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 gas company detector reads 5%, are we safe?
- 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: LEL/UEL

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





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

Gas/Vapor	LEL* (% vol)	UEL* (% vol)
Acetone	2.2	12.8
Benzene	1.2	7.8
Carbon Monoxide	12.5	74
Diesel	0.8	10
Ethylene Oxide	3.0	100
Gasoline	1.4	7.6
Hydrogen	4.0	75
Methane	5.0	15

1.8

1.5

2.0

1.2

11.4

7.8

9.5

7.1



MEK

n-Pentane

Propane

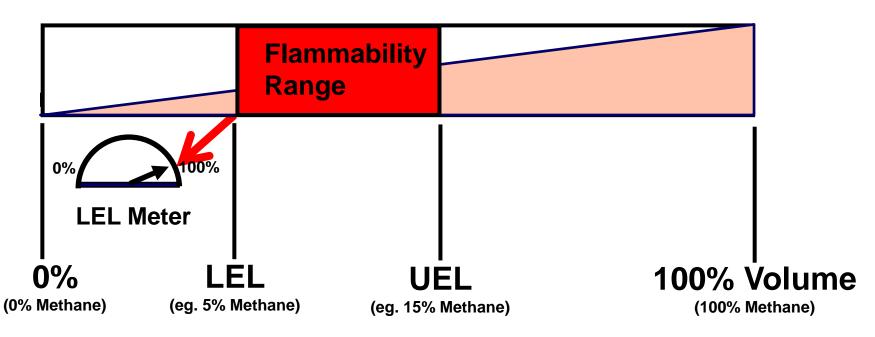
Toluene



Measuring Flammability

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

Gas Concentration







CW

- Wheatstone bridge catalytic bead
 - Response, calibration & correction factors
 - Poisons
- High range flammability
 - Dilution
 - Oxygen Displacement
- Thermal Conductivity (TC)
- Non-dispersive infrared (NDIR)
- Photoionization Detector (PID)
- Which technology should I trust





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





* Reference and photos courtesy of RKI Instruments





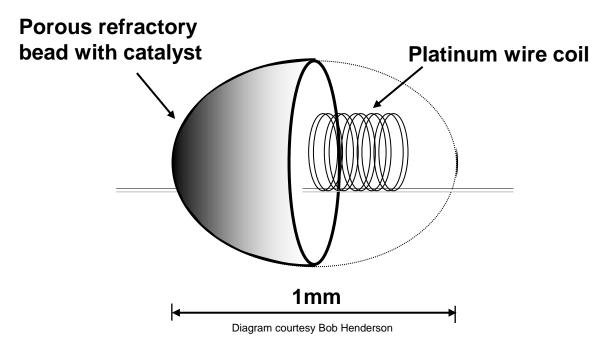


- According to Miriam Webster:
 - "a substance that enables a chemical reaction to proceed at a usually faster rate or under different conditions (as at a lower temperature) than otherwise possible
- Platinum or palladium are two catalysts commonly used in the catalytic bead to facilitate the exothermic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







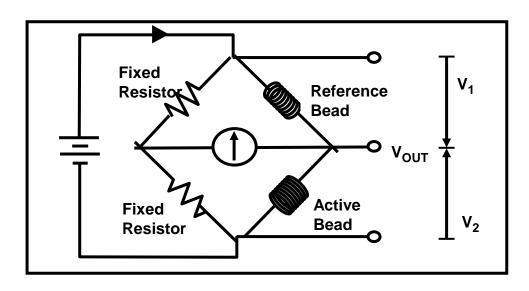


- A coiled wire is used to maximize the surface area of catalyst
- The catalyst is put into a porous ceramic bead to keep it from flexing like a "Slinky" and shorting out on itself
- This adds to the durability of the sensor









- 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







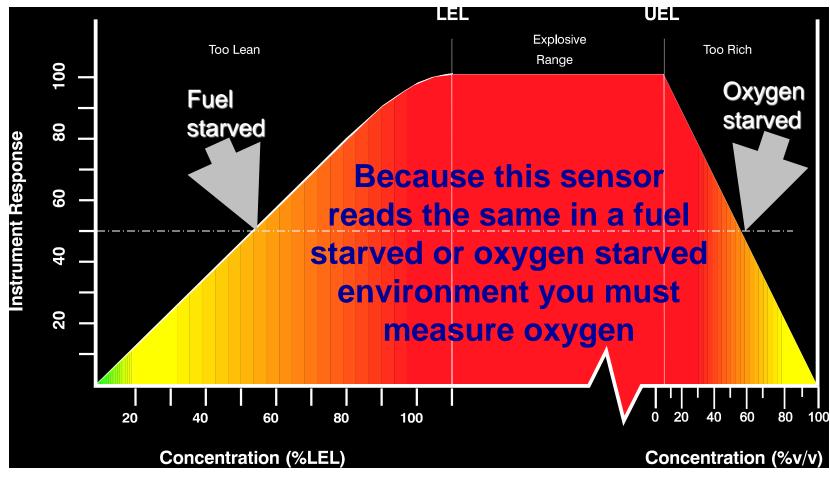


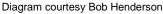
- The Wheatstone bridge catalytic bead sensor oxidizes or "burns" flammable gases and vapors so oxygen is a requirement for this sensor to operate
- Oxygen must also be measured first because the cat bead sensor produces the same amount of heat at a point below LEL where it is "fuel starved" or "too 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 as shown on the next chart by the line at 50% of LEL which demonstrates that the cat bead sensor can have the same reading below LEL and above UEL
- OSHA requires that oxygen is measured 1st because the regulation was written in a time when one might have an oxygen detector and a LEL detector rather than a multigas product
- If one measures more than 19.5% oxygen then the LEL sensor is definitely measuring below LEL not above UEL







