Capabilities and Limitations of the Latest LEL Sensors for Combustible Gas Measurement

Bob Henderson

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Robert E. Henderson

Speaker Biography

Bob Henderson is the President of GfG Instrumentation, Inc., a leading supplier of portable and fixed gas detection products. GfG's instruments are used in atmospheric monitoring applications all over the world.

Robert has over 38 years of experience in the design, marketing and manufacture of gas detection instruments. Robert is a past Chairman, and in-coming Chair of the AIHA Real Time Detection Systems Technical Committee. He is also a past Chairman and current member of the AIHA Confined Spaces Committee. He is also a past Chair of the Instrument Products Group of the ISEA. Robert has a BS in biological science and an MBA from Rensselaer Polytechnic Institute.

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Real-time technologies for measuring LEL combustible gas

- Catalytic (CC) LEL
- Photoionization Detection (PID)
- Infrared (IR) LEL
- Thermal conductivity (TCD)
- Metal oxide semiconductor (MOS)
- Molecular properties spectrometer (MPS)

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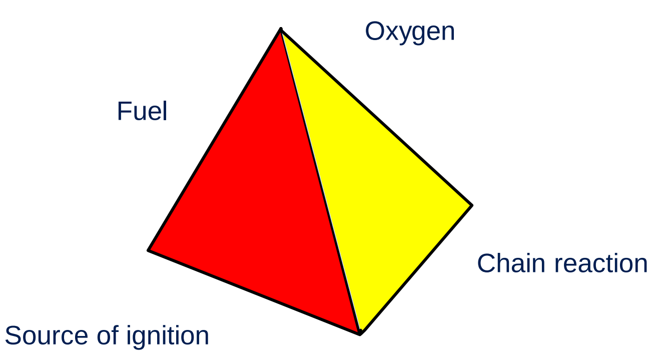
Fire Tetrahedron



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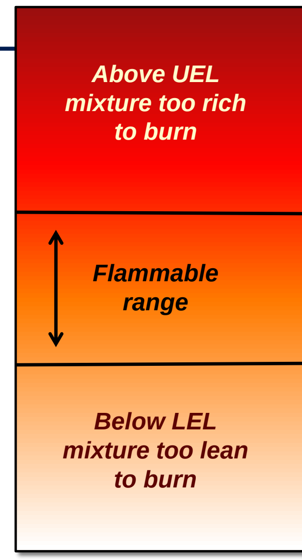
Explosive limits

- Lower Explosive Limit (LEL):
  - Minimum concentration of a combustible gas or vapor in air which will ignite if a source of ignition is present
- Upper Explosive Limit (UEL):
  - Most but not all combustible gases have an upper explosive limit
  - Maximum concentration in air which will support combustion
  - Concentrations which are above the UEL are too "rich" to burn



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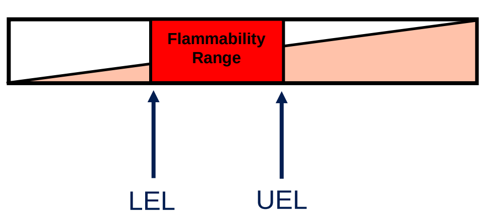
Different gases have different flammability ranges

Gas Concentration



Fuel Gas	LEL (%VOL)	UEL (%VOL)
Acetylene	2.2	85
Ammonia	15	28
Benzene	1.3	7.1
Butane	1.8	8.4
Carbon Monoxide	12	75
Ethylene	2.7	36
Ethylene oxide	3.0	100
Ethyl Alcohol	3.3	19
Fuel Oil #1 (Diesel)	0.7	5
Hydrogen	4	75
Isobutylene	1.8	9
Isopropyl Alcohol	2	12
Gasoline	1.4	7.6
Kerosine	0.7	5
Methane	5	15
MEK	1.8	10
Hexane	1.1	7.5
Pentane	1.5	7.8
Propane	2.1	10.1
Toluene	1.2	7.1
p-Xylene	1.1	7.0

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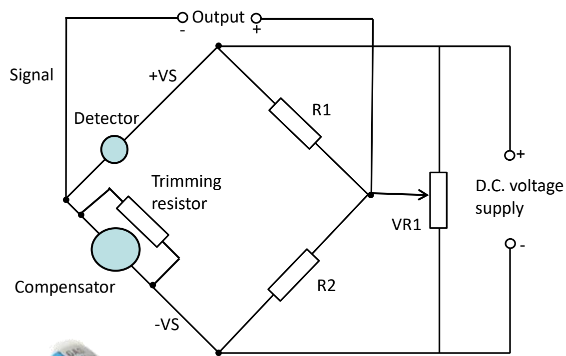
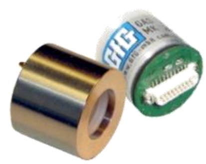
Catalytic “Hot Bead” Combustible Sensor

- Detects combustible gas by catalytic oxidation
- When exposed to gas oxidation reaction causes the active (detector) bead to heat
- Requires oxygen to detect gas!





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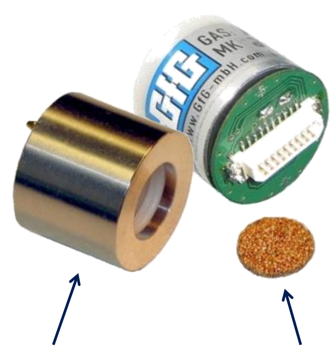
Traditional LEL sensors are “Flame proof” devices

- Flame proof sensors depend on physical barriers such as stainless-steel housings and flame arrestors to limit the amount of energy that can ever be released by the sensor



Stainless steel housing

Flame arrestor (sinter)

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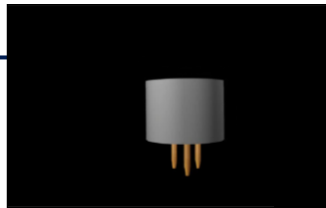
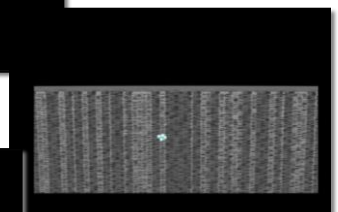
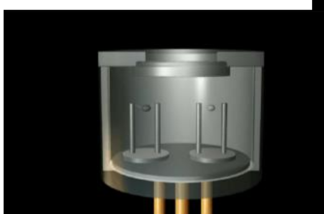
Catalytic Sensor Structure



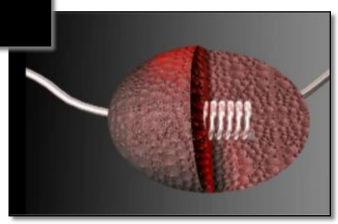
Catalytic combustion (CC) type LEL sensor is typically housed in robust, stainless steel flame proof enclosure



Gas molecules diffuse into sensor through flame arrestor



Once inside the sensor molecules diffuse to the active bead, where they are oxidized



Oxidation heats active bead to higher temperature. Difference in temperature is proportional to the concentration of gas.

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Stoichiometric formulas

- Stoichiometric is not an imported vodka
- Describes correct mixture of ingredients in a chemical reaction
- After the reaction is over, no surplus ingredients will be left
- In combustion, the stoichiometric ratio also is called the correct, ideal or perfect ratio:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2\ H_2O$$

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Conditions created by oxidation of large molecules affects performance of the sensor

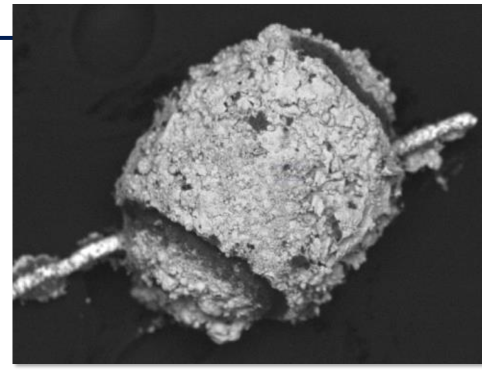
- Oxidation occurs on step-by-step basis and proceeds only when molecules are in physical contact with catalyst coated surfaces within the bead.
- The very hot reaction by-products create convective currents as they rapidly diffuse away from the catalyst surfaces in the bead.
- Water vapor produced by oxidation of larger molecules creates a significant net outward flux, impeding diffusion of new molecules into the into the bead.
- Oxidation of methane: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

  To oxidize one molecule CH_4 three molecules enter bead, and three molecules produced as by-products.
- Oxidation of pentane: $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$

  To oxidize one molecule of pentane, nine molecules enter bead, and 11 molecules produced as by-products.
- Oxidation of nonane: $C_9H_{20} + 14O_2 \rightarrow 9CO_2 + 10H_2O$

  To oxidize one molecule of nonane, 15 molecules enter bead, but 19 need to leave the sensor.

Image Courtesy Alphasense



300 µm

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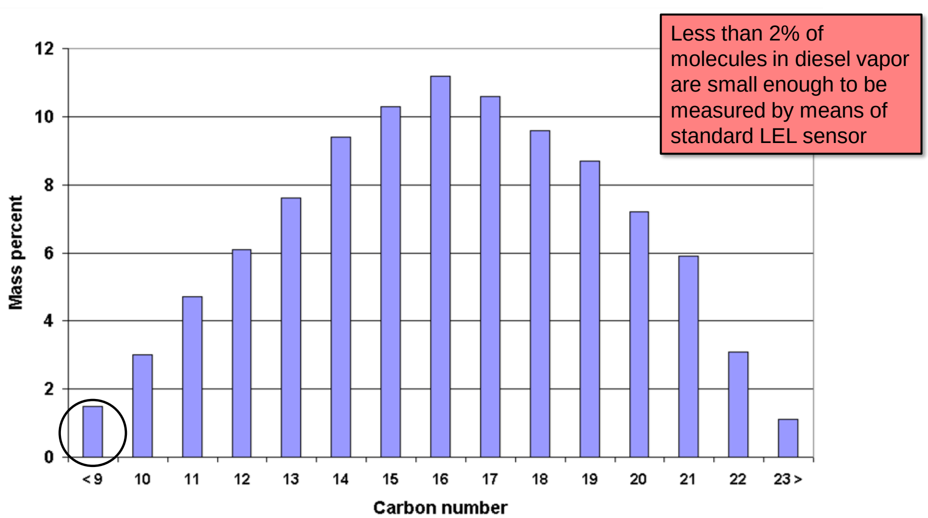
Typical carbon number distribution in No. 2 Diesel Fuel (liquid)



