in proportion to the concentration of the gas
- EC sensors are similar to dry cell batteries in construction
- Gas diffusing into sensor reacts at the surface of the sensing electrode
- The sensing 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



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

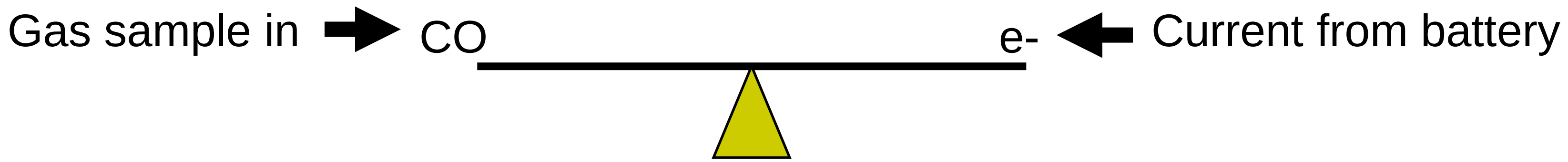


Consuming EC Sensors

- 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

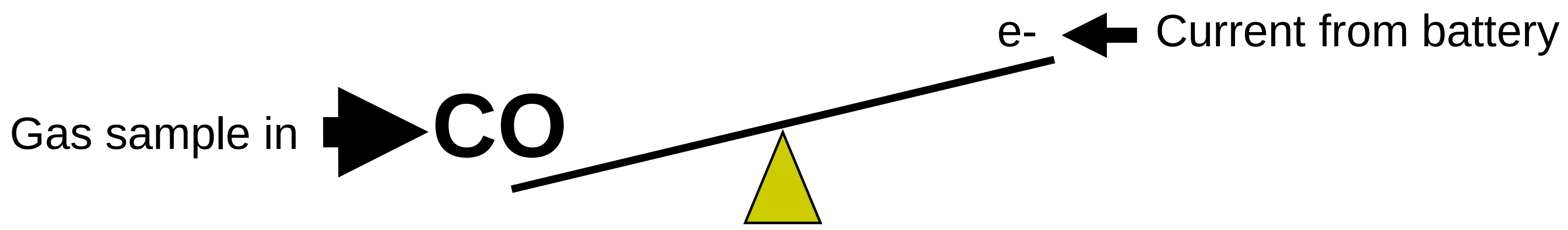
- Another way to look at EC sensors is that they are like a "see-saw"



- 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.

Topics: EC Sensors

- How Electrochemical (EC) toxic gas sensors work
- Understand basic sensor specifications and how they might impact decision-making

What do sensor specs mean?

- Just like human’s, 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 a sitting has killed people
- Understanding your sensors’ limitations will help you make better decisions
- Sensor limitations are defined in sensor specifications published by detector 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 detector 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)

What do sensor specs mean?

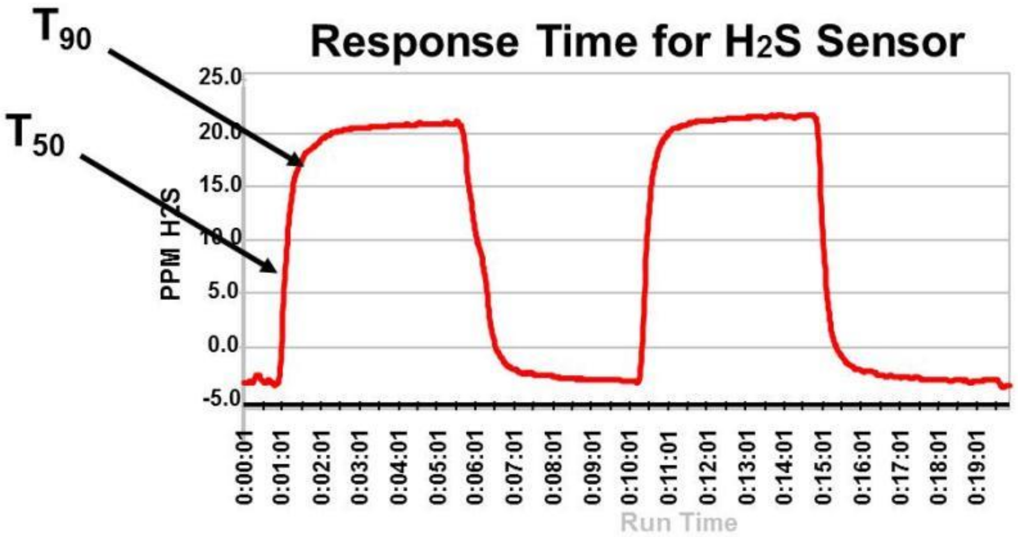
- **Range:** the normal operating concentration of a sensor where the best linearity is found. Exceeding the normal operating range may result in erroneous readings and long recovery times, but should not permanently damage the sensor as long as the Max Overload is not exceeded.
- **Max Overload:** The highest concentration of that the electrochemical cell can see before it is potentially irreversibly harmed. This rating is like the "Sensor IDLH." 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***

What do sensor specs mean?