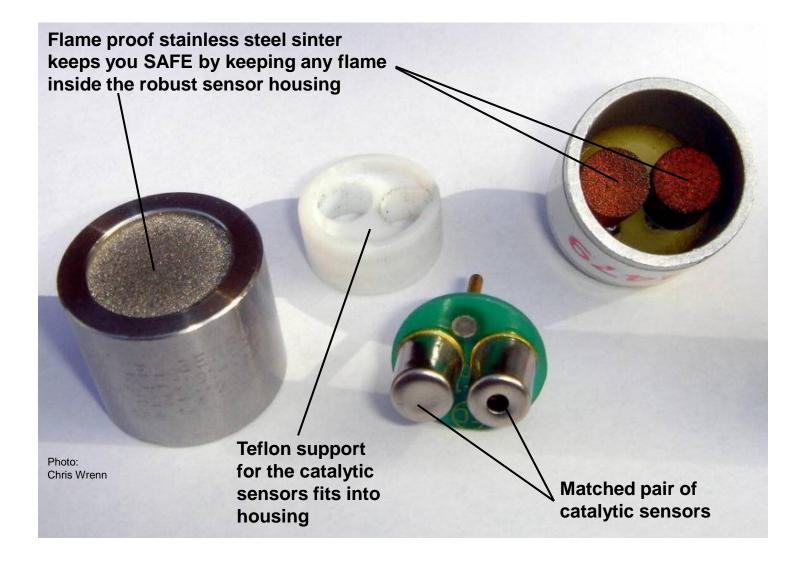






Making the Electric Stove Safe for Use in Flammable Atmospheres









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





CW

- Wheatstone bridge catalytic bead
 - Response, calibration & correction factors
 - Poisons
- High range flammability
 - Dilution
 - Oxygen Displacement
- Thermal Conductivity (TC)
- Non-dispersive infrared (NDIR)
- 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 detector doesn't agree with the contractor's detector



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







- Vapor pressure (review):
 - Tells us how readily a liquid (or solid) wants to evaporate into to a vapor state
 - Low vapor pressure chemicals don't want to make vapors
 - High vapor pressure chemicals want to become gases
 - A chemical with a vapor pressure over 1 ATM, 760 mm/Hg or Torr, 14.7 PSIA or 1,013 mb is a gas
 - Vapor pressures of over 40 mm/Hg are more likely to move around and are considered to be an inhalation or vapor hazard
 - Water has a vapor pressure of about 20/mm/Hg





- Boiling Point (review):
 - Another way to help us understand how readily a liquid wants to move to a vapor state
 - It is the temperature at which a liquid transitions to a gas
 - Low boiling point chemicals
 - Want to become vapors
 - Have relatively higher vapor pressures
 - Are relatively easier to measure with a vapor monitor
 - Ex: Gasoline
 - High boiling point chemicals
 - Don't want to become vapors
 - Have relatively lower vapor pressures
 - Are harder to measure with a vapor monitor
 - Ex: Diesel



Summary of VPs and BPs for some common hydrocarbons



Note that as the number of carbons increases the vapor pressure drops and the boiling point increases

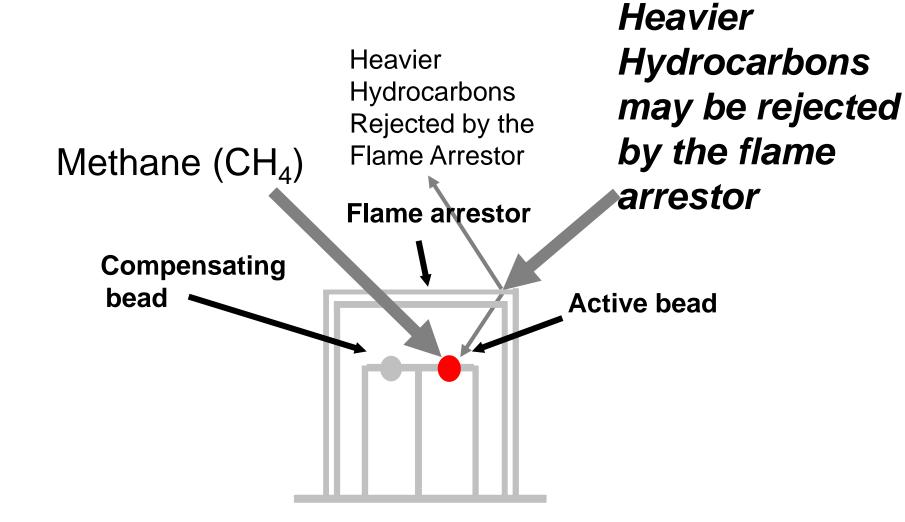
Name	Formula	Vapor Pressure (@20°C) mm Hg	Boiling Point (°C)	Boiling Point (°F)
Water	H2O	17.54	100	212
Ethane	C2H6	>760	-67	-89
Acetone	(CH3)2CO	200	13	56
Isopropanol	C3H8O	40	27	81
Propane	C3H8	>760	-43	-45
Methane	CH4	>760	-107	-161
Butane	C4H10	>760	-18	-0.5
Pentane	C5H12	465	2	36
Gasoline	C5-10	38-300	10-93	50-200
Hexane	C6H14	260	20	68
Heptane	C7H16	46	37	98
Octane	C8H18	5	52	126
Decane	C10H22	2	79	174
Diesel	C11-25	0.4	160-371	320-700
Dodecane	C12H26	0.3	102	216
Hexadecane	C16H34	~0.01	114	237
Docosane	C22H46	<0.001	164	327
Triacontane	C30H64	<0.0001	232	450

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Catalytic LEL Sensor Cut-Away





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

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)







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







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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 npentane scale so that the LEL sensor response is corrected to a more appropriate scale for most common gases and vapors







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- 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°F (260°C) compared with the ignition temperature of methane which is 999°F (537°C)
- 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







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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







- 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.