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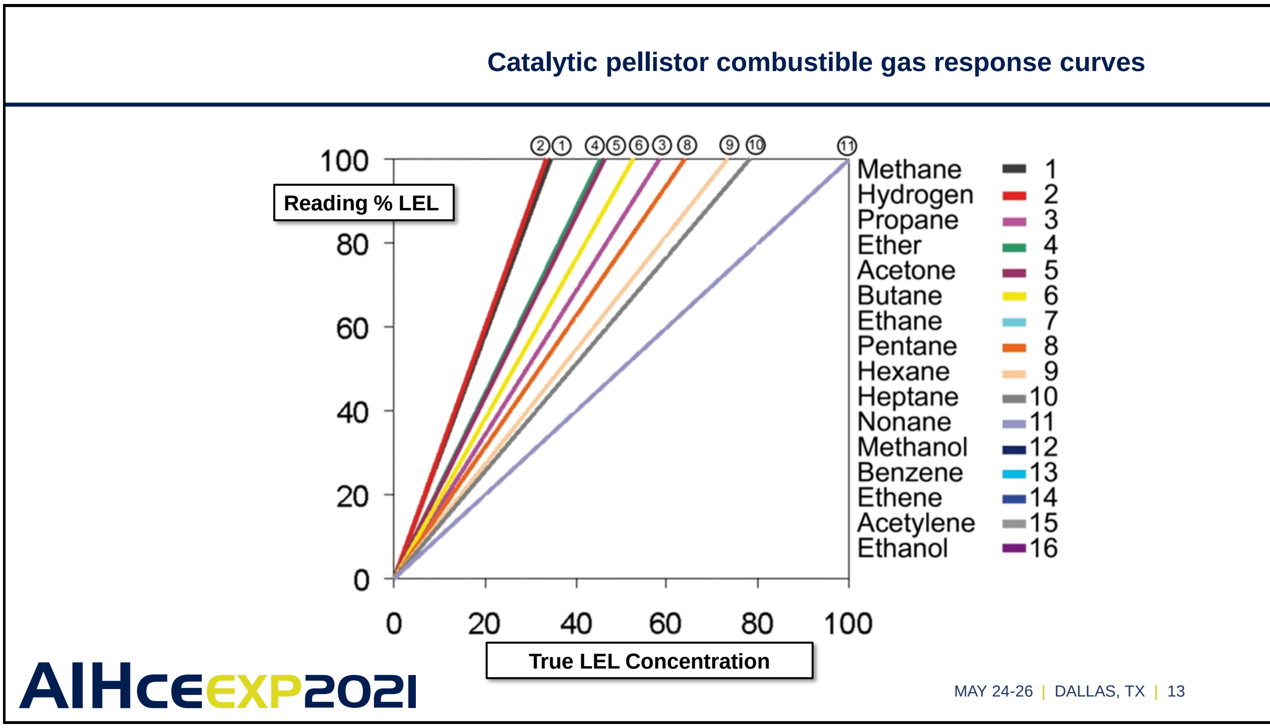
Catalytic pellistor combustible gas response curves
Reading % LEL
100
80
60
40
20
0
0
20
40
60
80
100
True LEL Concentration
Methane 1
Hydrogen 2
Propane 3
Ether 4
Acetone 5
Butane 6
Ethane 7
Pentane 8
Hexane 9
Heptane 10
Nonane 11
Methanol 12
Benzene 13
Ethene 14
Acetylene 15
Ethanol 16
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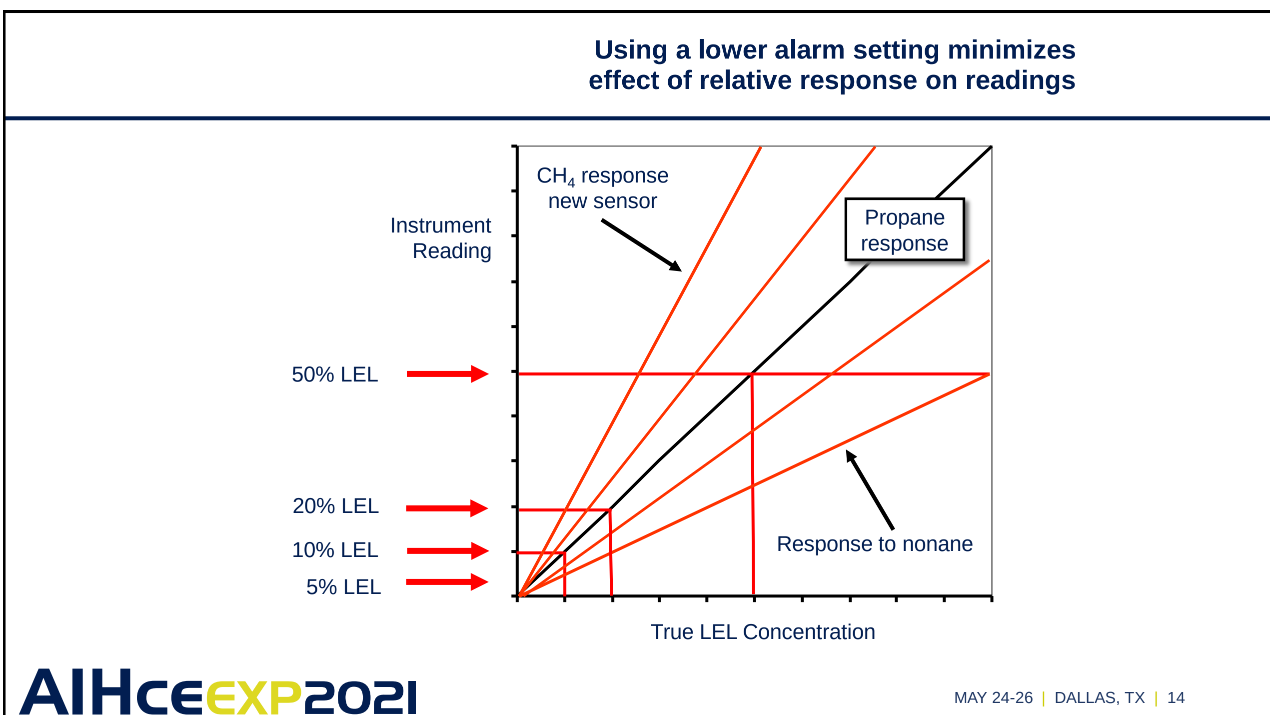
Using a lower alarm setting minimizes effect of relative response on readings
CH4 response new sensor
Propane response
Instrument Reading
50% LEL
20% LEL
10% LEL
5% LEL
Response to nonane
True LEL Concentration
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Typical catalytic LEL sensor relative responses*

Relative responses of 4P-75 catalytic LEL sensor			
Combustible gas / vapor	Relative response when sensor calibrated on pentane	Relative response when sensor calibrated on propane	Relative response when sensor calibrated on methane
Hydrogen	2.2	1.7	1.1
Methane	2.0	1.5	1.0
Propane	1.3	1.0	0.7
n-Butane	1.2	0.9	0.6
n-Pentane	1.0	0.8	0.5
n-Hexane	0.9	0.7	0.5
n-Octane	0.8	0.6	0.4
Methanol	2.3	1.8	1.2
Ethanol	1.6	1.2	0.8
Isopropanol	1.4	1.1	0.7
Acetone	1.4	1.1	0.7
Ammonia	2.6	2.0	1.3
Toluene	0.7	0.5	0.4
Gasoline (unleaded)	1.2	0.9	0.6

*Note: Response values differ between LEL sensor designs.
Values in the above table are for discussion only.

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Correction Factors

- Correction factor is the reciprocal of the relative response
- The relative response of 4P-75 LEL sensor (methane scale) to ethanol is 0.8
- Multiplying the instrument reading by the correction factor for ethanol provides the true concentration
- Given a correction factor for ethanol of 1.25, and an instrument reading of 40 per cent LEL, the true concentration would be calculated as:

40 % LEL	X 1.25	=	50 % LEL
Instrument Reading	Correction Factor		True Concentration

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Typical catalytic LEL sensor correction factors*

Correction factors for 4P-75 catalytic LEL sensor			
Combustible gas / vapor	Correction factor when sensor calibrated on pentane	Correction factor when sensor calibrated on propane	Correction factor when sensor calibrated on methane
Hydrogen	0.45	0.59	0.91
Methane	0.50	0.67	1.00
Propane	0.77	1.00	1.54
n-Butane	0.83	1.11	1.67
n-Pentane	1.00	1.33	2.00
n-Hexane	1.11	1.43	2.22
n-Octane	1.25	1.67	2.50
Methanol	0.43	0.57	0.87
Ethanol	0.63	0.83	1.25
Isopropanol	0.71	0.95	1.43
Acetone	0.71	0.95	1.43
Ammonia	0.38	0.50	0.77
Toluene	1.43	2.00	2.86
Gasoline (unleaded)	0.83	1.11	1.67

*Note: Correction factors differ between LEL sensor designs.
Values in the above table are for discussion only.

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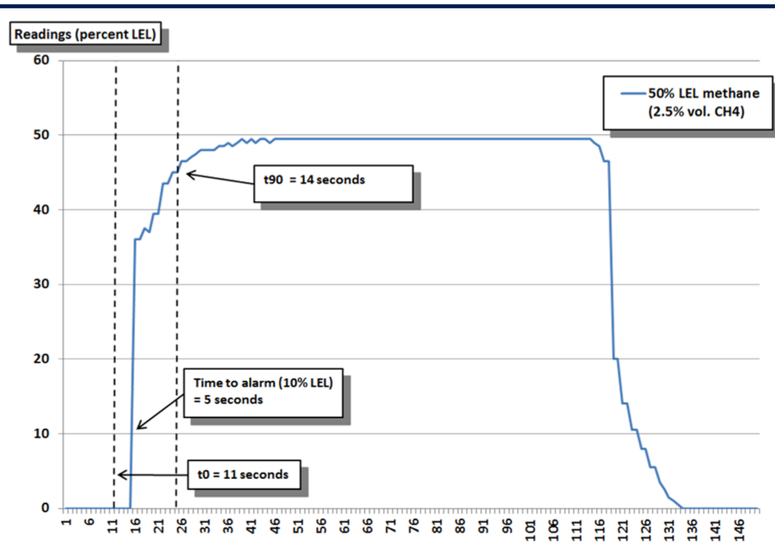
Typical catalytic percent LEL sensor response to 50% LEL methane (2.5% vol. CH_4)



