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Worldwide manufcaturer of gas detection solutions

TR 1002: Catalytic (CC) LEL and Infrared (NDIR) Combustible Gas Sensor Performance

January 28, 2013

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GfG Instrumentation

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Catalytic Combustible (Pellistor) LEL and Infrared (NDIR) Combustible Gas Sensor Performance

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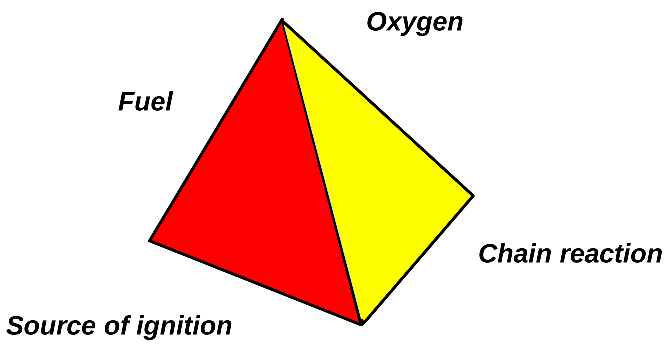
GFG Instrumentation Inc.
Ann Arbor, MI

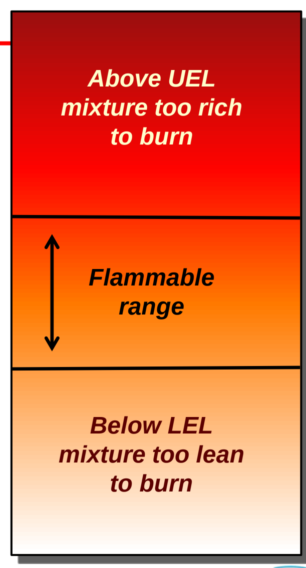
Explosive or Flammable Atmospheres

Fire Tetrahedron



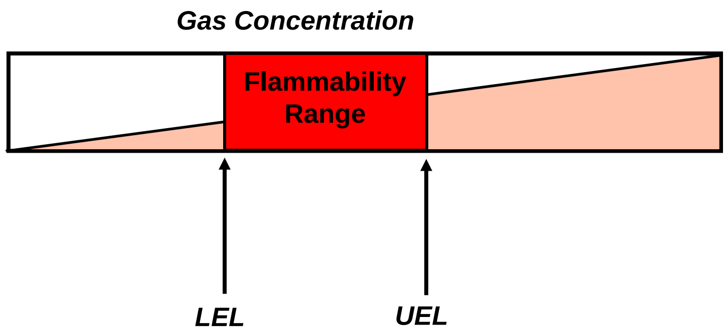
Explosive limits

- *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*

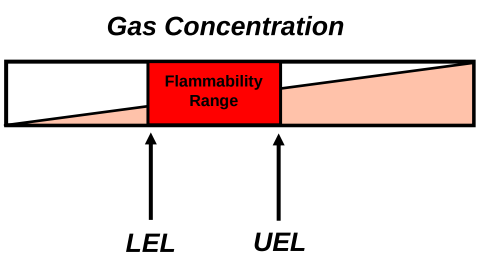


Flammability Range

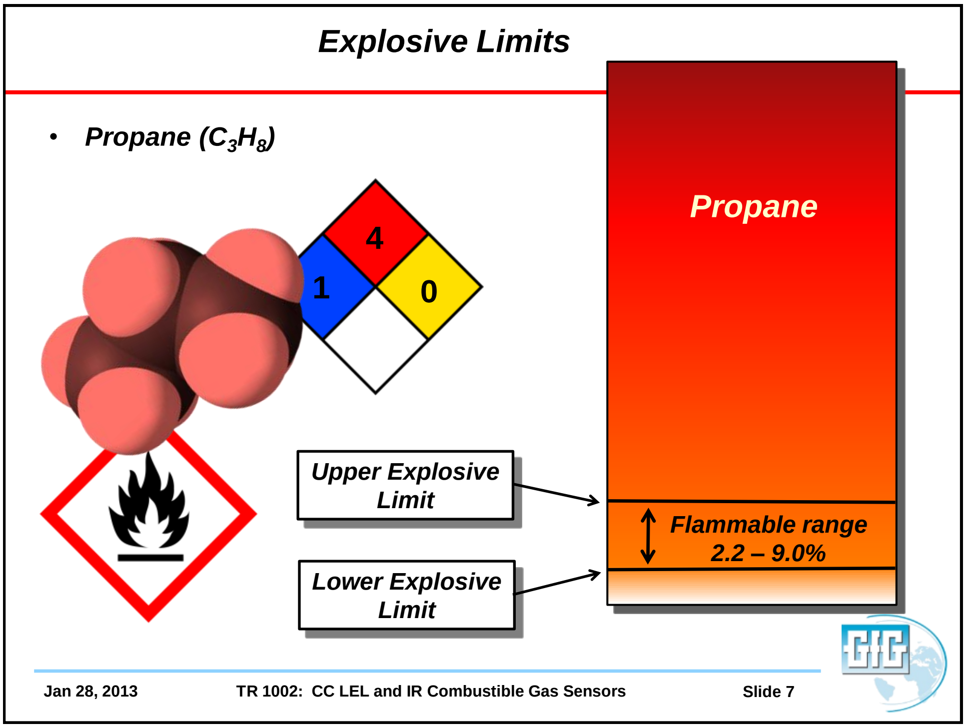
- ***The range between the LEL and the UEL of a combustible gas or vapor***
- ***Concentrations within the flammable range will burn or explode if a source of ignition is present***