- 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





- 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



- 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











- 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 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 detector 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 detector will automatically do the math to correct the detector 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
 - Radio calls should reference the measurement scale
 - "9% of LEL methane units"
 - "12% of LEL pentane units"
- Measurement scale is usually the calibration gas
- Correction factors allow you to change scale without changing calibration gas

Know your LEL detector measurement scale





- 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

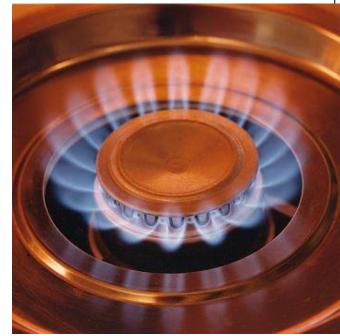


Photo courtesy of Oxford Classic Motor Club, www.oxcmc.org.uk

• n-pentane has an ignition temperature of just 500°F (260°C) compared with an ignition temperature of 999°F (537°C) 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

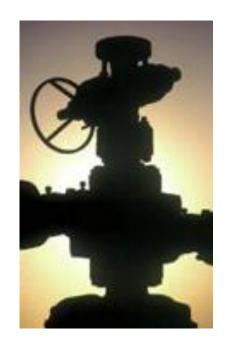
- A detector manufacturer calibration recommendation is a 4 gas mixture composed of pentane (25%LEL), O₂ (19%), CO (100 ppm) and H₂S (25 ppm)
- A fire department used bump gas canisters with methane (25% LEL), O₂ (15%), H₂S (75 ppm) and CO (200 ppm).
- "A detector successfully passed calibration with 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."



Gas Production Company Changes to a Methane Scale



- A gas production company used detectors with LEL sensors calibrated to a pentane scale
- They were exclusively dealing with "natural gas" or methane
- The personal safety detectors were "always going into alarm"
- Investigation demonstrated that they were calibrated to a pentane scale and they were going into alarm 100% too early, this caused the users to totally ignore all alarms
- Changing to a methane measurement scale reduced the false alarms and allowed the users to regain their confidence in their detectors





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 detector
- Contractor argued that they had a -10% of LEL reading on their detector and they were OK







- HazMat team used detector measuring in npentane which read 11% of LEL
- Contractor used detector measuring in methane with a reading of 6% of LEL (this detector also had a PID)
- Tank contained Toluene
- HazMat Team: O₂: 20.9, LEL: 11, CO: ~20, H₂S: 0
- Contractor: O₂: 20.9, LEL: 6, CO: ~20, H₂S: 0, PID: 2640





HazMat Team:

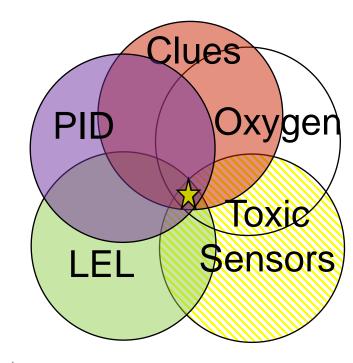
- 11%LEL_{pentane} x 1.06_{CF*Toluene} = 11.7%LEL_{Toluene}
- Contractor:
 - 6% LEL_{methane} x 1.9_{CF*Toluene} = 11.4%LEL_{Toluene}
- References:
 - 2640 ppm_{iso} x $0.5_{CF^*Toluene}$ = 1320 ppm_{Toluene} or 11% of LEL
 - 100% LEL_{Toluene} = 1.2% or 12,000 ppm_{Toluene}
 - 10% of LEL_{Toluene} =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











- 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



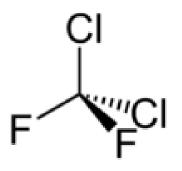




- So in this case the fire department and contractor detectors were not set to the same "volume" or measurement scales
- When the two detectors were corrected to the same "volume" they both "heard" the vapors at the correct level
- Later we will talk about using Photoionization Detectors (PIDs) for LEL 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.





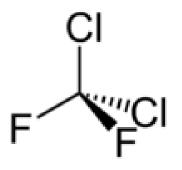




- Workers removing Freon (R-12) from a building HVAC system vented R-12 into the engineering space
- One worker succumbs another is taken to hospital
- HazMat team can see "shimmering" in the air when they make entry wearing PPE and SCBA
- Oxygen levels drop below 10%, PID reads nothing but LEL reads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





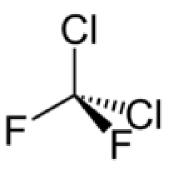




- Even though R-12 does not have an LEL value, it still can provide a reading on a catalytic sensor because the carbon at the center of the molecule will burn
- It won't read much; not all the way up to 100% LEL, but since it has carbon atoms it will burn some and cause a reading
 - Note that this "frees"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





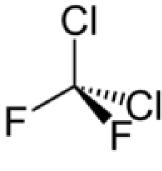




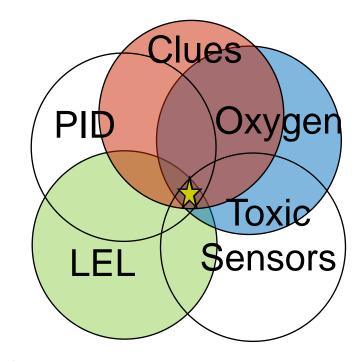
- A reading of 10% LEL to 12% LEL seems to be the highest reading R-12 may be able to reach
- It would need to be over 100% LEL to be flammable, but a catalytic sensor can burn it enough to cause a slight reading