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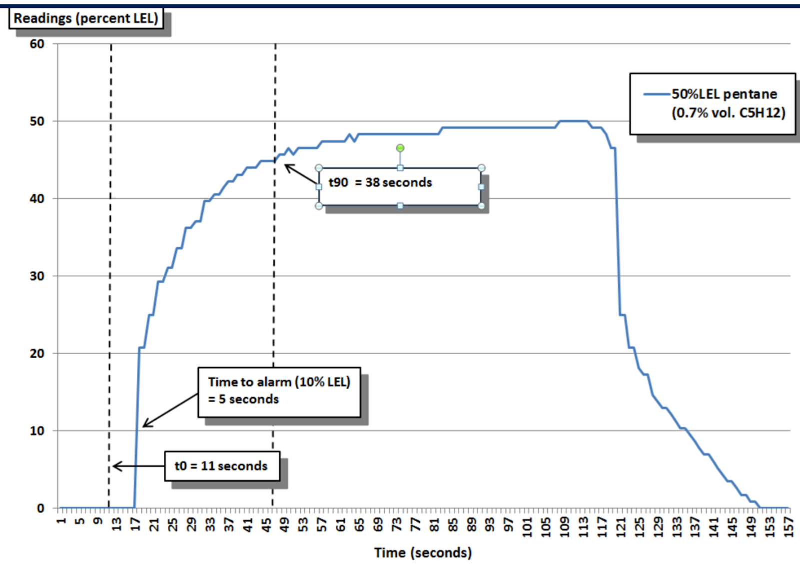
Typical catalytic percent LEL sensor response to 50% LEL pentane (0.7% vol. C_5H_{12})



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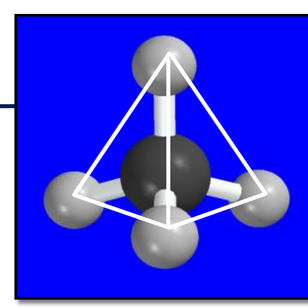
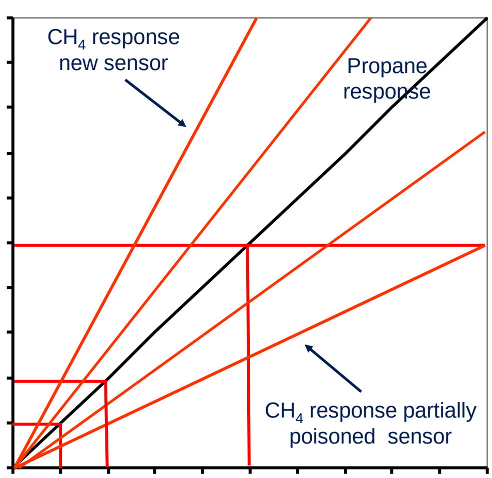
Response to methane over life of sensor





- Relative response to methane may change substantially over life of sensor

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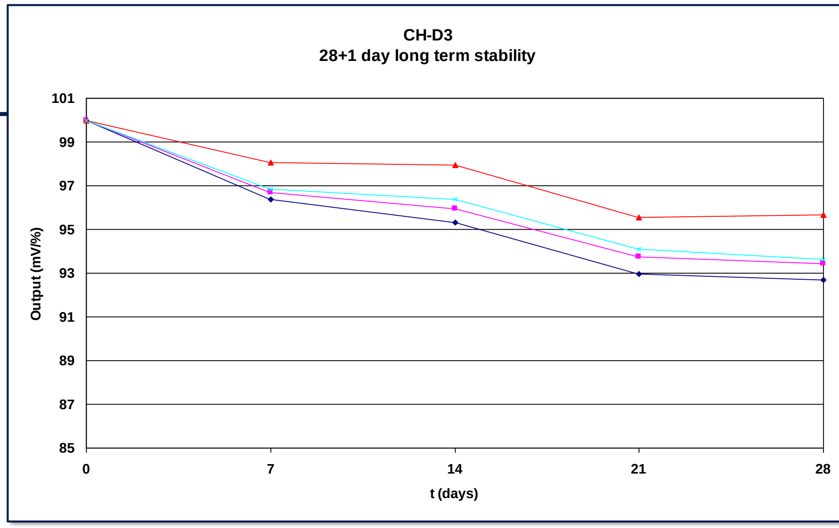
Pellistors must pass lengthy stability test during production (28 day +1day)

- Manufacturers burn in pellistor sensors by exposure to high concentration gas
- Quickly lose significant sensitivity, then stabilize, with much lower rate of additional loss
- Not easy to maintain required sensitivity!



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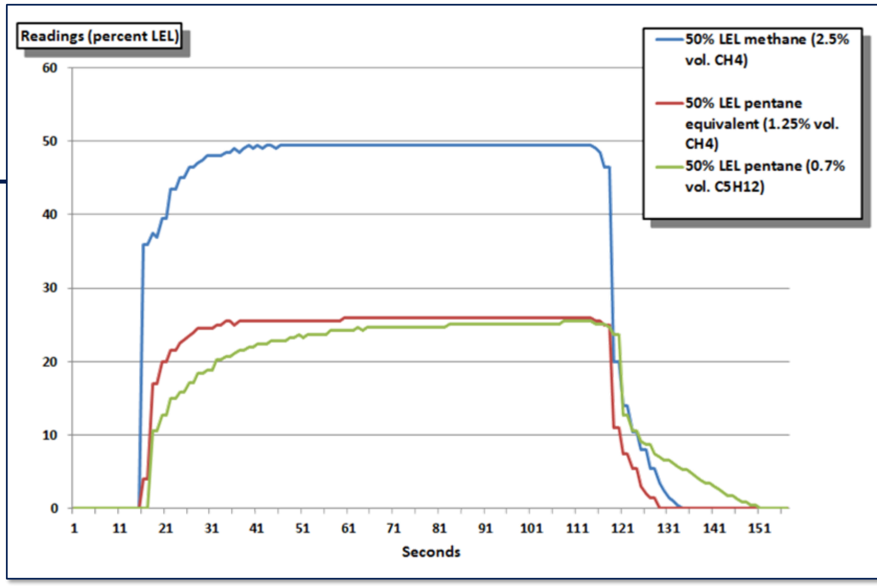
Methane based equivalent calibration gas mixtures

Combustible Gas / Vapor	*Relative response when sensor is calibrated to 2.5% (50% LEL) methane*	*Concentration of methane used for equivalent 50% LEL response*
Hydrogen	***1.1***	***2.75% CH4***
Methane	***1.0***	***2.5% Vol CH4***
Ethanol	***0.8***	***2.0% Vol CH4***
Acetone	***0.7***	***1.75% Vol CH4***
Propane	***0.65***	***1.62% Vol CH4***
n-Pentane	***0.5***	***1.25% Vol CH4***
n-Hexane	***0.45***	***1.12% Vol CH4***
n-Octane	***0.4***	***1.0% Vol CH4***
Toluene	***0.35***	***0.88% Vol CH4***

*Note: Correction factors differ between LEL sensor designs. Values in the above table are for discussion only.

CC LEL sensor response to 50% LEL methane (2.5% vol. CH_4), 50% LEL pentane (7.0% vol. C_5H_{12}) and 50% LEL "pentane equivalent" (1.25% vol. CH_4)



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Limitations of catalytic pellistor LEL sensors

- Poor response to larger molecules
- Slower response to larger molecules
- Easily poisoned
- Exposure to high concentration combustible gas damaging to sensor
- Must have minimum of 10% O_2 to accurately detect gas

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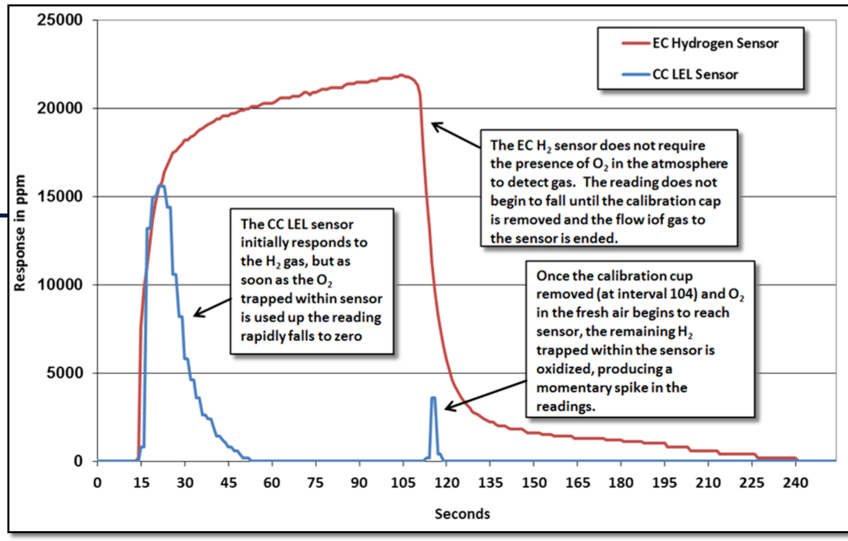
Response of electrochemical and LEL sensor to 5% LEL (20,000 ppm) H_2 in nitrogen



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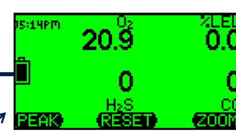
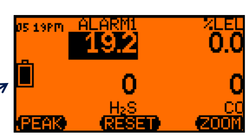
Effects of O_2 concentration on combustible gas readings

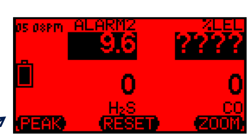
- Look at O_2 readings first!
- LEL readings may be affected if levels of O_2 are higher or lower than fresh air
- Catalytic LEL sensors require a minimum level of 10% oxygen to read LEL
- If the O_2 concentration is too low the LEL reading should be replaced with question marks or an alarm message



Readings in fresh air



Readings in O_2 deficient air



Readings when O_2 too low for LEL sensor

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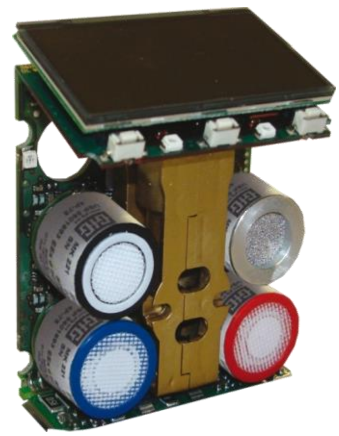
Over-Limit Protection

- LEL sensor designed to detect 0-100% LEL concentration of flammable gas
- Catalytic LEL sensors can be damaged by exposure to higher than 100% LEL concentrations
  - To prevent damage, sensor is switched OFF, the alarms are activated, and instrument shows an "OL" message (Over Limit)
- Techniques for high range combustible gas measurement:
  - Dilution fittings
  - Thermal Conductivity (TCD), infrared (NDIR) and Molecular Properties Spectrometer (MPS) are all able to measure high range combustible gas up to 100% volume