- Electrochemical 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

Sensors don't respond instantly

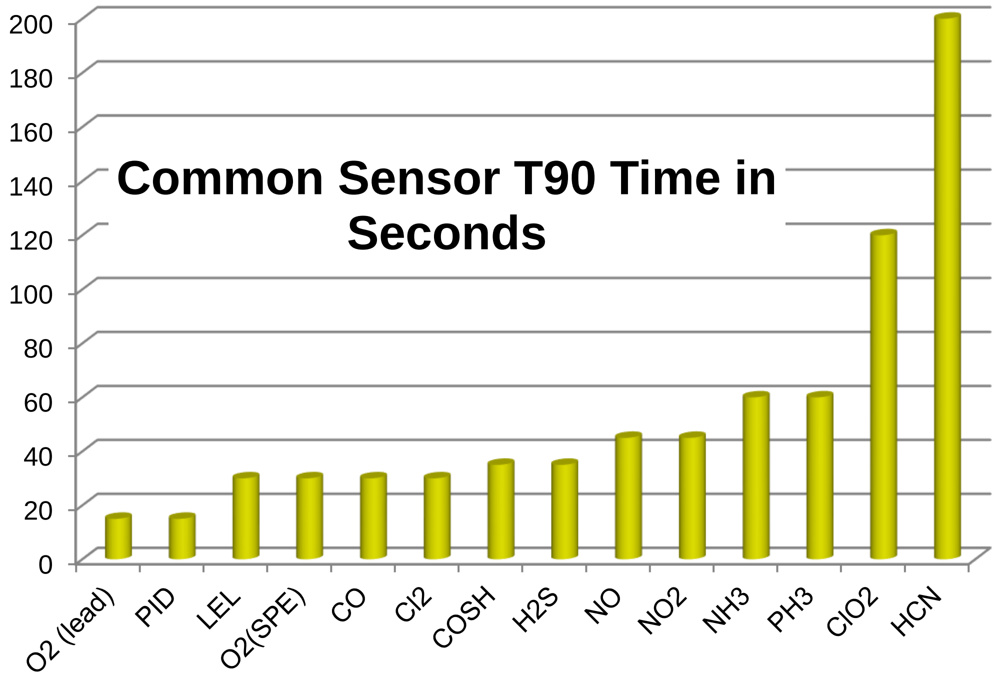
- **Response Time:** time for sensor to reach its final stable reading. Typically called T_{90},or time to 90% of response and usually expressed in seconds.



- ***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***

Sensors don't respond instantly

- The common O_2, LEL, CO, H_2S and PID 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 detector, 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 take significantly longer to respond



Sample tubing will effect response time

- Response time increases on pumped detectors when extension tubing is used
- As a rule of thumb with a safety margin, for most detectors 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
- 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 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
  - Corrosive and reactive gases such as NH_3, Cl_2, ClO_2, HCl, HCN and NO_2 may be absorbed particularly by Tygon tubing
  - 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, H_2S, PH_3, SO_2 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 NH_3 and HCl can be absorbed into the water, reducing or eliminating response
  - Water can block flow and can destroy sensors and detectors
  - Always watch for moisture in your sample line

What do sensor specs mean?

- **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!
- ***Personal gas detectors are designed to protect people and largely they can live where people live***

Electrochemical Toxic Sensors

Advantages

+ Continuous Readings
+ Proven Technology
+ Reasonably Specific

Disadvantages

– "Exotic" sensors can be expensive to purchase and to calibrate
– "Exotic" sensors typically have 1 year life

Course Agenda

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  - The Importance of Calibration

PIDs as your basic sniffer

Training Agenda

- What is a PID?
- Making Decisions with a PID

Why are PIDs important?

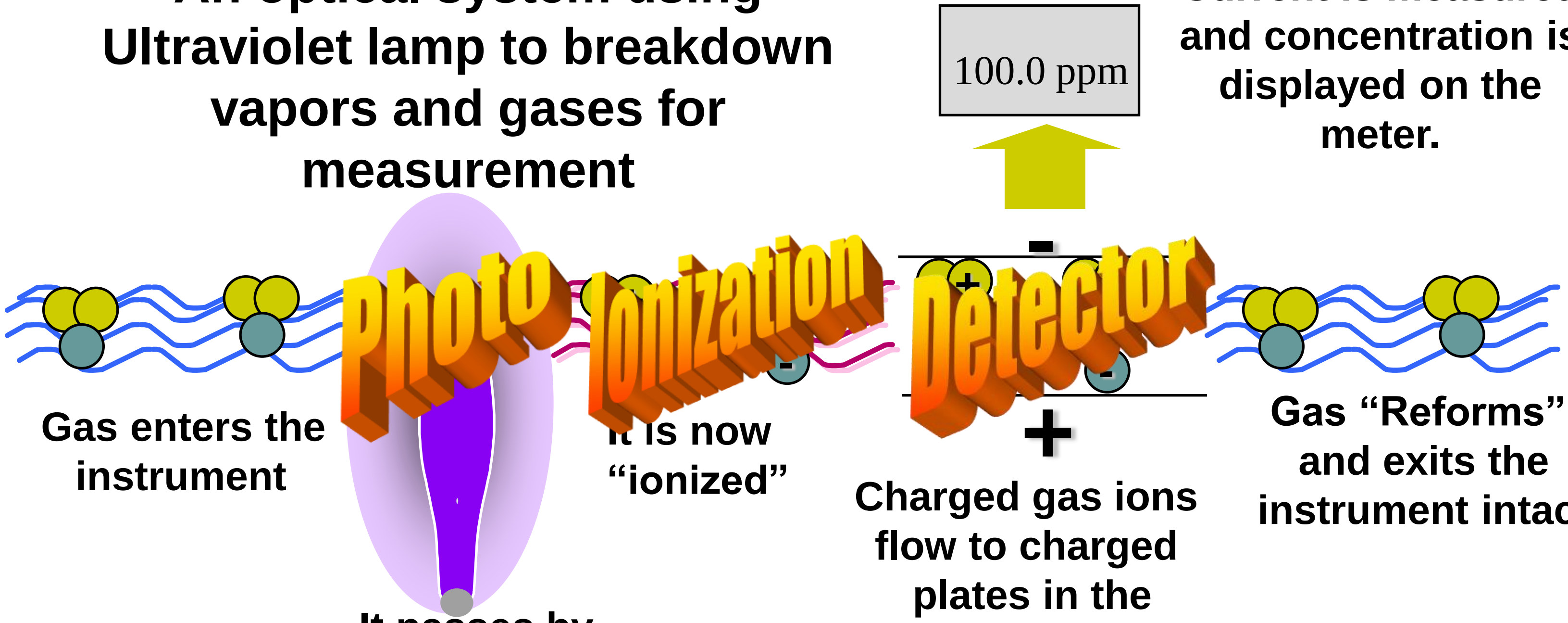
- After oxygen, flammability and your basic electrochemical toxic sensors, broadband sensors like PIDs are one of your best tools to quickly identify if something is out there
- On their own, PIDs will not tell you what that “something” is, but they can often quickly tell you where it is coming from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

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
- A PID is a very sensitive broad spectrum detector, like a “low-level LEL”

How does a PID work?