Different gases have different flammability ranges



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


Explosive Limits
• Propane (C_3H_8)
4
1
0
Propane
Upper Explosive Limit
Lower Explosive Limit
Flammable range 2.2 – 9.0%
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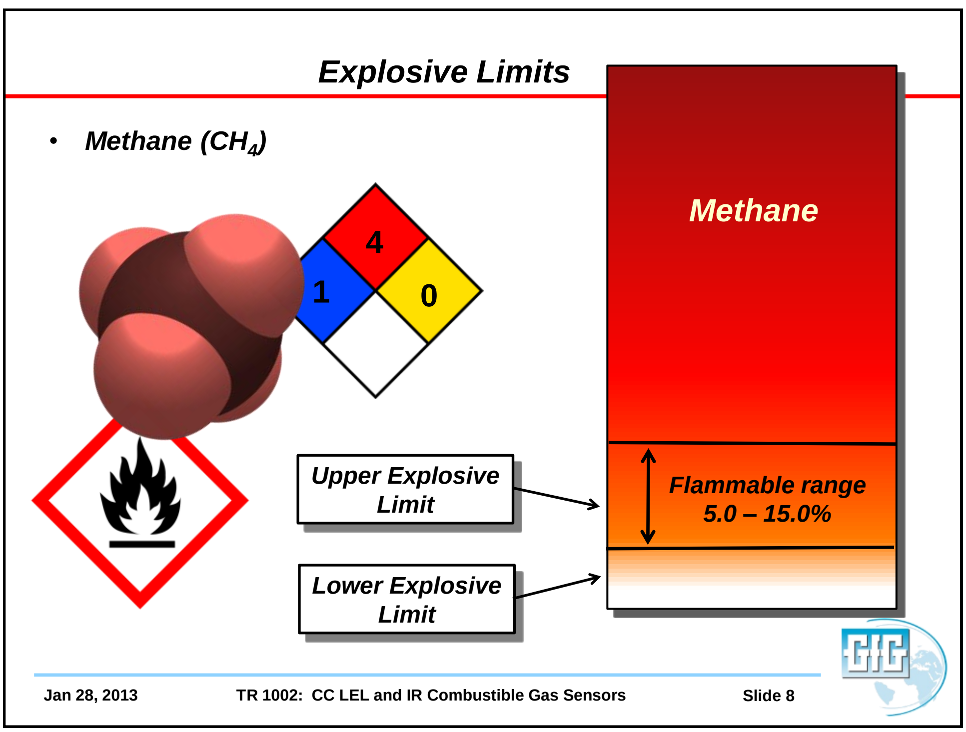
Explosive Limits
• Methane (CH_4)
4
1
0
Methane
Upper Explosive Limit
Lower Explosive Limit
Flammable range 5.0 – 15.0%
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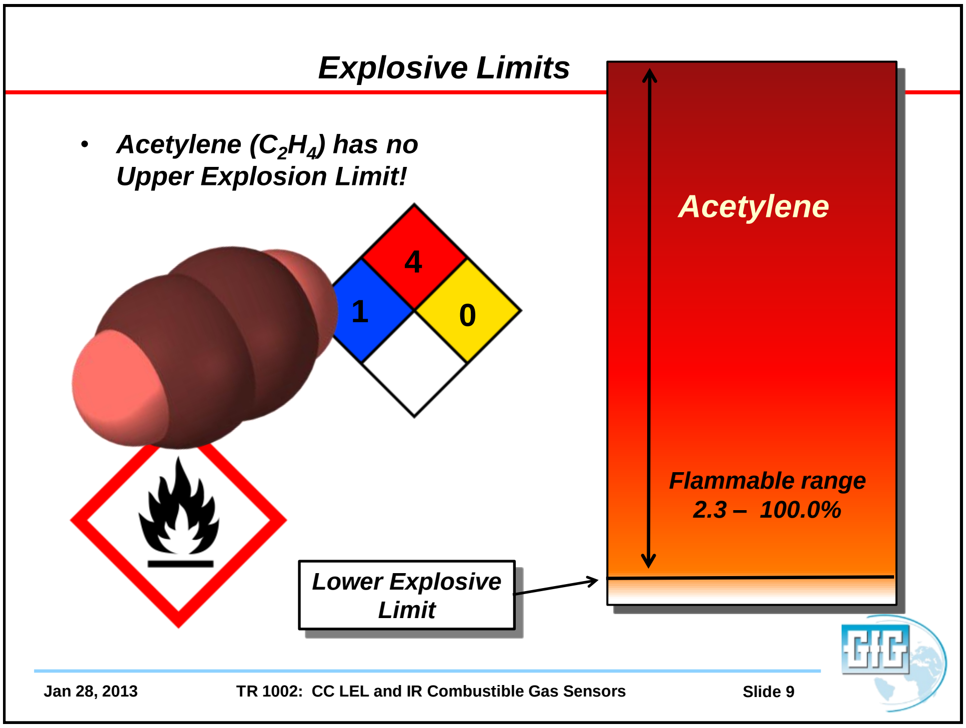
Explosive Limits