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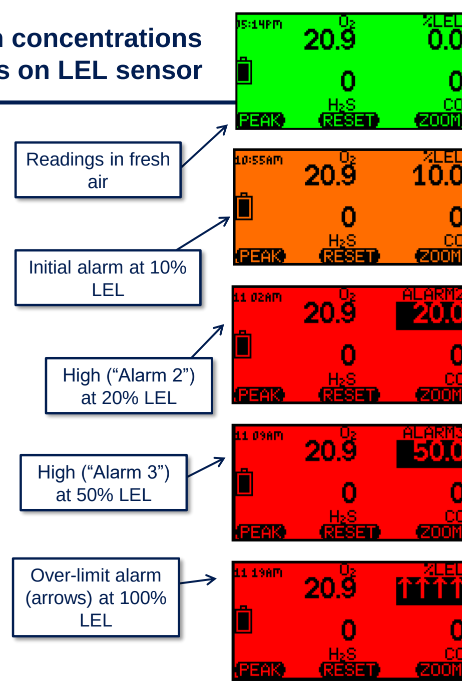
Effects of high concentrations of gas on LEL sensor

- When doing atmospheric testing we concerned with the LEL not the UEL. Why is that?
  - Work is not permitted in areas where the concentration of gas exceeds safety limits!
  - If the explosive gas concentration is too high there may not be enough oxygen for the LEL sensor to detect properly
  - Concentrations above 100% LEL can damage the LEL sensor



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Combustible sensor poisons

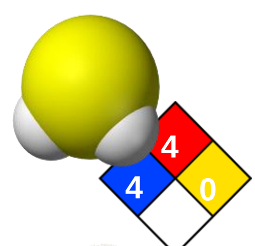
- Combustible sensor poisons:
  - Silicones (by far the most virulent poison)
  - Hydrogen sulfide

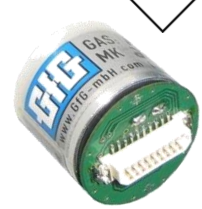
> Note: The LEL sensor includes an internal filter that is more than sufficient to remove the H_2S in calibration gas. It takes very high levels of H_2S to overcome the filter and harm the LEL sensor

  - Other sulfur containing compounds
  - Phosphates and phosphorus containing substances
  - Lead containing compounds (especially tetraethyl lead)
  - High concentrations of flammable gas!
- Combustible sensor inhibitors:
  - Halogenated hydrocarbons (Freons®, trichloroethylene, methylene chloride, etc.)

Effects of H_2S on combustible gas sensors

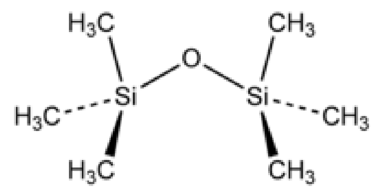
- H2S affects sensor as inhibitor AND as poison
  - Inhibitors like trichloroethane and methylene chloride leave deposit on active bead that depresses gas readings while inhibitor is present
  - Sensor generally recovers most of original response once it is returned to fresh air
- H2S functions as inhibitor BUT byproducts of catalytic oxidation become very corrosive if they build up on active bead in sensor
  - Corrosive effect can rapidly (and permanently) damage bead if not "cooked off" fast enough
  - How efficiently bead "cooks off" contaminants is function of:
    - Temperature at which bead is operated
    - Size of the bead
    - Whether bead under continuous power versus pulsing the power rapidly on and off to save operating energy.





"Silicone resistant" vs. "standard" pellistor type LEL sensors

- "Silicone resistant" combustible sensors have an <u>external</u> silicone filter capable of removing most silicone vapor before it can diffuse into the sensor
  - Silicone vapor is the most virulent of all combustible sensor poisons
  - Filter also slows or slightly reduces response to heavier hydrocarbons such as hexane, benzene, toluene, xylene, cumene, etc.
  - The heavier the compound, the greater the effect on response



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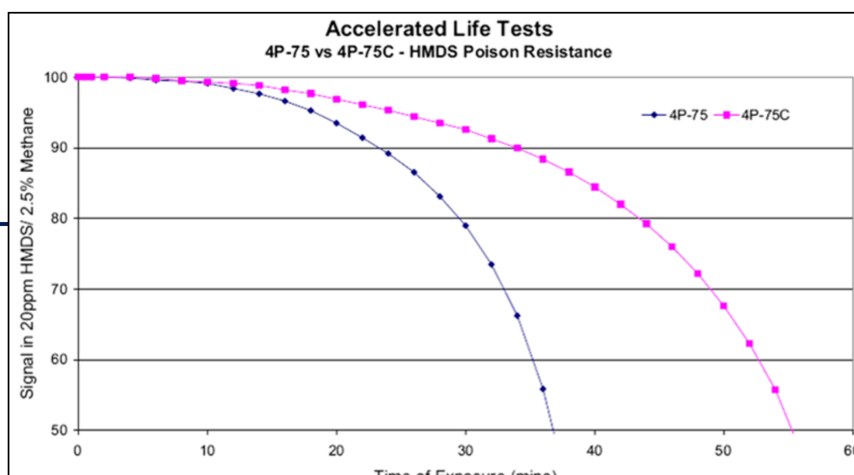
Effects of hexamethyldisiloxane (HMDS) on pellistor sensor



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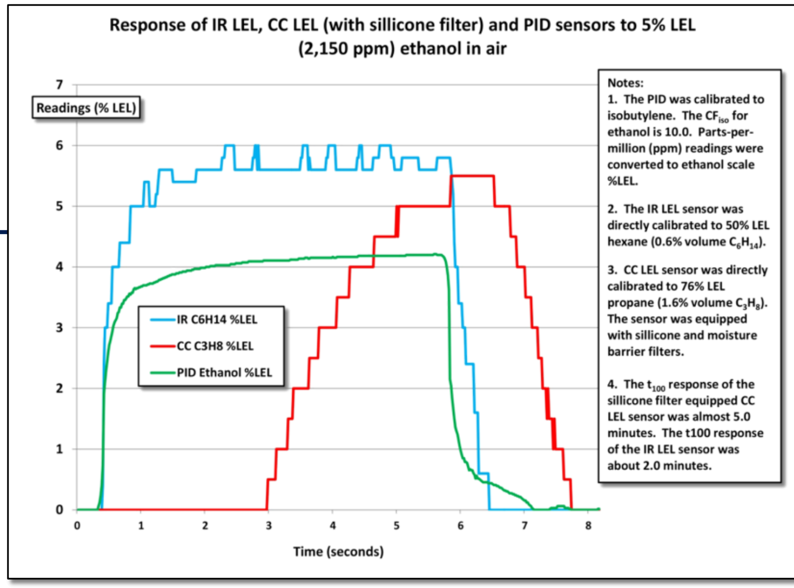
Effects of silicone filter on LEL sensor performance



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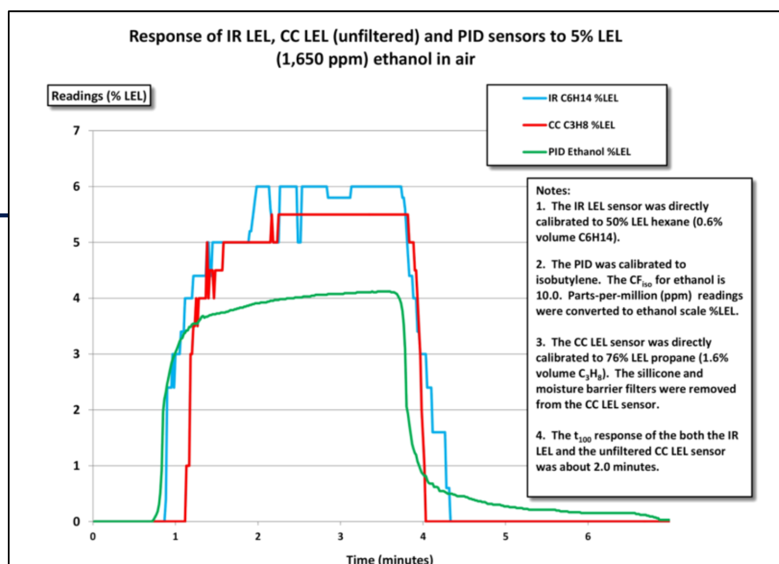
Effects of silicone filter on LEL sensor performance



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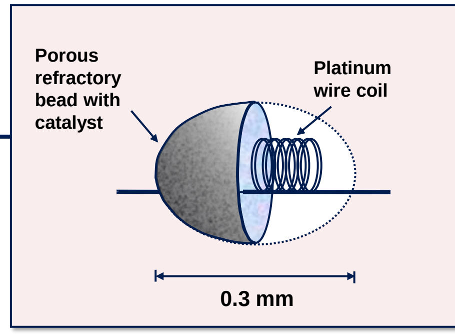
CC LEL sensors need time to warm up

- To reduce power consumption and improve IS and speed of response, size of pellistor bead much smaller in current generation CC sensors
- Volume of pellistor bead (a sphere): $V = 4/3 \pi r^3$
- Since most catalyst sites are within the bead (not on the surface of the bead), when you decease the radius of the bead by "x", you reduce the volume of the bead (and number of catalyst sites) by "x" to the third power (x^3)
- So, smaller low power LEL sensors are easier to poison
- Because compensator bead is now so much larger compared to the active bead, takes longer for the beads to reach thermal equilibrium at the working temperature (≈ 550°C)



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Standard "catalytic" LEL sensor advice

- Whatever the brand, allow enough time for full stabilization prior to performing fresh air zero
  - Always perform fresh air zero, even if display shows reading of 0% LEL
  - Digital filtering near zero may mask readings that are slightly above or below zero
  - Wait until sensors fully warmed up after initially turning instrument on before performing a fresh air zero
  - Especially important to allow sensor to stabilize fully when there is a large difference in temperature between where the instrument is turned on (usually indoors) and actually used
- Perform functional test before each day's use!
  - Use methane-based test gas mixture OR if you use a different gas (e.g. propane or pentane) challenge the sensor with methane periodically to verify the sensor has not lost sensitivity to methane

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Bump Test

- "Bump test" (function check) is a <u>qualitative</u> test in which the sensors are exposed to gas for a time and at a concentration to activate all of the alarms to at least the lower alarm settings
- "Bump test" confirms that gas is capable of reaching the sensors, that the response time (time to alarm) after gas is applied is within normal limits, and that the alarms are activated and function properly
- Takes 20-45 sec. to perform
- "Bump test" does <u>not</u> verify the accuracy of the readings of the sensors when exposed to gas

Calibration check

- "Calibration check" is a <u>quantitative</u> test using a traceable source of known concentration test gas to verify that the response of the sensors is within the manufacturer's acceptable limits
  - For instance, a manufacturer might specify that readings in a properly calibrated instrument should be within ±10% of the value of the gas applied
  - If this is the pass / fail criterion, when 20 ppm H_2S is applied, readings must stabilize between 18 ppm and 22 ppm in order to pass the test
- Different manufacturers are free to publish different requirements

Perform "Bump Test" or "Calibration Check" before each day's use!