LEL Sensors Reads Freon







★ =Freon

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





CW

- Wheatstone bridge catalytic bead
 - Response, calibration & correction factors
 - Poisons
- High range flammability
 - Dilution
 - Oxygen Displacement
- Thermal Conductivity (TC)
- Non-dispersive infrared (NDIR)
- Photoionization Detector (PID)
- Which technology should I trust







- 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











- Fire department complained of short LEL sensor life
- Detectors were stored on a rubber mat on top of a diamond plate storage cabinet
- Silicon caulk was used to glue down rubber mat
- Once the mat was removed and replace and the silicone caulk was eliminated the sensor issues disappeared







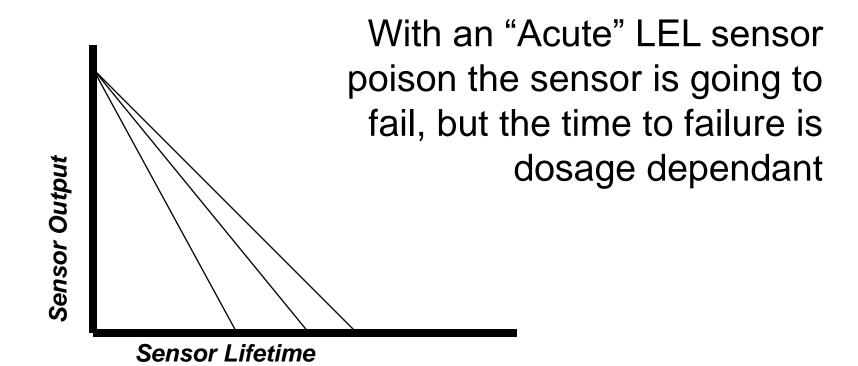


- 4 gas detector customer put their detector in a custom heavy duty, waterproof storage case
- The customer made a custom foam insert to store everything neatly
- The LEL sensor in the detector was not lasting long
- Investigation determined that the custom foam was glued into the case with silicone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















- 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: H₂S, CS₂
 - Hydride gases: like phosphine (PH)
 - Halogenated Hydrocarbons: Refrigerants ("Freon"), trichloroethylene, methylene chloride
 - Styrene







- 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 detector remains in alarm







Hot dogs kill LEL sensors

- The confined space detector in a hot dog plant was only getting 6 months out of its LEL sensor
- The "tubes" for the hot dog meat are made from edible rayon
- Edible rayon is made by treating high grade wood pulp with CS₂ (Carbon Disulfide)
- CS₂ is extremely capable at disabling catalytic beads
- Switching to another LEL detection technology was recommended because the plant wasn't about to change their process
- PID was suggested as an alternative detector of flammability because it is resistant to CS₂ poisoning and it can also make toxicity decisions in atmospheres containing CS₂ (TWA = 20 ppm)







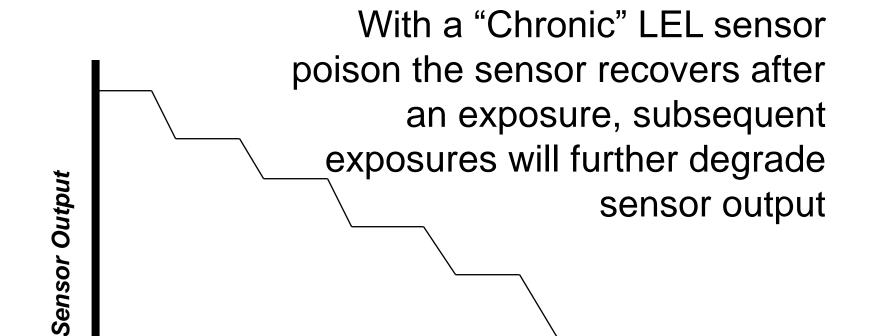
- Pulp plant customer complains of getting short life out of their LEL sensors
- The plant stinks with H₂S and mercaptans which are chronic LEL sensor toxins
- PIDs are best for the turpentine areas but methane is present so PID can't do it alone
- Could use NDIR and PID





Sensor Lifetime









<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 low vapor pressure combustibles like diesel, jet fuel and kerosene
- Not sensitive enough for toxicity measurements (wakes up ~300-500 ppm)





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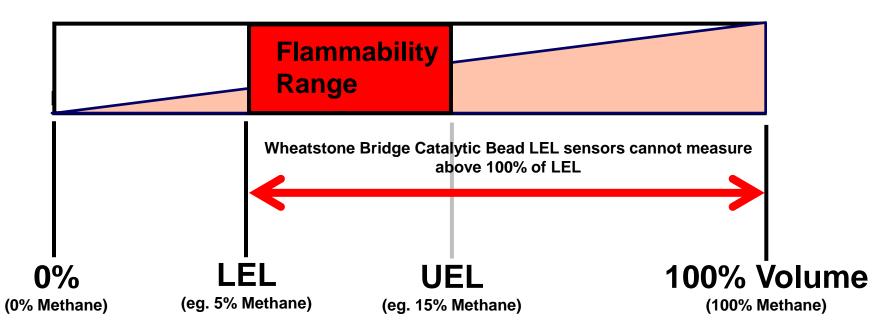




High Range Catalytic Bead Sensor Limitations

 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

Gas Concentration









- Techniques for high range combustible gas measurement
 - Dilution fittings
 - Calculation by means of oxygen displacement
 - Thermal Conductivity (TC) sensors
 - Non-dispersive Infrared (NDIR)