Acetylene (C_2H_4) has no Upper Explosion Limit!
4
1
0
Acetylene
Flammable range
2.3 – 100.0%
Lower Explosive Limit
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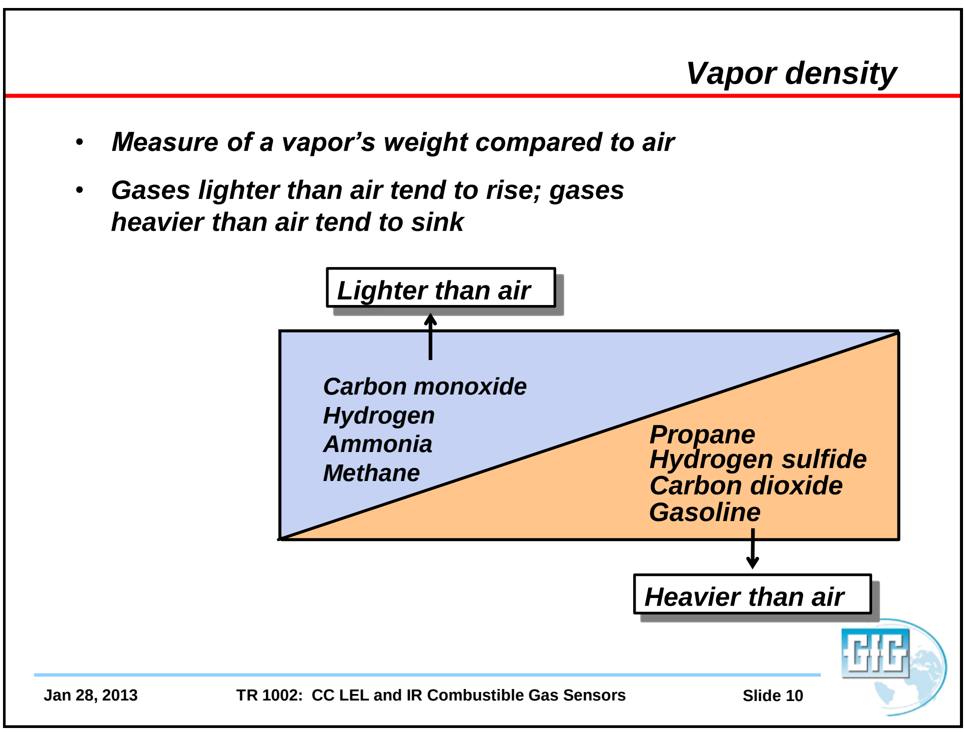
Vapor density
Measure of a vapor's weight compared to air
Gases lighter than air tend to rise; gases heavier than air tend to sink
Lighter than air
Carbon monoxide
Hydrogen
Ammonia
Methane
Propane
Hydrogen sulfide
Carbon dioxide
Gasoline
Heavier than air
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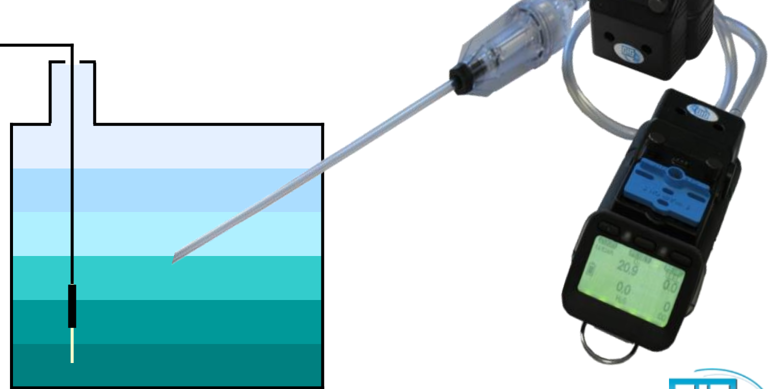
Stratification