- Perform "Bump test" or "Calibration check" before each day's use in accordance with the manufacturer's instructions using an appropriate test gas
- Any instrument that fails test must be adjusted by means of a "full calibration" procedure before further use, or taken out of service
- If environmental conditions that could affect instrument performance are suspected, verification of calibration should be made on a more frequent basis
- Events that could adversely affect readings (e.g. dropping or immersion), should trigger reverification of fitness before further use

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Periodic Calibration

- "Full calibration" is two step procedure that includes both "Fresh air" and "Span" calibration
- "Span" calibration defined as quantitative adjustment of instrument's response to match a desired value compared to known traceable concentration of calibration gas
- Follow manufacturer guidelines!
  - Calibration should be conducted periodically as required by the manufacturer, or whenever "Bump test" and / or "Calibration check" results indicate one or more of the sensors require adjustment
  - The calibration procedure, including the concentration of gas applied, method used to apply gas, and method used to adjust the readings are determined by the manufacturer

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What about using photoionization detectors for LEL measurement?

- Optimized for ppm measurement
- Not linear at high concentrations
- Not certified for LEL measurement

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Volatile organic compounds (VOCs)

- VOCs are organic chemicals or mixtures characterized by tendency to evaporate easily at room temperature
- Familiar VOCs include:
  - Solvents
  - Paint thinner
  - Nail polish remover
  - Gasoline
  - Diesel
  - Heating oil
  - Kerosene
  - Jet fuel
  - Benzene
  - Butadiene
  - Hexane
  - Toluene
  - Xylene
  - Many others

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Why use photoionization detector equipped instruments?

- For most VOCs, long before you reach a concentration sufficient to register on a combustible gas indicator, you will have easily exceeded the toxic exposure limits for the contaminant
- PID equipped instruments are generally the best choice for measurement of VOCs at exposure limit concentrations
- Whatever type of instrument is used to measure these hazards, it is essential that the equipment is used properly, and the results are correctly interpreted

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Combustible sensor limitations

Contaminant	LEL (Vol %)	Flashpoint Temp (ºF)	OSHA PEL	NIOSH REL	TLV	5% LEL in PPM
Acetone	2.5%	-4ºF (-20 ºC)	1,000 PPM TWA	250 PPM TWA	500 PPM TWA; 750 PPM STEL	1250 PPM
Diesel (No.2) vapor	0.6%	125ºF (51.7ºC)	None Listed	None Listed	15 PPM	300 PPM
Ethanol	3.3%	55ºF (12.8 ºC)	1,000 PPM TWA	1000 PPM TWA	1000 PPM TWA	1,650 PPM
Gasoline	1.3%	-50ºF (-45.6ºC)	None Listed	None Listed	300 PPM TWA; 500 PPM STEL	650 PPM
n-Hexane	1.1%	-7ºF (-21.7 ºC)	500 PPM TWA	50 PPM TWA	50 PPM TWA	550 PPM
Isopropyl alcohol	2.0%	53ºF (11.7ºC)	400 PPM TWA	400 PPM TWA; 500 PPM STEL	200 PPM TWA; 400 PPM STEL	1000 PPM
Kerosene/ Jet Fuels	0.7%	100 – 162ºF (37.8 – 72.3ºC)	None Listed	100 mg/M3 TWA (approx. 14.4 PPM)	200 mg/M3 TWA (approx. 29 PPM)	350 PPM
MEK	1.4%	16ºF (-8.9ºC)	200 PPM TWA	200 PPM TWA; 300 PPM STEL	200 PPM TWA; 300 PPM STEL	700 PPM
Turpentine	0.8	95ºF (35ºC)	100 PPM TWA	100 PPM TWA	20 PPM TWA	400 PPM
Xylenes (o, m & p isomers)	0.9 – 1.1%	81 – 90ºF (27.3 – 32.3 ºC)	100 PPM TWA	100 PPM TWA; 150 PPM STEL	100 PPM TWA; 150 STEL	450 – 550 PPM

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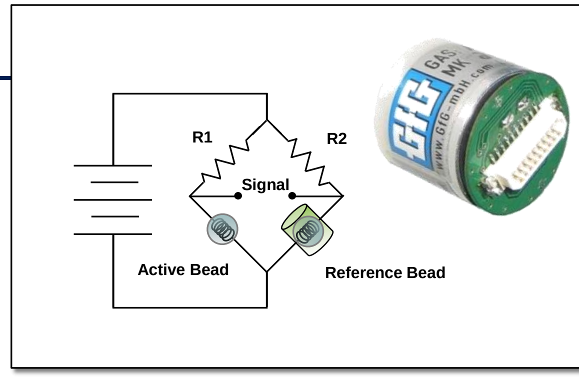
Thermal conductivity (TCD) combustible gas sensors

- Specialized type of sensor most frequently used to detect high range concentrations of combustible gas (especially natural gas)
- Very similar to Wheatstone type LEL sensor, EXCEPT the active bead is not treated with catalyst
- Depend on differences in density of atmosphere to measure gas



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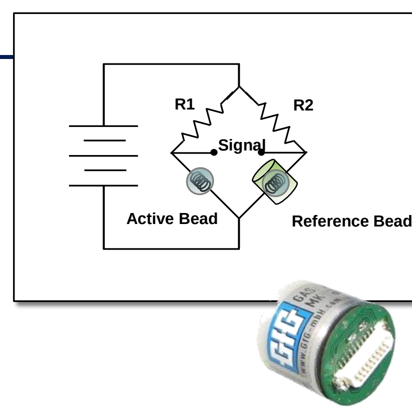
Thermal conductivity (TCD) combustible gas sensors

- Two beads strung onto opposite arms of Wheatstone bridge circuit
- Neither bead treated with catalyst
- Reference bead isolated from the air being monitored in sealed or semi-sealed chamber
- Active bead exposed to atmosphere being monitored
- Beads heated to operating temperature
- Detection depends on "air-conditioning" effect of gas on the active bead
  - Lighter than air gas (such as hydrogen or methane), attenuates the atmosphere, causing the active bead to dissipate heat more efficiently
  - If a heavier than air gas is present (such as propane) the bead is insulated by the denser atmosphere
- Difference in temperature between the two beads is proportional to the amount of combustible gas present in the atmosphere being monitored



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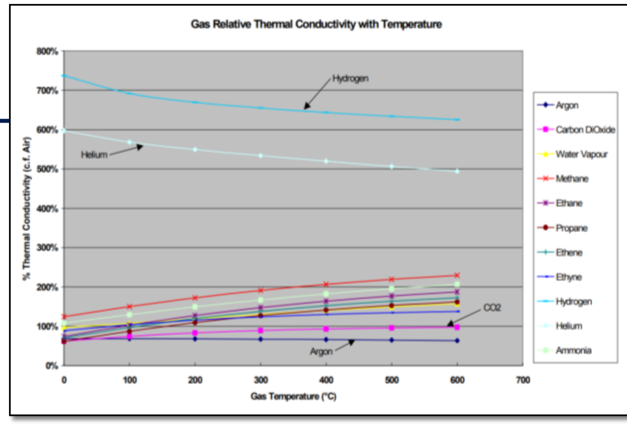
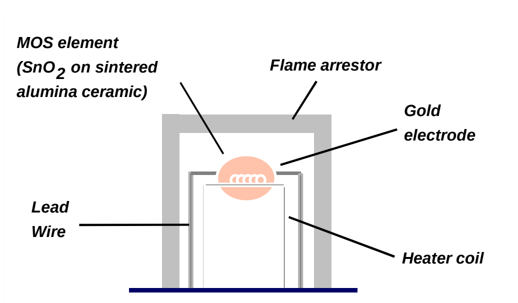
Thermal conductivity (TCD) combustible gas sensors

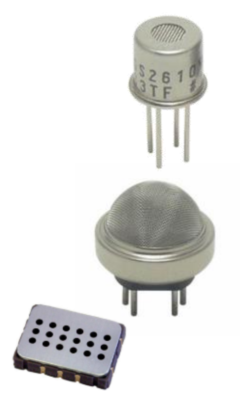


- Benefits
  - Able to detect gas up to 100% volume concentration
  - Gases with similar densities (such as methane and ethane) have similar response
  - Often included in same instrument as catalytic LEL sensor
- Limitations
  - Changes in the makeup of the air being tested can affect readings
  - Not recommended for use in confined spaces where there is the potential for oxygen deficiency, or air that contains elevated concentrations of nitrogen or carbon dioxide
  - Generally, only used when measured gas is present in fresh air
  - Do not use if background gas mixture is unknown or variable

MOS Detection Mechanism

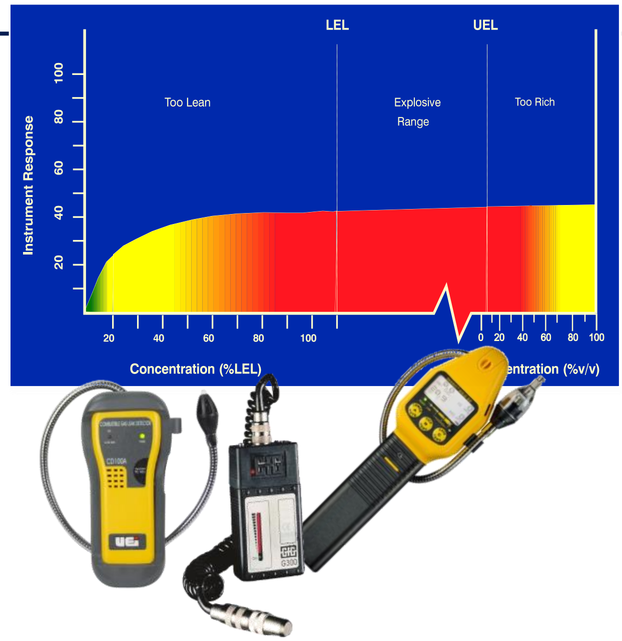
- Sensing element:
  - Tin dioxide (SnO2) on sintered alumina ceramic
  - In clean air electrical conductivity low
  - Contact with either oxidizing or reducing gases (such as CO, combustible gas and ammonia) increases conductivity
  - Sensitivity to specific gases depends on temperature of sensing element





MOS sensor capabilities and limitations

- Benefits:
  - Broad range response (including refrigerants and halogenated solvents)
  - Detection in ppm range or lower concentration
  - Inexpensive
  - Good for qualitative measurement or leak detection
  - Long life
- Limitations:
  - Non-linear signal
  - Qualitative rather than numerical reading
  - Affected by temperature and humidity conditions (sensor can "go to sleep" in very low humidity)
  - Damaged by same inhibitors and poisons that harm catalytic LEL sensors