- Gas detectors can benefit from continuous sample dilution for several reasons including:
 - Adding enough oxygen to inert sample gases to allow proper function of LEL and electrochemical sensors
 - Bringing concentrated samples into the linear measurement range of the sensor
 - Reducing humidity, methane, or other matrix gases that can affect the target gas readings
 - Reducing possible damage to some sensors at high exposures
- Dilution fittings usually attach between a length of sample hose and the detector, but right at the detector. They assume that the user and the detector are in "clean" air with 20.9% oxygen in it
- One product uses a second flow transducer controlled dilution pump to accurately dilute the sample gas

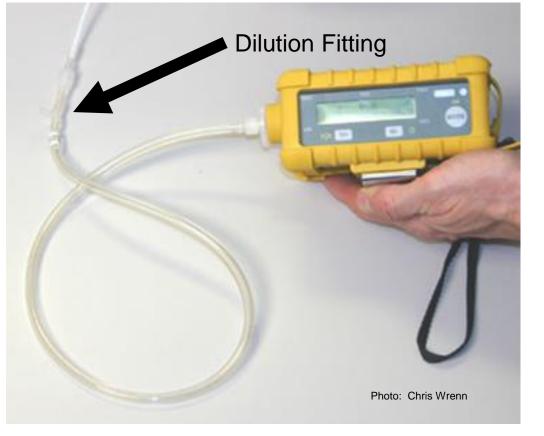




- Dilution fittings add a controlled amount of clean air to the sample mixture
- Some dilution fitting capable detectors automatically calculate the corrected reading accounting for the dilutant gas













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- Air is 20.9% or 209,000 ppm oxygen (O₂)
- Air is 78% or 790,000 ppm nitrogen (N₂)
- A decrease in O₂ concentration from 20.9% to 20.8% means that there
 may be 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% O₂ so that means that the other 80% of N₂ must be displaced too
 - 20/80 = 1000/x then x is 4000 and 4000+1000= 5000
- Many gas monitor manufacturers put a "dead-band" around 20.9% oxygen forcing the meter to read "20.9" when the real concentration is 20.8-21.0. This can reduce the perceived "jumpiness" of oxygen sensors but effectively means that you won't see any change until you have over 10,000 ppm of something









- 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% catalytic 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 and is NOT an effective alarm for LEL levels of gases & vaoprs
- 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





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Why Thermal Conductivity Sensors?

- Thermal Conductivity (TC) sensors are commonly used by gas utility workers for their flammability decisions because of their very wide range of detection
- While these workers need to stay at safe, they are not limited to staying below the LEL, they may even need to stay above the UEL to be safe
- For example, when a big gas main leaks it may not be practical to shut down the main because all the downstream customers will have their gas turned off





Why Thermal Conductivity Sensors?

- When the gas turns back on there could numerous fire threats because of people who don't relight their pilot lights, filling their residences with flammable gas just waiting to find a source of ignition
- In order to weld an active gas line, gas utility workers will check to see if their working environment is above the UEL and then weld up the hole in the gas main
- As long as they stay above the UEL the spark from the welder will not ignite the gas.





How Does TC Work?

- Air is about 20% Oxygen, 80% Nitrogen
- Nitrogen does not conduct heat well
- This is why down parkas keep us warm, the nitrogen in air retards heat transfer
- Flammable gases conduct heat much better than nitrogen
- As flammable gases replace nitrogen in a gas matrix, the matrix will be better at conducting heat
- Were we to replace the nitrogen in our down parka with propane, not only will we become potential flammable but we will not be warm either









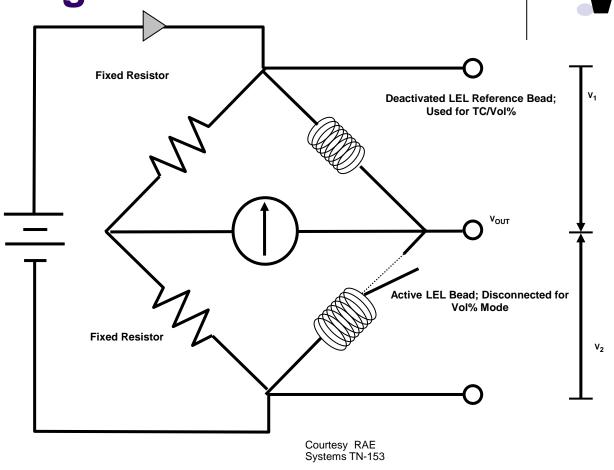
- Imagine a one burner electric stove
- We set the stove to "Low" heat which uses a certain amount of power
- As thermally conductive flammable gases replace the nitrogen in the atmosphere then more power will be required to keep the electric stove burner at "Low" heat
- The more power required to keep maintain "Low" the more thermally conductive gas there is in the atmosphere







- Some manufacturers make combo TC/Vol sensors where the TC coil is part of a Wheatstone bridge that is integral to the LEL sensor
 - LEL: the coil acts as the reference bead and the catalytically active bead is connected to the bridge
- TC/Vol: the active bead is disconnected and only the deactivated reference bead is used.