An optical system using Ultraviolet lamp to breakdown vapors and gases for measurement



Gas enters the instrument

It passes by the UV lamp

It is now "ionized"

Charged gas ions flow to charged plates in the sensor and current is produced

Current is measured and concentration is displayed on the meter.

Gas "Reforms" and exits the instrument intact

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

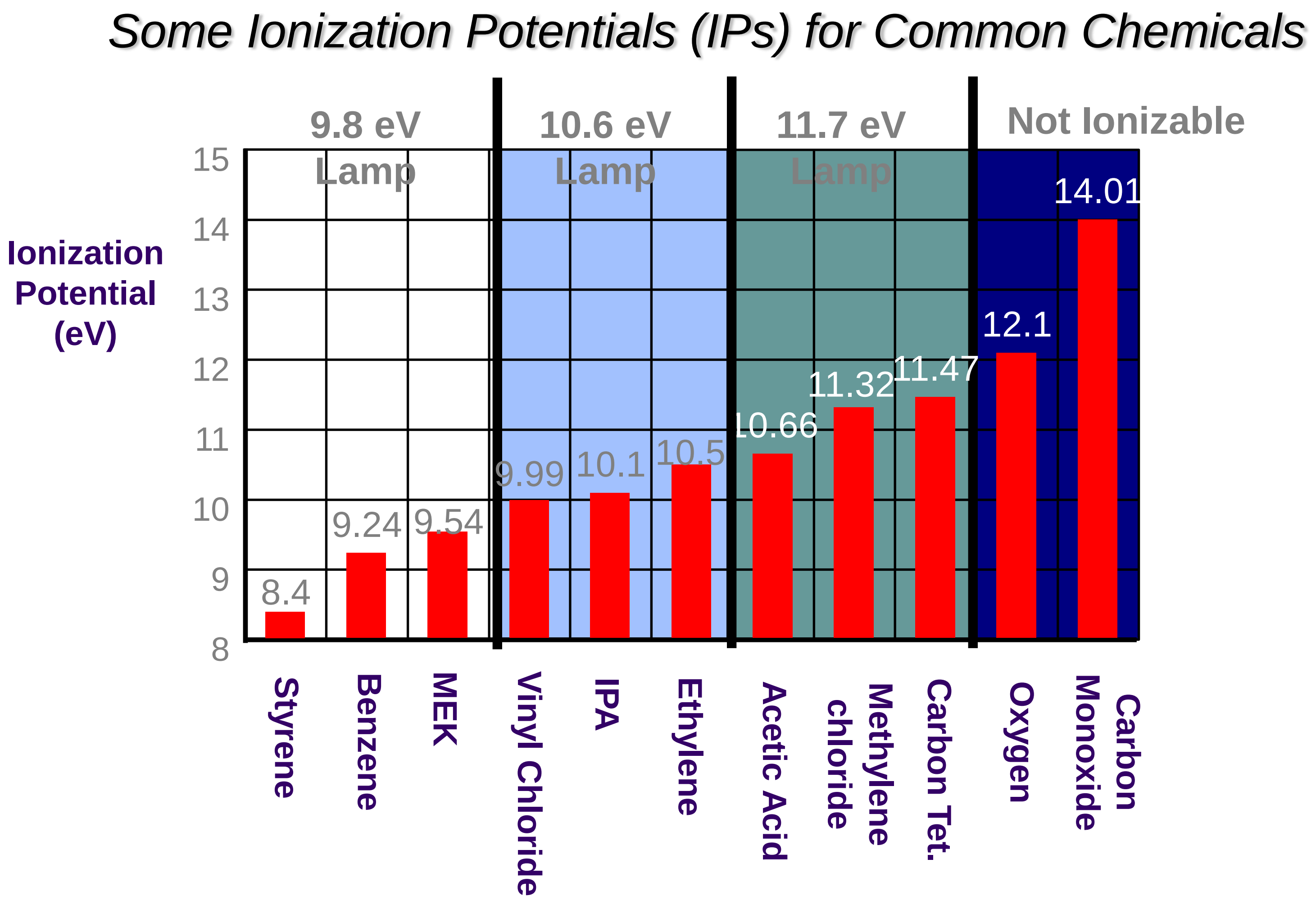
What does a PID Measure?

Ionization Potential

- IP determines if the PID can “see” the gas
- If the IP of the gas is less than the eV output of the lamp the PID can “see” it
- Ionization Potential (IP) does not correlate with the Correction Factor
- Ionization Potentials are found in the NIOSH Pocket Guide, many chemical texts and PID manufacturer correction factor charts (for example RAE System TN-106)

If the “wattage” of the gas or vapor is less than the “wattage” of the PID lamp then the PID can “see” the gas or vapor!

What does a PID Measure?