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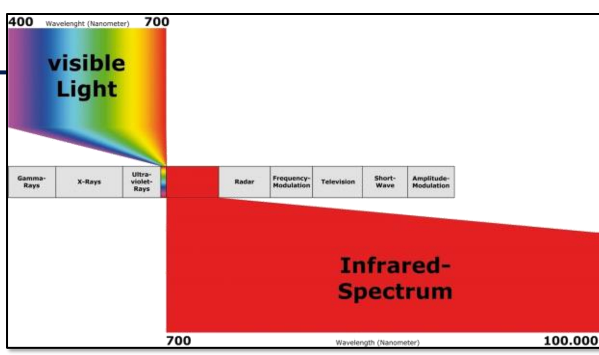

Non-dispersive infrared (NDIR) sensors

- Many gases absorb infrared light at a unique set of wavelengths
- In NDIR sensors the amount of IR light absorbed is proportional to the amount of target gas present
- IR absorption has advantages of high sensitivity, low cross-sensitivity, long life, and resistance to contamination
- IR absorption employed in both very high-performance laboratory analyzers and in very low-performance systems (e.g. inexpensive, non-intrinsically safe hand-held CO_2 detectors)

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Non-dispersive infrared (NDIR) sensors

- When infra-red radiation passes through a sensing chamber containing a specific contaminant, only those frequencies that match one of the vibration modes are absorbed
- The rest of the light is transmitted through the chamber without hindrance
- The presence of a particular chemical group within a molecule thus gives rise to characteristic absorption bands
- Non-dispersive IR sensors measure at a specific range of wavelengths associated with a particular gas or class of gases

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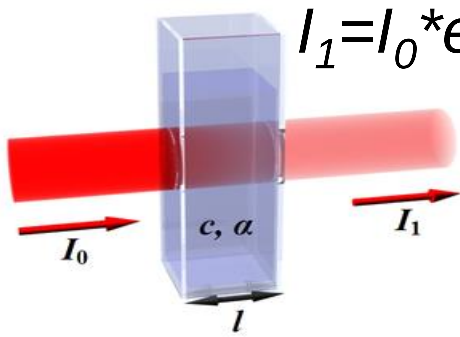
Beer-Lambert Law

$$I_1=I_0*e^{-\alpha L c}$$



Optical path-length matters...

- I_0 is the intensity of the incident light
- I_1 is the intensity after passing through the material
- L is the distance that the light travels through the material (the path length)
- c is the concentration of absorbing species in the material
- α is the absorption coefficient or the molar absorptivity of the absorber

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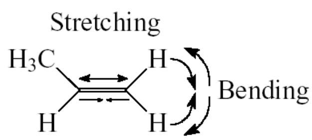
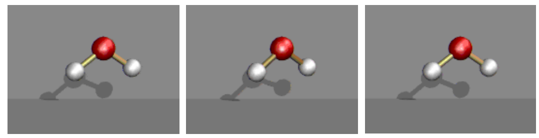
Energy Absorbed by "Bond Stretching" and "Bending" Vibration

- Must have a COVALENT CHEMICAL BOND



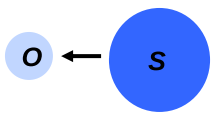


Symmetric Stretch

Asymmetric Stretch

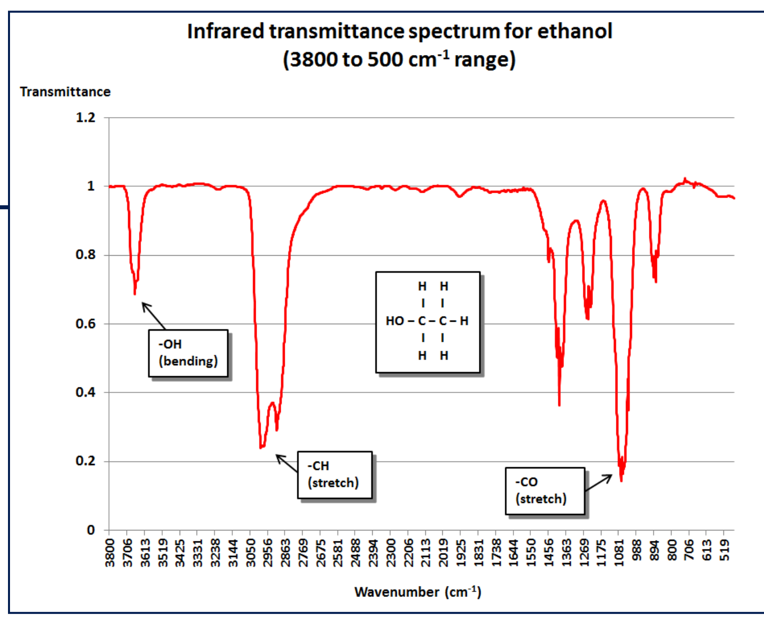
Bend

Nonlinear Molecules



Linear molecules: SO

Geometry and specific bonds in molecule give rise to IR spectrum



Requirements for IR Absorption

- Lower quantum levels must be "populated"
- Dipole moment (degree of charge imbalance) must change with the vibrational "motion"
- CO_2 and CH_4 absorb IR
- Homonuclear diatomics such as hydrogen DO NOT absorb IR
- IR-transparent gases:
  - H_2
  - N_2
  - O_2
  - F_2
  - Cl_2
  - Hg_2
  - Ar

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NDIR sensors commonly used in portable instruments

GfG IR sensor (Note longer pathlength)

MIPex "MEMS" extreme low power miniaturized IR LEL sensor

"4 Series" sized format used by City Tech, Dynament and E2V infrared sensors (Note shorter pathlength)

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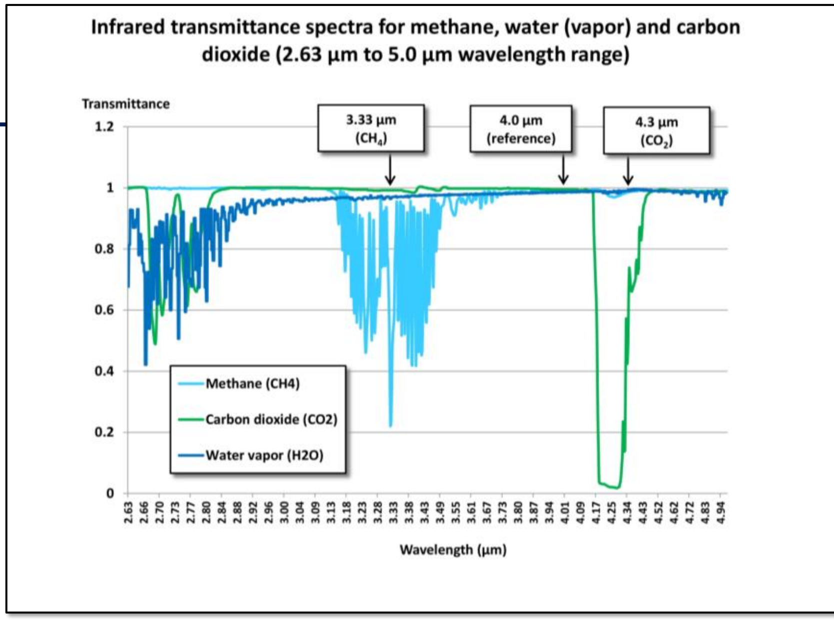

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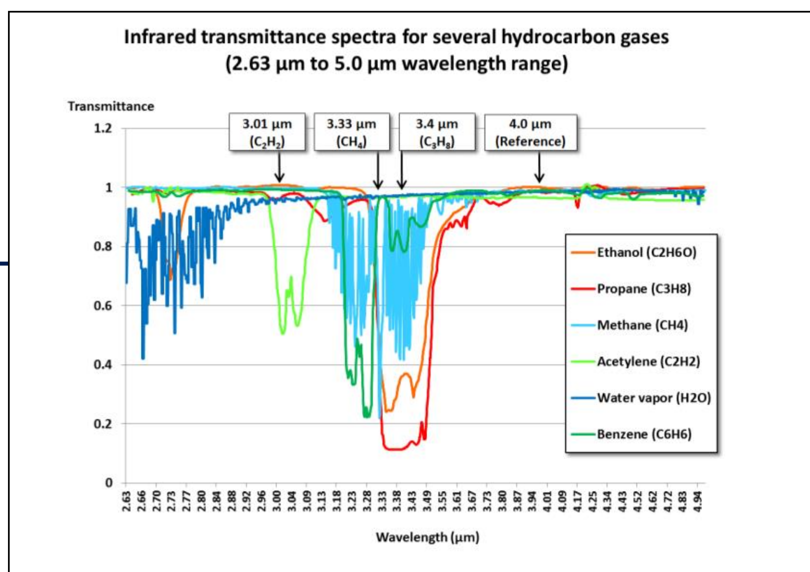
Wavelengths typically used for IR LEL measurement



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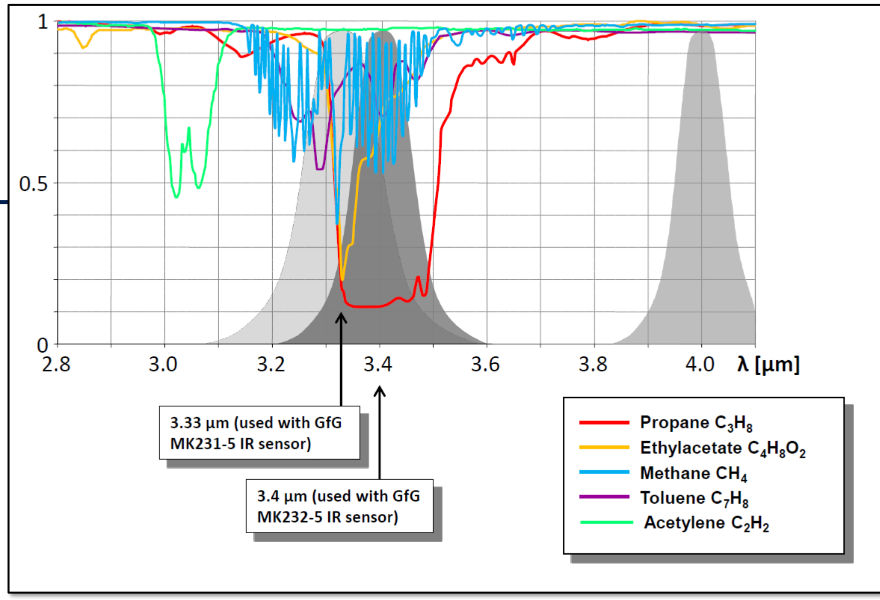
LEL measurement at 3.33µm vs. 3.4µm