TC sensors for combustible gases

- Each type of gas has a unique TC and thus a unique relative response
- The gas does not need to be combustible
- No oxygen is required for its operation
- Almost any gas can be measured as long as it has a different TC than the matrix gas
 - For example, CO₂ can be measured in air or H₂ in argon
 - The TC may be either higher or lower than that of the matrix gas
- TC Sensors often display in % volume NOT % of LEL
 - 100% of LEL Methane is 5% by volume on a TC sensor







Gas/Vapor	Thermal Conductivity	Sensitivity (%)
Hexane	0.45	45
Butane	0.66	66
Argon	0.7	70
Carbon dioxide	0.7	70
Propane	0.7	70
Water	0.74	74
Acetylene	0.78	78
Ethylene	0.78	78
Ethane	0.9	90
Carbon monoxide	0.97	97
Air (reference)	1	100
Methane	1.45	145
Neon	1.87	187
Helium	5.5	550
Hydrogen	6.8	680

^{*} These correction factors are for example ONLY, consult your manufacturer for response factors for your TC detector





- A fire department responded to fast food restaurant where a pregnant woman fell
- Woman said that she felt light headed and dizzy after going into a basement to get supplies
- Driver and officer recon the basement and almost don't get back up the steps
- HazMat responds and wearing SCBA show low O₂, no LEL and no PID readings
- Because they couldn't find anything in the basement's atmosphere they decided to try another detector





Natural Gas Detector "Lies" to a HazMat Team

- They got their natural gas detector off the rig and went back in the basement
- It reads high levels of flammable gas!
- Now they thought that they had a flammable atmosphere
- But both the cat bead LEL and PID readings did not change
- Perhaps it had to do with the natural gas detector's TC sensor?

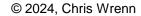






Gas/Vapor	Thermal Conductivity	Sensitivity (%)	
Hexane	0.45	58	
Butane	0.66	66	
Argon	0.7	70	
Carbon dioxide	0.7	70	
Propane	0.7	70	
Waller	0.74	7	
Acetylene	0.78	78	
Ethylene	0.78	78	
Ethane	0.9	90	
Carbon monoxide	0.97	97	
Air (reference)	1	100	
Methane	1.45	145	
Neon	1.87	187	
Helium	5.5	550	
Hydrogen	6.8	680	

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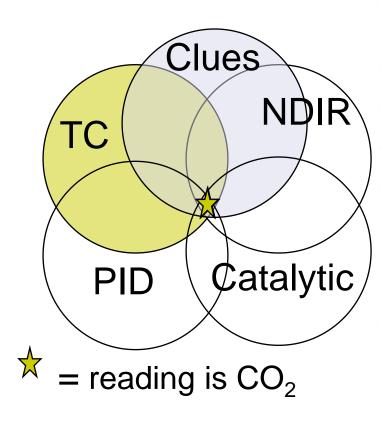
Natural Gas Detector "Lies" to a HazMat Team

- It turns out that the cryogenic carbon dioxide (CO₂) tank in the basement of the fast food restaurant was leaking
- The TC natural gas detector was only designed for measuring natural gas, so it figured that the change in thermal conductivity was due to flammable gas because propane and CO₂ have the same thermal conductivity









 Clues: Slip trip and fall at fast food restaurant

NDIR: no reading

• Catalytic: no

PID: no reading

TC: CO₂ leaking from the cryogenic container fooled the TC sensor because CO₂ has about the same TC as propane

If the Catalytic bead AND PID don't show flammability it most likely isn't flammable





<u>Advantages</u>

 Great for high range measurements up to 100% by volume

+ Do not require oxygen

<u>Disadvantages</u>

Secondary measurement (uses cooling affect)

Gases with different TCs in the matrix can cause "false" alarms
Less sensitive at low levels (0-10% of LEL)









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NDIR Sensors for combustible gases

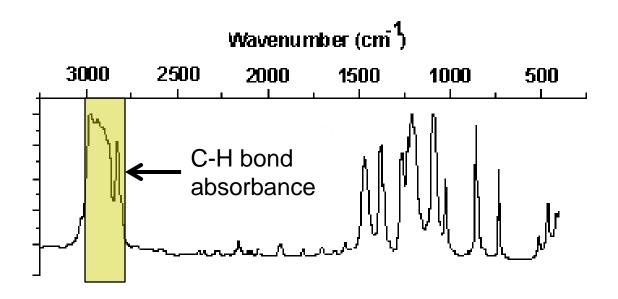
- Non Dispersive InfraRed (NDIR) sensors use the absorption of infrared light to make gas measurements
- Many molecules can absorb infrared light, causing them to bend, stretch or twist
- The amount of IR light absorbed is proportional to the concentration
- The energy of the photons is not enough to cause ionization, and thus the detection principle is very different from that of a photoionization detector (PID)
- Ultimately, the energy is converted to kinetic energy, causing the molecules to speed up and thus heat the gas





NDIR Sensors for combustible gases

C-H bonds (common to MANY flammable hydrocarbon gases and vapors) absorb in the range 3.3-3.5 µm (2800-3000 cm-1), depending on the structure of the rest of the molecule. Many compounds have similar C-H bonds and this absorbance is suitable to detect a range of hydrocarbons non-selectively









- Essentially the NDIR sensor looks for the "shadows cast" by C-H bonds when IR light is shined through gases/vapors with C-H bonds
- The darker the shadow the higher the concentration
 - This is the "Beer-Lambert" law

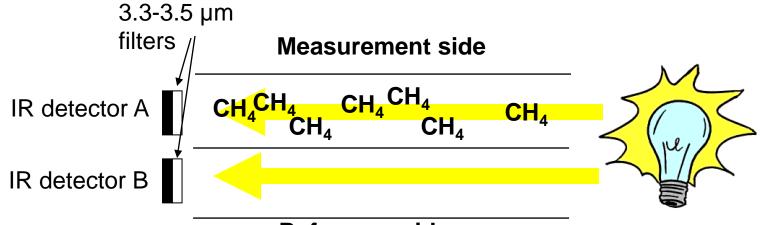






NDIR sensors for combustible gases

- Light passes through the gas sample and is absorbed in proportion to the amount of C-H bonds present
- The filter in front of the detector removes all the light except that at 3.3-3.5 μm, corresponding to C-H bonds
 - The more C-H bonds the more signal so NDIR sensors are more responsive to larger hydrocarbons than to smaller ones which is the opposite case of the cat bead sensor
- Reference detector provides a real-time signal to compensate the variation of light intensity due to ambient or sensor changes
- Concentration = Detector B Detector A