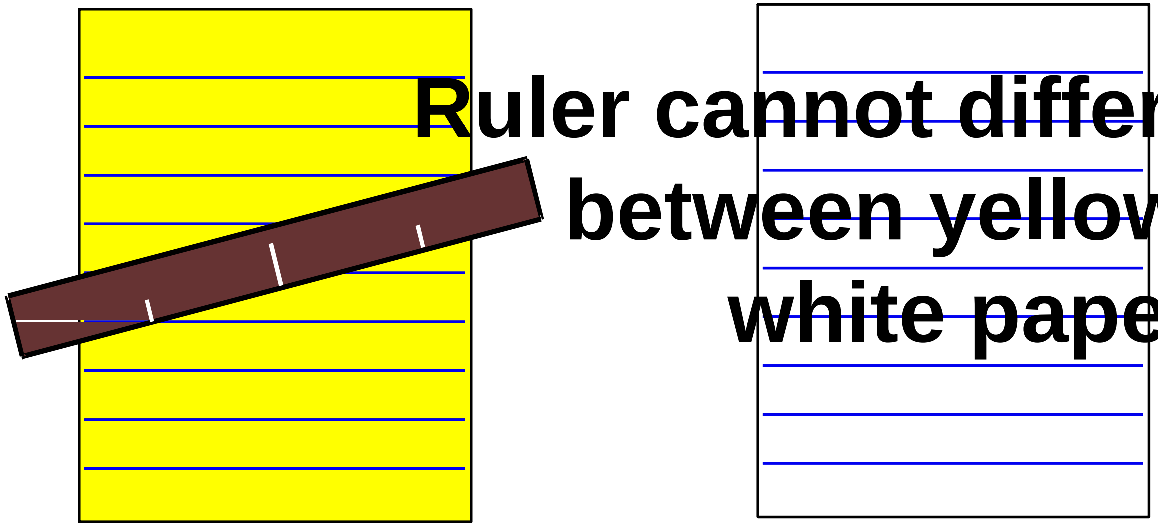


Why mostly 10.6 eV and not 11.7 eV Lamps?

- 9.8 & 10.6 provide more specificity
- 10.6 lasts 24-36 months
- 10.6 provides best resolution
- 10.6 costs less ($195)
- 11.7 is required for high energy compounds like Methylene Chloride
- 11.7 crystal absorbs water and degrades
- 11.7 lasts about 2-3 months
- 11.7 costs more ($295 and higher)

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

Training Agenda

- What is a PID?
- Making Decisions with a PID

PID Alarms: the 50/50 Rule

When Measuring in Isobutylene Units and set to 50 ppm RAE PIDs will protect from over 50 of the most common Chemicals:

- Acetone
- Cyclohexane
- Diesel Fuel
- Ethyl alcohol
- Ethylbenzene
- Gasoline
- Heptane, n-
- Hexane, n-
- IPA
- Jet Fuel
- MEK
- MIBK
- MPK
- Nonane
- Octane, n-
- Pentane
- Stoddard Solvent
- Styrene
- Tetrahydrofuran
- Toluene
- Trichloroethylene
- Xylene

Guidelines for PID use

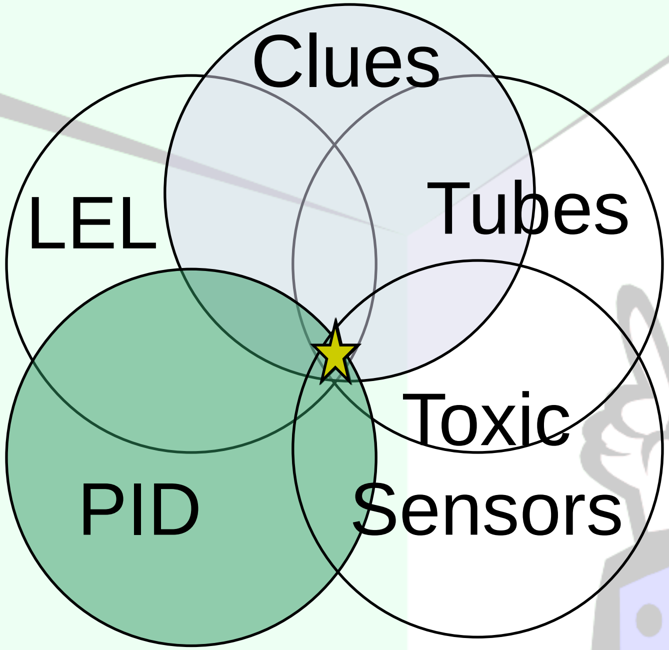
- **1 ppm:** may be nothing in outdoor environment but for IAQ it definitely means that something is going on (assumes properly calibrated PID)
- **10 ppm:** something is definitely going on outside
- **50 ppm:** mask up (or 50% of most TWAs)
- **100 ppm:** TWA has most likely been exceeded
- **1000 ppm:** 10% of LEL and therefore IDLH has most likely been exceeded
- **10,000 ppm** (or 1% by volume): 100% of LEL has most likely been exceeded

Apartment Bldg. CO Detector

- Portable CO detector showed no CO
- CO Colorimetric tube found no CO
- PID read 100 ppm
- Investigation revealed spray painting had taken place
- Home CO detectors use less filtered CO sensors that can respond readily to hydrocarbons

Hor

Apartment Bldg. CO Detector



★ =spray paint set off home CO detector

- Clues: Apartment CO call, smells like paint solvent
- Tubes: no reading on CO tube
- Toxic Sensors: 0 ppm reading on CO
- PID: 100 ppm reading on PID
- LEL: no reading on LEL

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

Which PID for Me?

- Multigas with PID
  - Like your Swiss Army Knife or Leatherman
  - If you have only one tool this should be it

- Straight PID
  - Like your DeWalt 18volt driver
  - While the Leatherman has a Phillips screwdriver on it you wouldn’t hang drywall with it
  - Best for decon and leak detection or situations where the gas in question could kill other sensors

Course Agenda

- Why do we need Detection Technologies?
- Measuring Atmospheric Hazards
  - Oxygen
  - Combustible Gases & Vapors
  - Detecting Toxic Gases & Vapors
    - Understanding Exposure Limits (Alphabet Soup)
    - Electrochemical Sensors
    - PID as your basic sniffer
- Getting the Most From Your Meters
  - Caring for your detectors
  - The Importance of Calibration

Care of CSE detectors

- Aside from sensor failure, much of Confined Space detector failure is due to abuse
- Training should emphasize users to respect this life support system

"You wouldn't drop your cell phone in a puddle or throw it against the wall so treat your Confined Space detector with the same respect"

Storage of CSE detectors

- Temperature extremes can lead to both battery and sensor failure
- Hot temperatures can "cook" electrochemical sensors causing "desiccation" and early failure
- Cold temperatures can slow chemical reactions and reduce or eliminate electrochemical sensor response
  - Refrigerators and freezers slow chemical processes so our food doesn't spoil