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Combustible gas NDIR sensor advantages and limitations

- Limitations:
  - Molecule must include chemical bonds that absorb at the wavelength(s) used for measurement
  - Not all combustible gases can be detected!
    - "Diatomic" molecules like hydrogen (H_2) cannot be detected at all
    - Gases with double and triple bonds (like acetylene) detect poorly or not at all at some measurement wavelengths
    - NDIR sensors with short optical path-lengths may have limited ability to measure gases with lower relative responses
- Advantages:
  - Sensor cannot be poisoned
  - Does not require oxygen to detect gas
  - Can be used for high-range combustible gas measurement
  - Responds well to large hydrocarbon molecules that cannot be measured by means of standard LEL sensor

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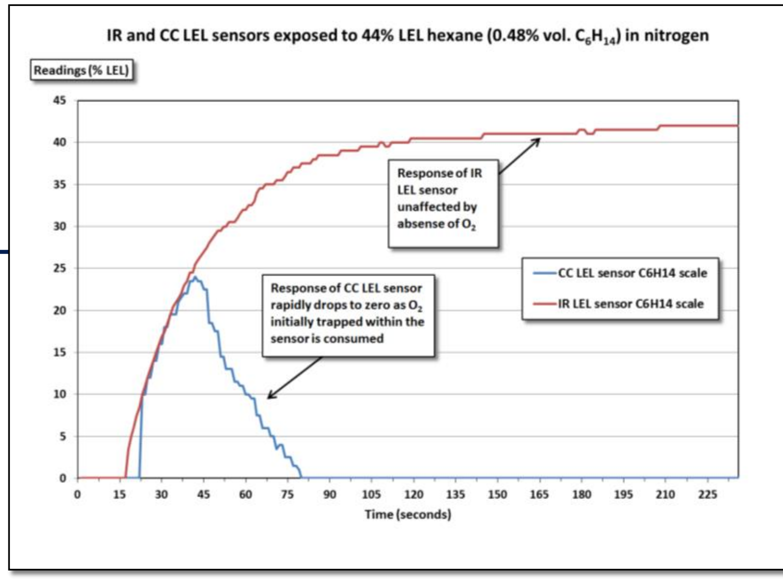
IR LEL sensor performance unaffected by the absence of oxygen



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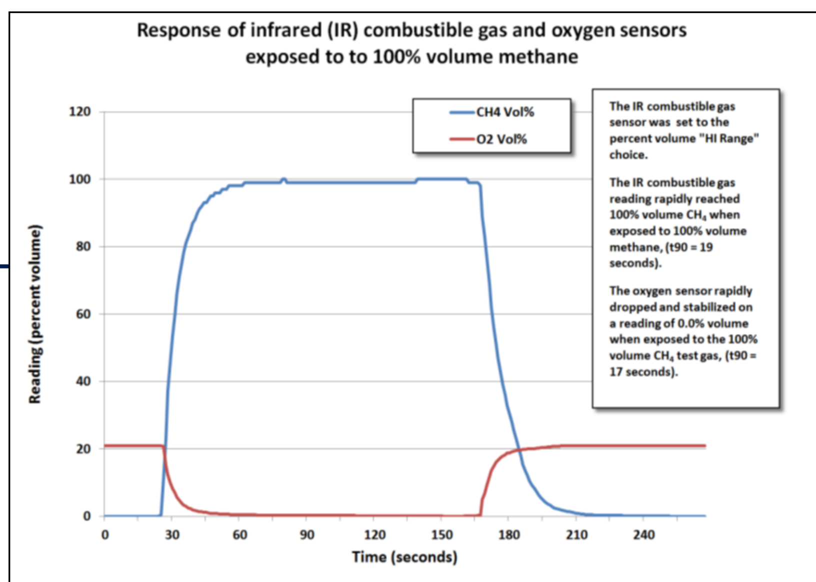
IR combustible sensors can be used for high range measurement up to 100% volume gas



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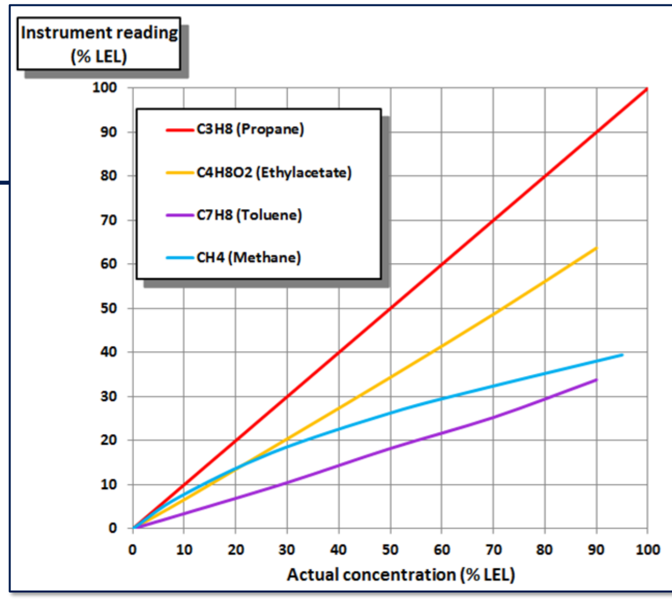
Response of NDIR LEL sensor (3.33 µm, 44 mm path) to various target gases

- Shape of raw NDIR CH_4 curve (at 3.33 µm) is less linear than other detectable gases
- CH_4 curve can be mathematically corrected (normalized) against the response curves of other gases of interest



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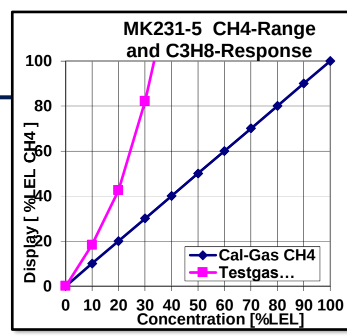
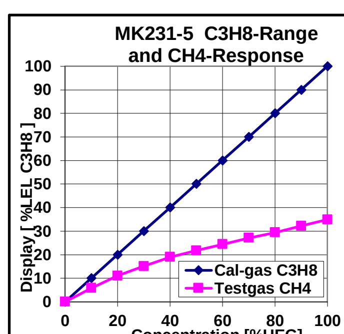
NDIR sensor performance

- When CH_4 is present, direct calibration to methane is the most conservative approach
- Calibration to CH_4 generally overestimates uncorrected readings for other aliphatic hydrocarbons; the higher the concentration the greater the overestimation
- Calibration to other aliphatic hydrocarbons (such as propane or hexane) underestimates uncorrected readings for methane;
- However, readings can be automatically corrected by choosing response curve from on-board library
- When other aliphatics are present, calibration to propane provides the most accurate response





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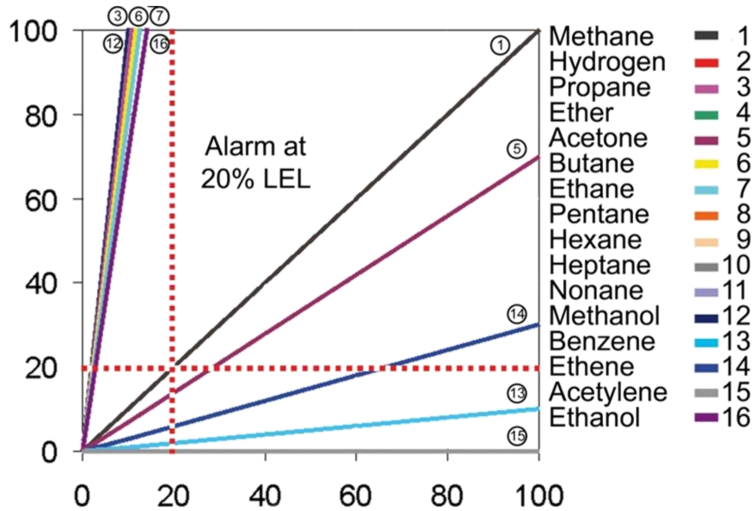
Linearized 3.33 µm NDIR combustible gas response curves



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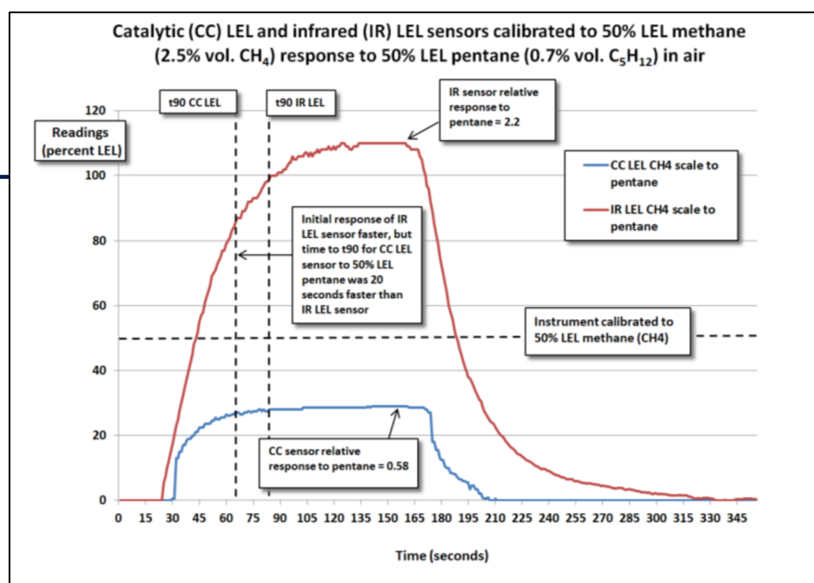
Relative response of pellistor and infrared sensors to n-Pentane