NDIR & Flame Arrestors

- Historically NDIR sensors used a high-power light source so a flame arrestor was required
- New photo-diode NDIR sensors use a low power IR light source and are intrinsically safe so a flame arrestor is not required
- Nevertheless, this does not solve the problem that NDIR combustible gas sensors will miss many common flammable gases



NDIR LEL sensors will miss some flammable gases



- Flammable gases and vapors that lack the C-H bond will not be seen by the NDIR LEL sensors
- Some examples of flammable gases/vapors that NDIR LEL sensors miss
 - The BIG 4: Acetylene (C₂H₂), Hydrogen (H₂), Carbon Monoxide (CO), Ammonia (NH₃)
 - Although acetylene (C₂H₂) has two C-H bonds, the presence of a triple bond between the two carbon atoms so reduces absorbance that it renders the molecule unmeasurable at 3.33-3.4 μm which is where most NDIR combustible sensors are measuring
 - "Diatomic" molecules like oxygen (O₂) and hydrogen (H₂) do not absorb infrared light.
 - Other hydride gases: Phosphine (PH₃), Arsine (AsH₃)
 - Carbon Disulfide (CS₂)
- NOTE: NDIR can also be used for Carbon Dioxide (CO₂) measurements, BUT CO₂
 absorbs at a different wavelength so NDIR dedicated to combustible gases will not
 work for CO₂





Advantages

- Can measure to 100%
 by volume
- + Do not require oxygen
- + Resist poisons



<u>Disadvantages</u>

- Secondary
 measurement
 (measures IR
 absorption of the C-H
 bond)
- Misses some common combustible gases
- Often more expensive





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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 measure in ppm and we've been talking about % of LEL and % Volume
- Multiply % Volume by 10,000 to get ppm
- LEL Gasoline is 1.4% by volume or 14,000 ppm
- 10% of LEL Gasoline is 1,400 ppm

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







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



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

^{**} Divide ppm by the chemical correction factor for your PID





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

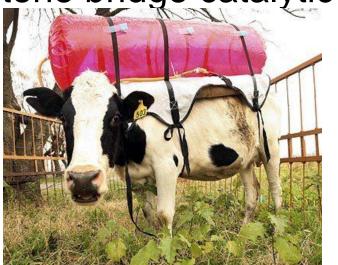




- If you can see "it" like pouring it out of a can onto the ground then the PID is probably better
- If it is a gas that you can never "see" then the wheatstone bridge catalytic bead sensor is better

 If the ionization potential of "it" is greater than 10.6eV then the wheatstone bridge catalytic

bead sensor is better











<u>Advantages</u>

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



<u>Disadvantages</u>

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





CW

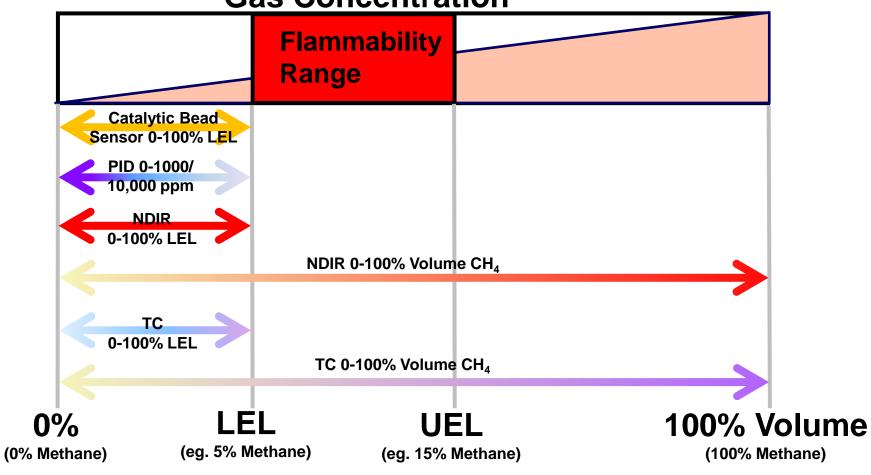
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CW

Combustible Sensors Compared









Combustible sensors compared

- 100% of LEL on cat bead sensor is 5% by volume on a TC sensor in methane
 - 5% of LEL is SAFE, so if you don't know that you are reading % volume you may mistakenly think you are safe
- 1000 ppm on PID ~ 10% of LEL





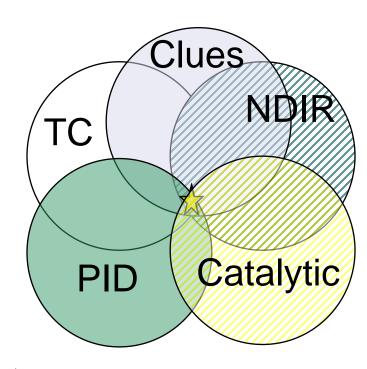
Wing tank LEL

- Entrants can see and smell jet fuel but their catalytic LEL detectors read nothing
- Catalytic LEL sensor takes a long time see jet fuel
 - Cold detectors will take time to warm up the thermal mass of the explosion-proof LEL sensor housing and this can impact response time for low vapor pressure chemicals
 - A manufacturer customized their detector with a 20 minute warm-up timer so the jet fuel had the best chance of getting to the LEL sensor without condensing on a cold explosionproof sinter
- Aircraft maintenance exposes sensor to poisoning silicone compounds
- PID alarm for toxicity (50 ppm) in addition to LEL (800 ppm)
- PIDs are used to make LEL decision