Storage of CSE detectors

- Freezing temperatures can even rupture electrochemical sensors when the aqueous electrolyte freezes

"Store detectors in areas where you would like to work"

Detectors can operate for periods in temperature extremes, but you still cannot "Cheat" physics

Charging CSE detectors

- Watch charging temperatures
  - Unless designed for in-case charging, the foam in cases can hold the heat of charging which can damage detectors, sensors and batteries
  - NiMH batteries should charge between 32-104^{o}F (0-40^{o}C), charging below 32^{o}F/0^{o}C may cause leakage of battery electrolyte
  - NiCad batteries should charge between 41-86^{o}F (5-30^{o}C), charging below 32^{o}F/0^{o}C may build up gas in the battery

When to replace sensors

- As long as sensors pass their calibration test then they are good to use
  - If they don't calibrate they need to be replaced

A Responsible Party

- Somebody needs to be “in charge” of your meter program
- Without someone in charge it ends up being run by “not me” and the program suffers
  - Calibrations slip
  - Spares aren’t purchased
  - Detectors get abused

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)

Course Agenda

- Why do we need Detection Technologies?
- Measuring Atmospheric Hazards
  - Oxygen
  - Combustible Gases & Vapors
  - Detecting Toxic Gases & Vapors
    - Understanding Exposure Limits (Alphabet Soup)
    - Electrochemical Sensors
    - PID as your basic sniffer
- Getting the Most From Your Meters
  - Caring for your detectors
  - The Importance of Calibration

Calibrate or Die

The importance of calibration

Topics

- Why do we calibrate?
- What types of calibrations are there?
- How much calibration is enough?
- How to calibrate
- Where do I calibrate?
- Calibration can help improve your confidence in your meter

Why Calibrate?

- The importance of calibration for handheld gas and vapor detectors cannot be under-emphasized because many sensors fail to an unsafe state
  - An LEL sensor indicates a safe atmosphere when it reads zero but when it fails it also reads zero.
  - A Chlorine sensor indicates a safe atmosphere when it reads zero but when it fails it also reads zero
- While some sensors, like oxygen, usually fail to a safe or alarming state, they can benefit from calibration to restore their accuracy
- The only way to assure that sensors are working correctly is to apply a gas to them to “calibrate” them and make sure that they are working correctly so that users don’t die!

Why Calibrate?

- OSHA 1910.146 (the “CSE” standard) requires use of a “calibrated” instrument
- Identifies loss of sensitivity, failing or failed sensors
- Many sensors fail to an unsafe state
- Increases/restores operator confidence in their meter

Regular calibration guards against any unexpected loss of sensitivity

Calibration Improves User Confidence

- Gas detectors are a “Flashlight” allowing people to “see” toxic gases and flammable vapors
- You wouldn’t go into a dark basement without checking the operation of your flashlight
- Don’t go into a “dark” confined space without checking the operation of your detector
- Manual calibration helps to maintain “muscle memory” and user confidence in their detector

Topics: Calibration

- Why do we calibrate?
- What types of calibrations are there?
- How much calibration is enough?
- How to calibrate
- Where do I calibrate?
- Calibration can help improve your confidence in your meter

Calibration Types

- **“Bump”:** a qualitative test where the detector is shown calibration gas and all the sensors show response and alarms
  - Checks to show that the sensors AND alarms work
  - Could be as simple as exhaling into an oxygen sensor or showing a PID a marker pen
  - Pump check if applicable
- **“Calibration Check”:** a quantitative test where the detector is shown calibration gas of a known and traceable value and the user verifies that the readings correspond to ±10% of calibration gas values
  - Pump check if applicable

Calibration Types

- **“Full Calibration”:** the detector is shown calibration gas and readings are adjusted (automatically or manually) to the certified cal gas values following the manufacturer’s procedure
- **“Factory Calibration:”** the detector is returned to a certified factory facility for testing and adjustment (most new detectors do not have this requirement)

Calibration Check Catches a Bad CO Sensor

- A fire department took a multi-gas detector that had been calibrated that day to a CO call
- The fixed CO detector went into alarm every time the furnace was turned on, but the FD CO sensor only read 0
- A maintenance man’s CO detector show 60 ppm when the FD CO sensor still read 0
- Upon returning to the station the FD CO was “successfully” recalibrated
- But the detector did not respond to CO when it was applied to the detector (a “bump” or “calibration check”)

Calibration Check Catches a Bad CO Sensor

- It’s possible that that FD didn’t fully understand how to calibrate their detector
- But the “calibration check” did catch the problem
- When in doubt, a “bump” or a “calibration check” is always helpful

Topics: Calibration

- Why do we calibrate?
- What types of calibrations are there?
- How much calibration is enough?
- How to calibrate
- Where do I calibrate?
- Calibration can help improve your confidence in your meter

How Much Calibration is Enough?

- Follow manufacturers written recommendations
  - Don’t rely on unsupported verbal assurance from distributors or manufacturers concerning calibration requirements
  - If manufacturer says that you can calibrate LESS than one a month (every 6 months for example) then make sure this is documented IN WRITING
- Calibration frequency should also be driven by the level of threat
  - The higher or more frequent the risk, the more frequent calibration should take place

ISEA Calibration Statements

- The International Safety Equipment Association (ISEA, www.safetyequipment.org) is the leading organization of manufacturers of safety and health equipment including environmental detectors
- ISEA has developed "ISEA Statement on Validation of Operation For Direct Reading Portable Gas Monitors " (3/5/2010) to ensure definition consistency in all documentation, and to emphasize the need to validate the operational capability of portable gas detectors
  - http://www.safetyequipment.org/userfiles/File/calibration_statement-2010-Mar4.pdf