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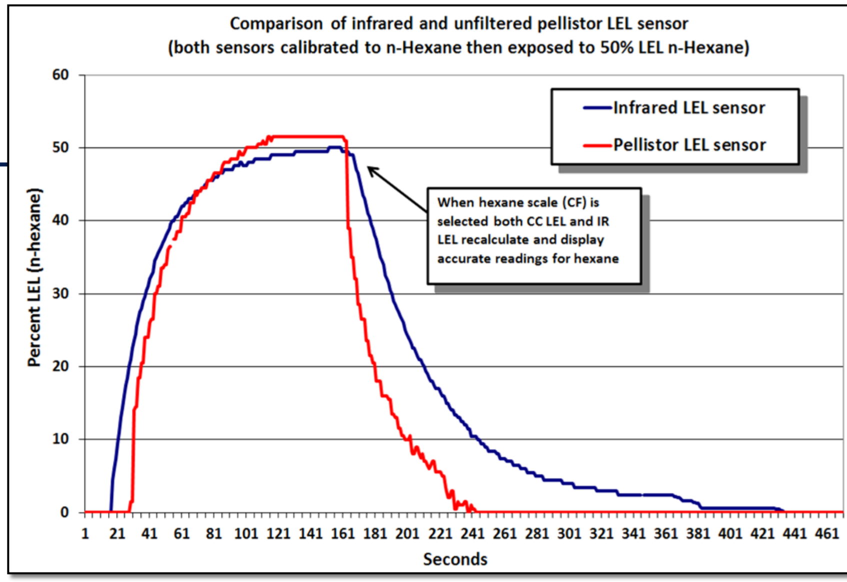
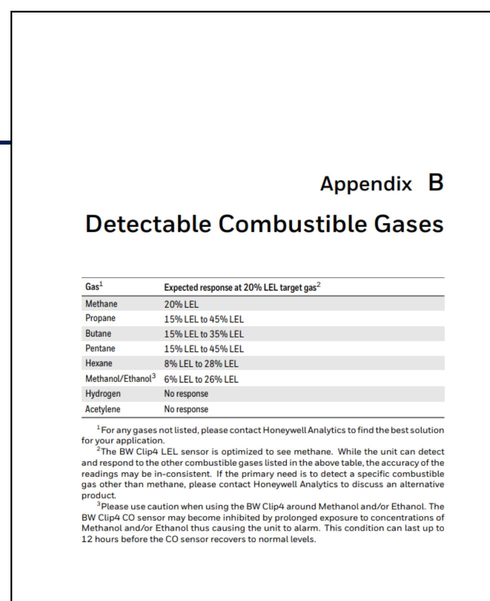
Corrected response of catalytic LEL and IR LEL sensors to 50% LEL n-Hexane

- Both sensors were calibrated to 50% LEL n-Hexane
- Readings for both sensors are now very close to the true 50% LEL concentration
- Initial response of IR sensor is slightly quicker than the pellistor sensor
- However, the time to the final stable response (T100) is virtually identical for both sensors, (about 150 seconds)



Performance of IR LEL sensors differs from performance of catalytic LEL sensors

- Read the owner's manual!
- Make sure to verify with manufacturer before attempting to use the sensor to measure unsaturated hydrocarbons, aromatic VOCs or other gases not specifically listed in the owner's manual!



Appendix B

Detectable Combustible Gases

Gas[1]	Expected response at 20% LEL target gas[2]
Methane	20% LEL
Propane	15% LEL to 45% LEL
Butane	15% LEL to 35% LEL
Pentane	15% LEL to 45% LEL
Hexane	8% LEL to 28% LEL
Methanol/Ethanol[3]	6% LEL to 26% LEL
Hydrogen	No response
Acetylene	No response

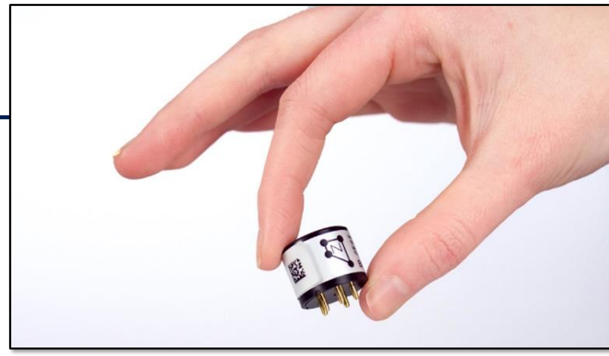
[1] For any gases not listed, please contact Honeywell Analytics to find the best solution for your application.

[2] The BW Clip4 LEL sensor is optimized to see methane. While the unit can detect and respond to the other combustible gases listed in the above table, the accuracy of the readings may be in-consistent. If the primary need is to detect a specific combustible gas other than methane, please contact Honeywell Analytics to discuss an alternative product.

[3] Please use caution when using the BW Clip4 around Methanol and/or Ethanol. The BW Clip4 CO sensor may become inhibited by prolonged exposure to concentrations of Methanol and/or Ethanol thus causing the unit to alarm. This condition can last up to 12 hours before the CO sensor recovers to normal levels.

Molecular Properties Spectrometer

- Smart sensor with built-in environmental compensation
- Automatic multi-gas detection
  - Detects, sorts and quantifies individual and mixtures of multiple gases
  - Calibrated for all detectable gases by performing a single calibration with methane
- Extremely low power — 29 mW average
- Intrinsically safe
- Extremely poison-resistant
- Factory does not require periodic calibration (bump test still required)
- 5-year expected lifetime



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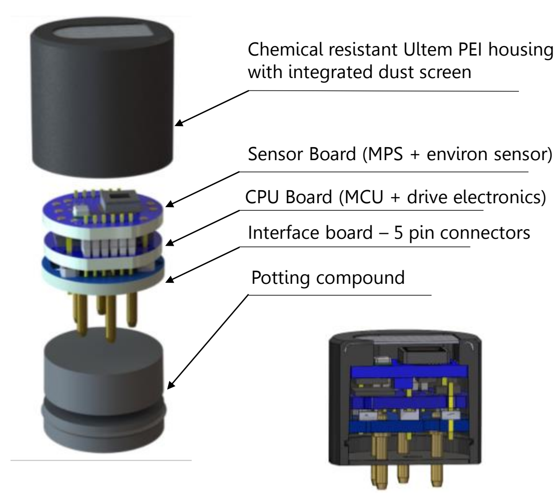
MPS principle of detection

- The Molecular Property Spectrometer (MPS) Flammable Gas Sensor's transducer is a micro-machined membrane with an embedded Joule heater and resistance thermometer
- MEMS transducer is mounted on a PCB and packaged inside enclosure open to ambient air
- Parallel ridges in the MEMS transducer differentially trap gas molecules of different sizes
- Joule heater used to rapidly heat atmosphere between the ridges
- Presence of a flammable gas causes changes in the thermo-conductive properties of the air/ gas mixture that are measured by the transducer
- Sensor data are processed by algorithms to report concentration sorted into classes and concentrations of combustible gas



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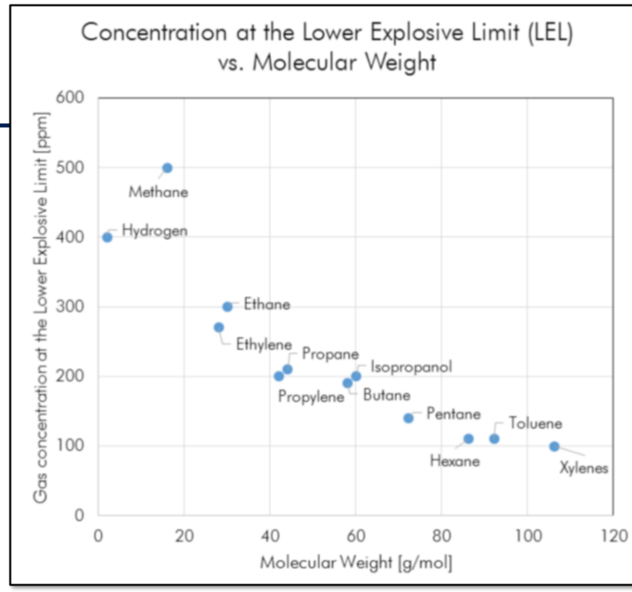
Relationship between LEL concentration and molecular weight (density)

- Le Chatelier's mixing rule is commonly used for estimating the %LEL of mixtures of flammable gases in air
- It states the composite %LEL of a mixture depends on the mole fraction, *x*, of each gas present and each gas' current percentage of its respective lower-explosive-limit concentration:

$$\%LEL_{mix} = \frac{1}{\sum \frac{x_i}{\%LEL_i}}$$

- This relationship generally applies for *average* molecular weight as well; that is, a gas mixture with an average molecular weight equal to that of pentane will have a composite %LEL concentration similar to that of pentane
- Makes reading uniquely accurate for mixtures of flammable gas



MPS accuracy and detectable gases

- The MPS sensor capable of detecting most common flammable gases/vapors
- Accurate for methane across full environmental range
- Other gases typically meet published tolerances; but performance is optimized for accuracy near STP conditions
- High concentration CO_2 or unusual background inert gas mixtures may affect readings

Gas	Formula	Detection Range	Accuracy (at 50 %LEL)
butane	C_4H_{10}	0-100 %LEL	±5 %LEL
ethane	C_2H_6	0-100 %LEL	±5 %LEL
hexane	C_6H_{14}	0-100 %LEL	±8 %LEL
hydrogen	H_2	0-100 %LEL	±5 %LEL
isobutane	$HC(CH_3)_3$	0-100 %LEL	±5 %LEL
isobutylene	C_4H_8	0-100 %LEL	±5 %LEL
isopropanol	C_3H_8O	0-100 %LEL	±10 %LEL
methane	CH_4	0-100 %LEL	±3 %LEL
MEK	C_4H_8O	0-100 %LEL	±5 %LEL
octane	C_8H_{18}	0-100 %LEL	±5 %LEL
pentane	C_5H_{12}	0-100 %LEL	±5 %LEL
propane	C_3H_8	0-100 %LEL	±5 %LEL
propylene	C_3H_6	0-100 %LEL	±5 %LEL
toluene	C_7H_8	0-100 %LEL	±10 %LEL
xylene	C_8H_{10}	0-100 %LEL	±10 %LEL

MPS gas classifications

CLASS 1: Hydrogen
Molecular weight: 2.0 [g/mol]
Density: 0.09 [kg/m3]
carbons: 0

+HC **CLASS 2: Hydrogen Mixture**
Average Molecular weight: 2-14 [g/mol]
Density: 0.1-0.6 [kg/m3]
carbons: varies

CLASS 3: Methane/Natural Gas
Average Molecular weight: 16-19 [g/mol]
Density: 0.6-0.9 [kg/m3]
Typical # carbons: 1-2

CLASS 4: Light Gas (or Light Gas Mixture)
Average Molecular weight: 25-65 [g/mol]
Density: 1.2-2.5 [kg/m3]
Typical # carbons: 2-3
Likely Gases: Ethane, Propane, Butane, Isopropanol

CLASS 5: Medium Gas (or Medium Gas Mixture)
Average Molecular weight: 55-90 [g/mol]
Density: 2.5-4.25 [kg/m3]
Typical # carbons: 3-7
Likely Gases: Pentane, Hexane

CLASS 6: Heavy Gas (or Heavy Gas Mixture)
Average Molecular weight: 90+ [g/mol]
Density: 4.1+ [kg/m3]
Typical # carbons: 7+
Likely Gases: Toluene, Xylenes (aromatic hydrocarbons)

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Thank You!

Bob Henderson
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