Wing tank LEL





- Clues: wing tank containing jet fuel residue
- NDIR: Ok for LEL but not sensitive enough for toxicity
- Catalytic: little or no reading, may take 20 minutes when it does respond
- PID: 800 ppm in jet fuel units is 10% of LEL
- TC: 10% of LEL too low to read

★ =800 ppm of JP-8 is
10% of LEL

O₂: 20.9, LEL: 0, CO: 0, H₂S: 0, PID: 800





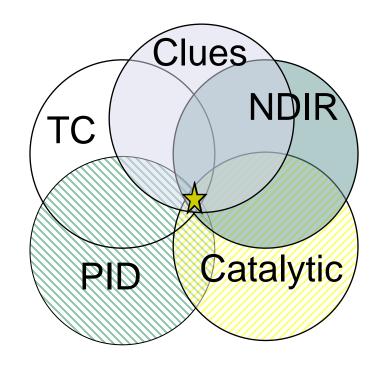


- Operator using a properly calibrated detector did not measure flammable levels of turpentine but was severely burned in a turpentine flash during hot work
- Catalytic LEL sensor just can't see turpentine
- Sulfur compounds in Pulp & Paper act as chronic poisons to LEL sensor that at its best can barely see turpentine
- detectors now have LEL and PID because other flammable gases like methane may be present that the PID cannot "see"



Pulp & Paper Turpentine LEL





★ =800 ppm of
 Turpentine is 10%
 of LEL

- Clues: turpentine recovery unit
- NDIR: good reading
- Catalytic: no reading for turpentine but required because methane may be present
- **PID:** 800 ppm in turpentine units or 10% of LEL but no methane reading
- TC: 10% of LEL too low to read

O₂: 20.9, LEL: 0, CO: 0, H₂S: 0, PID: 800







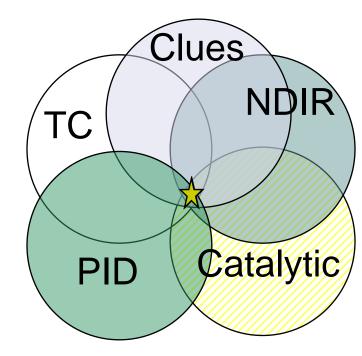


- In the spring of 2010 a fuel oil delivery truck mistakenly delivered to the wrong address in northern VA
- The wrong house had a disconnected oil fill tube because the house had been converted to natural gas
- The driver "delivered" nearly 700 gallons before realizing that the house was only supposed 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

NDIR: good reading

 Catalytic: little or no reading, may take 20 minutes when it does respond

 PID: 250 ppm fuel oil units or 2.5% of LEL

• TC: 10% of LEL too low to read

O₂: 20.9, LEL: 0, CO: 0, H₂S: 0, PID: 278





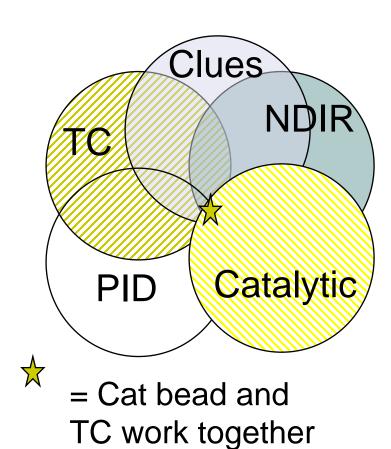
Natural gas well head

- Operators need to test natural gas well-head for purity
- Operators are also concerned about flammable levels of natural gas in their work area
- Operators choose to use product with dual range catalytic/TC sensor









- Clues: Natural gas wellhead
- NDIR: good reading
- Catalytic: great for flammability in the area prior to sampling the well head but sampling the well-head overranges the sensor
- PID: low reading from mercaptans and contaminants
- TC: perfect for the highrange purity reading





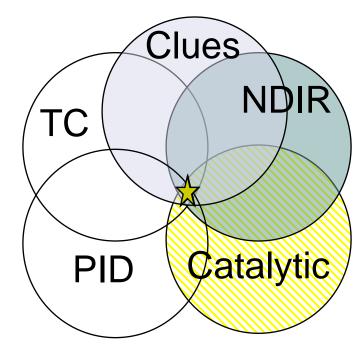


- Since halocarbons like "Freon" have been prohibited to use as a propellant they switched to flammable hydrocarbons like butane and octane and required LEL detection in their work areas
- Antiperspirant compounds like aluminum chlorohydrate are acute poisons for the catalytic bead sensors
- Recommend NDIR sensors for LEL decisions



Antiperspirant Plant



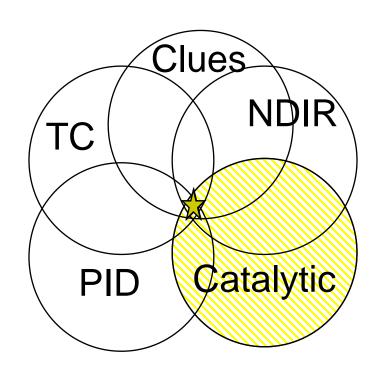


- Clues: Antiperspirant plant with cat bead poisons as part of the process
- NDIR: good reading, good solution
- Catalytic: marginal, only lasts 3 months
- PID: no reading because the blowing agents are not ionizable with 10.6eV lamp
- **TC**: not sensitive enough





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
- Know your application and choose your sensors appropriately
- 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
 - Start with a relatively high vapor pressure liquid like acetone or lacquer thinner
 - 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









Gas Detectors need Gas Detectives to come to the right conclusion

Ammonia

PERC

Benzene

Carbon Disulfide

Styrene

Carbon Monoxide

Xylene









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"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, text or email me and we'll work through it

610-659-4507

Check out <u>www.DetectionGeek.com</u> for downloads of slides and whitepapers