Calibration Frequency

- The following recommendations are either taken from or comply with ISEA recommendations
  - The safest course of action is daily check
    - Fresh air calibration (make sure that the air is CLEAN)
    - Expose the sensors to known concentration test gas before each day's use ("Bump" or "Calibration Check")
    - This test is very simple and takes only a few seconds to accomplish
    - With pumped units ALWAYs check pump flow/alarm during daily check
      - Connections, filters and tubing can fail
      - Leaks can dilute & diminish readings
  - Adjust span ("Full Calibration") should be done at regular intervals in accordance with instructions provided by the detectors manufacturer, company or regulatory agency policy
    - **Best practice is AT LEAST once a month or when necessary**

“Busting” the 30 day calibration “Myth”

- It seems that “calibrate every 30 days” is the most common recommendation verbally given by many distributors and sales reps, but this is often not a safe enough course of action
- According to ISEA: “Validation of an instrument’s operability should be conducted if any of the following conditions or events occurs during use:”
  - “Chronic exposures to, and use in, extreme environmental conditions, such as high/low temperature and humidity, and high levels of airborne particulates.”
  - “Exposure to high (over range) concentrations of the target gases and vapors”
    - Could be found on any HazMat call or overhaul detection assignment
  - “Chronic or acute exposure of catalytic hot-bead LEL sensors to poisons and inhibitors. These include volatile silicones, hydride gases, halogenated hydrocarbons, and sulfide gases”

“Busting” the 30 day calibration “Myth”

- “Chronic or acute exposure of electrochemical toxic gas sensors to solvent vapors and highly corrosive gases.”
- “Harsh storage and operating conditions, such as when a portable gas detector is dropped onto a hard surface or submerged in liquid. Normal handling/jostling of the detectors can create enough vibration or shock over time to affect electronic components and circuitry”
  - Like living on a vehicle
- “Change in custody of the detector”
  - Like any shift change
- “Change in work conditions that might have an adverse effect on sensors.”
- “Any other conditions that would potentially affect the performance of the detector.”

Detectors are designed for the industrial TWA environment

- Most gas detection equipment was designed for industrial detection where levels are expected to be at or near TWA values
  - Calibration recommendations are largely based upon detector use in the industrial TWA environment
- For applications where concentrations can exceed TWA values moving to IDLH and even higher (like first responders) more calibrations may be required
  - Calibrate after calls that over-ranged or otherwise “stressed” the detector
  - Calibrate at shift changes so that a detector that was inadvertently stressed by the previous shift performs properly for the next shift

Topics: Calibration

- Why do we calibrate?
- What types of calibrations are there?
- How much calibration is enough?
- How to calibrate
- Where do I calibrate?
- Calibration can help improve your confidence in your meter

Types of calibration

- First, ALWAYs follow your manufacturer's recommendation about calibration requirements
- Diffusion products are easy, just flow to the detector with an appropriate manufacturer recommended constant flow regulator
- Pumped units have many more options
  - ***Always check for pump flow on a daily basis by clogging the inlet and looking for a "pump" alarm***

Flow matching calibration

- Generally the preferred method of calibrating a pumped detector is using some form of matched flow calibration

Flow matching regulator calibration

- + A flow matching regulator mechanically matches gas flow to the pump's flow rate
- + If pump isn't flowing well the regulator won't open and the cal should fail
- + Conserves gas
- – Can be expensive to purchase regulator
- – Weak pumps may not open the regulator, sometimes this goes undetected

Flow matched vs. constant flow calibration

- While a flow matched calibration is preferred, many manufacturers will accept a constant flow regulator for use with their pumped units
  - For example pump draws at 250cc/min so regulator should flow at 250 cc/min
  - Using a 250cc/min regulator with a 500cc/min pump could starve the sensors of calibration gas or draw in ambient air leading to an inaccurate calibration
- The pumped device is connected directly to the tubing from the constant flow regulator
- Relatively inexpensive
- Easy to execute
- – May have accuracy variations if flow rate of pump is radically different from that of the regulator

Automated calibration

- + Automated “docking” stations help to reduce operator error by automating the calibration process
- + Manufacturer’s have a variety of calibration procedures, some do a full calibration daily, some do a daily “bump” and periodic calibration but all are designed to make sure that the meter is ready for use when you remove it from its charge/cal. cradle
- + Automates calibration, can document calibration
- – Can be expensive to implement
- – Tends to lock users into one vendor so customers don’t select ‘best of breed’ products in each detection segment
- – Discourages uses from touching the detector and developing good “muscle memory” during manual calibration

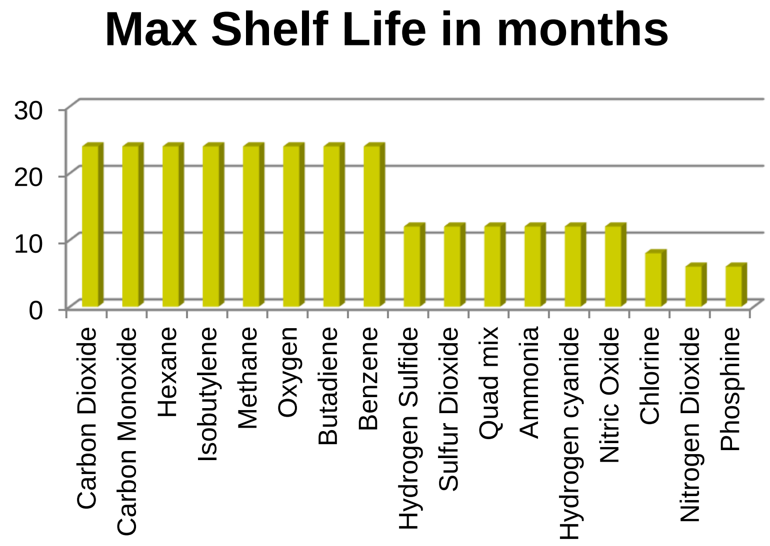
Bad Calibration from a “Docking Station”

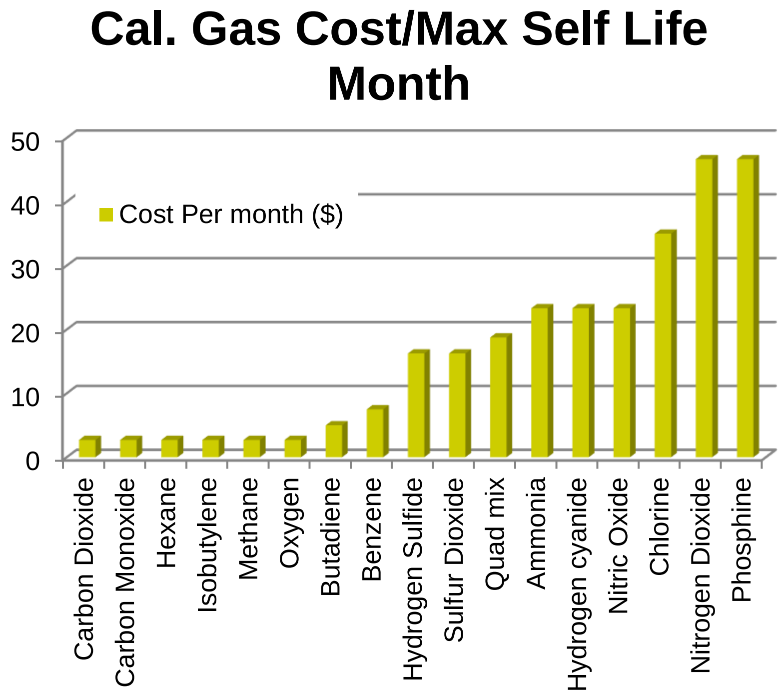
- After receiving new detectors and new docking stations a customer called their distributor to say that their new meters were “acting funny”
- When removed from their docking cradle the meters had very unstable readings, this was unexpected because the customer had a lot of experience using the previous generation of this detector doing manual calibrations
- Doing a “Calibration Check” with a bottle of calibration gas demonstrated that the calibration was not correct
- After a manual calibration was performed the meter performed as expected
- It was found that the docking station was improperly set up and the calibration gas was plumbed into the wrong input ports
- **Lesson:** it is a good idea to do a Calibration Check of meters after a docking station is set up and after calibration cylinders have been replaced

Virtually any calibration is better than no calibration!

- One can get caught up in calibration procedure on things like whether a flow-matching calibration is best
- Don’t lose sight of the fact that virtually ANY calibration is better than no calibration!

Calibration Gas Expiration





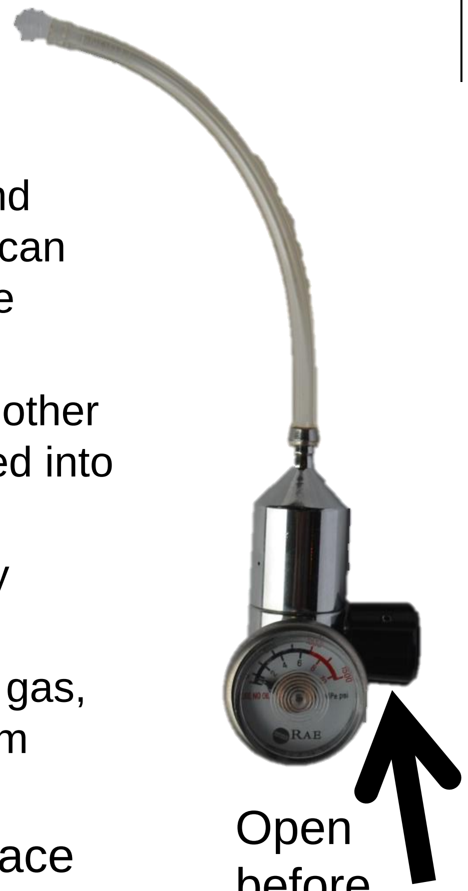
- Calibration gas will last as long as 24 months and as little as 6 months depending on the gas
- ***Never use expired gas***
- Some gases can be very expensive to own

Calibration Gas

- Combustible gas sensor cal gas and multi-sensor, all-in-one or “quad gas” cal gas all have some amount of oxygen (16-20.9% O_2) in them or else the combustible gas won’t work
  - Oxygen concentrations below 20.9% allow “spanning” of the oxygen sensor

Calibration Gas "Hygiene"

- Users can cause calibration gas to go prematurely "bad"
  - Repeated introduction of small amounts of moisture, oxygen and other contaminants carried into cylinders by a closed regulator can affect the concentrations of the small amounts of highly reactive gases like Cl_2
  - When a closed regulator is screwed onto a cylinder the air and other contamination between its threads and the closed valve is forced into the cylinder
  - Oxygen, moisture and contaminates can quickly degrade highly reactive calibration gases.
  - It is best to open a regulator prior to attaching it to a cylinder of gas, this keeps any moisture and contamination on the regulator from entering the gas cylinder
- Regulators and cylinders should be stored in a clean, dry place
  - According to one gas vendor storage of calibration gas cylinders in temperatures as high as 120-150ºF should not shorten their shelf-life or otherwise degrade their contents



Open before screwing onto gas cylinder

Don’t be afraid of Calibration

- Modern designs make calibration easy and automatic
- Keep the Calibration Materials With the Instrument!
- All-In-One Calibration Mixtures Make Functional Testing Easy!
- Don’t buy a sensor unless you are willing to calibrate it!

Calibration: Record keeping

- Documentation is critical!
- Without good records you cannot defend or explain your procedures (docking stations usually automate this)
- If you don't have the records to prove it was being done right -- it wasn't!

Date	Time	Instrument	Serial Number	Cal Gas	Concentration	Lot Number	Expiration/ Mfg. Date	Calibrated By

Topics: Calibration

- Why do we calibrate?
- What types of calibrations are there?
- How much calibration is enough?
- How to calibrate
- Where do I calibrate?
- Calibration can help improve your confidence in your meter

Calibrate wherever you need to regain confidence in your detector

- Docking stations are increasingly used by many to calibrate their detectors, but these fixed systems may not be immediately accessible when one loses confidence in their detector (ex: fire dept. HazMat team)
- Mobile users may want to consider carrying calibration gas on their vehicle to restore confidence in their detector when in the field away from their docking station
- A small calibration cylinder can quickly help restore confidence in a detector
- Always calibrate in a well ventilated area

Photo by Luke Sloan

Where do I calibrate?

- Always follow your manufacturer's recommendations
- It is ideal to calibrate under a fume hood
- If lacking a fume hood, use a well ventilated area so that the calibration gases don't affect you or others
- Always calibrate in a clean environment so that contaminants don't affect the calibration
- Some detectors do a "fresh air" or zero when turned on so they must be turned on in a clean environment

Topics: Calibration

- Why do we calibrate?
- What types of calibrations are there?
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Unsafe Zero Calibration

- A HazMat officer was making an entry into a sewage pump station for preplanning. All the right confined space entry operations and permitting were completed.
- Upon entry to the confined space the officer immediately exited feeling difficulty in breathing and light headedness. He thought it was from drinking too much coffee and a long night at the station.
- They then went to the next confined space to preplan, but this time he could tell from experience that the atmosphere was most likely bad. So he asked him to check it.
- The attendant lowered the tubing into the space and then turned the confined space detector on. The officer was alarmed but waited until the attendant gave the “everything is normal” sign.

Unsafe Zero Calibration

- The officer asked the attendant to take the tubing out of the space and re-zero the unit in a clean atmosphere
- With a fresh air calibration complete, he lowered the tubing back in the space. The unit immediately went into alarm for high H_2S, and low O_2.
- If they had entered the space this time, the odds are they would have collapsed
- ***Some detectors zero themselves when turned on. If they are turned on while sampling a contaminated atmosphere they will zero out that atmosphere***

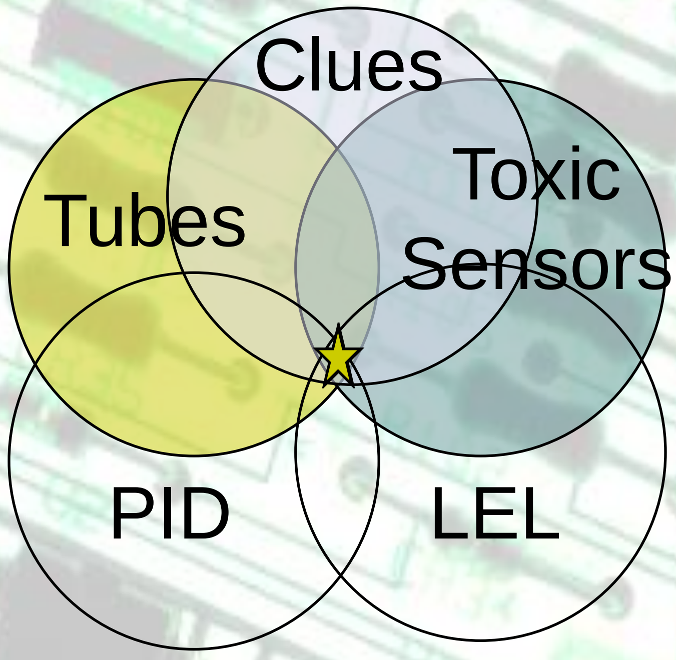
Printed Circuit Board Plant

- CO sensor indicated 35-45 ppm in printed circuit board plant with styrene, xylene, acetone and other aromatics and ketones
- Jumped to false conclusion that CO sensor was bad or responding to hydrocarbons
- Fresh aired detector outside plant and still had high CO in plant

Printed Circuit Board Plant

- Calibrated with CO gas and still had high CO in plant
- Checked with CO colorimetric tube and registered 50 ppm CO reading
- Investigated plant and found shrink-wrap machine pumping out 150 ppm CO in worker breathing zone

Printed Circuit Board Plant



★ =CO from shrink wrap machine

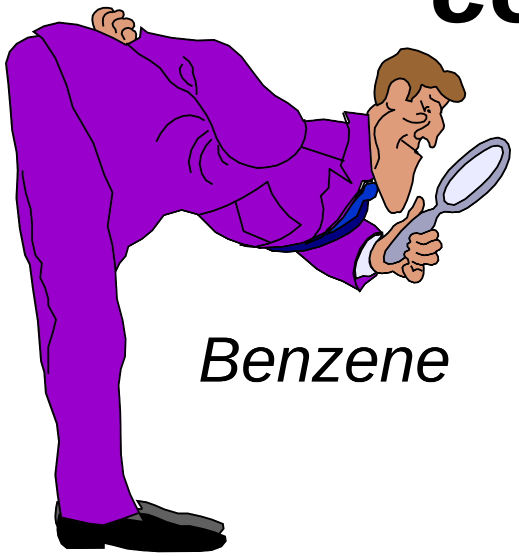
- **Clues:** Printed circuit board plant
- **Toxic Sensor:** 35-45 ppm reading on CO
- **LEL:** no reading on LEL
- **PID:** no reading on PID
- **Tubes:** 50 ppm reading on CO tube

O_2: 20.9, LEL: 0, CO: ~50, H_2S: 0, PID: 0

My detector failed calibration, what next?

- If any sensor fails calibration in a detector, and any remedial steps don’t address the problem, then the sensor needs to be replaced or the detector repaired and recalibrated before use
- Any detector that has failed calibration and has not been repaired, should not be used
- Any detector that has failed calibration, has been repaired and subsequently passed calibration is safe for use
- If any sensor in a multi-gas detector has failed, then the entire detector should be put out of service until it can be fully repaired and calibrated
  - “Only my oxygen sensor failed calibration, can I still use it?”
    - **NO**

Gas Detectors need Gas Detectives to come to the right conclusion



Carbon Disulfide

Ammonia

Styrene

Carbon Monoxide

Benzene

PERC

Xylene

Questions?

chriswrenn@att.net

"Still confused but at a higher level"

If you'd like a copy of this presentation or the white papers mentioned please email me or give me your information

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

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

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