- *Atmospheric hazards in confined spaces form layers*
- *Check all levels!*



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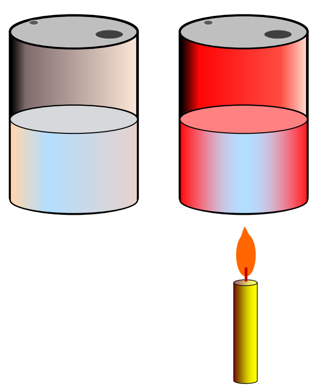
Vaporization is a function of temperature

- *Vapors are the gaseous state of substances that are either liquids or solids at room temperatures*
  - *Gasoline evaporates*
  - *Dry ice (solid carbon dioxide) sublimates*
- *Increasing the temperature of the combustible liquid increases the amount of vapor produced*



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Flashpoint Temperature

- *Temperature at which a combustible liquid gives off enough vapor to form an ignitable mixture*

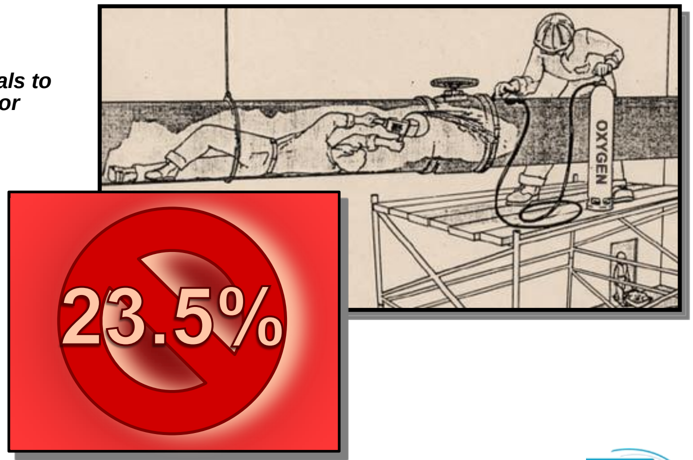
	Degrees F	Degrees C
Gasoline (aviation grade)	- 50 °F (approx.)	- 45 °C (approx.)
Acetone	0 °F	- 18 °C
Methyl ethyl ketone	24 °F	- 4 °C
Ethanol (96 %)	62 °F	17 °C
Diesel oil	100 - 190 °F	38 - 88 °C

Flammable and combustible liquid classifications (OSHA 29 CFR 1910.106)

	Flash Point Temp °F	*Boiling Point °F*	*Examples*
Class IA flammable liquid	*Below 73 °F*	*Below 100 °F*	*Methyl ethyl ether Pentane Petroleum ether*
Class IB flammable liquid	*Below 73 °F*	*Above 100 °F*	*Acetone Ethanol Gasoline Methanol*
Class IC flammable liquid	*At or above 73 °F*	*Below 100 °F*	*Styrene Turpentine Xylene*
Class II combustible liquid	*At or above 100 °F*	*Below 140 °F*	*Fuel oil no. 44 (Diesel) Mineral spirits Kerosene*
Class IIIA combustible liquid	*At or above 140 °F*	*Below 200 °F*	*Aniline Carbolic acid Phenol Naphthalenes Pine oil*
Class IIIB combustible liquid	*At or above 200 °F*		

Oxygen Enrichment

- *Proportionally increases rate of many chemical reactions*
- *Can cause ordinary combustible materials to become flammable or explosive*
- *According to OSHA 1910.146, any CS atmosphere with an O_2 higher than 23.5% is dangerously enriched*
- *OSHA 1912 Subpart B and NFPA specify 22.0% as hazardous*



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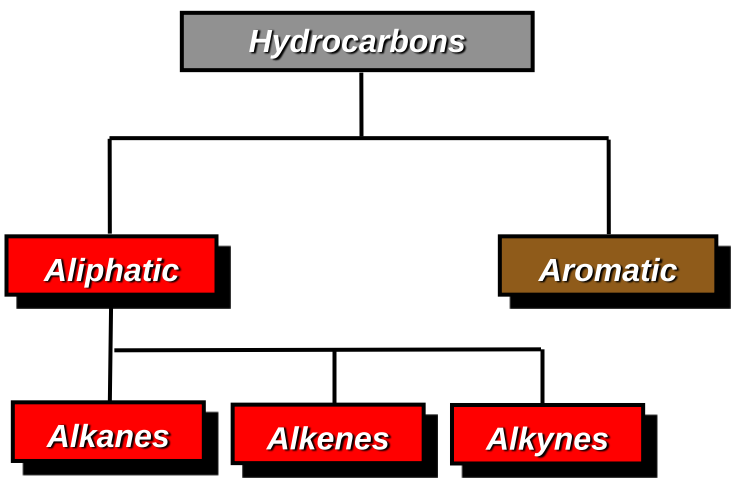
Classes of Hydrocarbons



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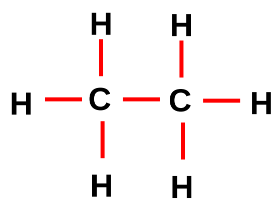
Hydrocarbons

Aliphatic

Alkanes

- *Alkanes are hydrocarbons in which all of the bonds are single bonds*



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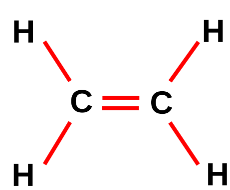
Hydrocarbons

Aliphatic

Alkenes

- *Alkenes are hydrocarbons that contain a carbon-carbon double bond*



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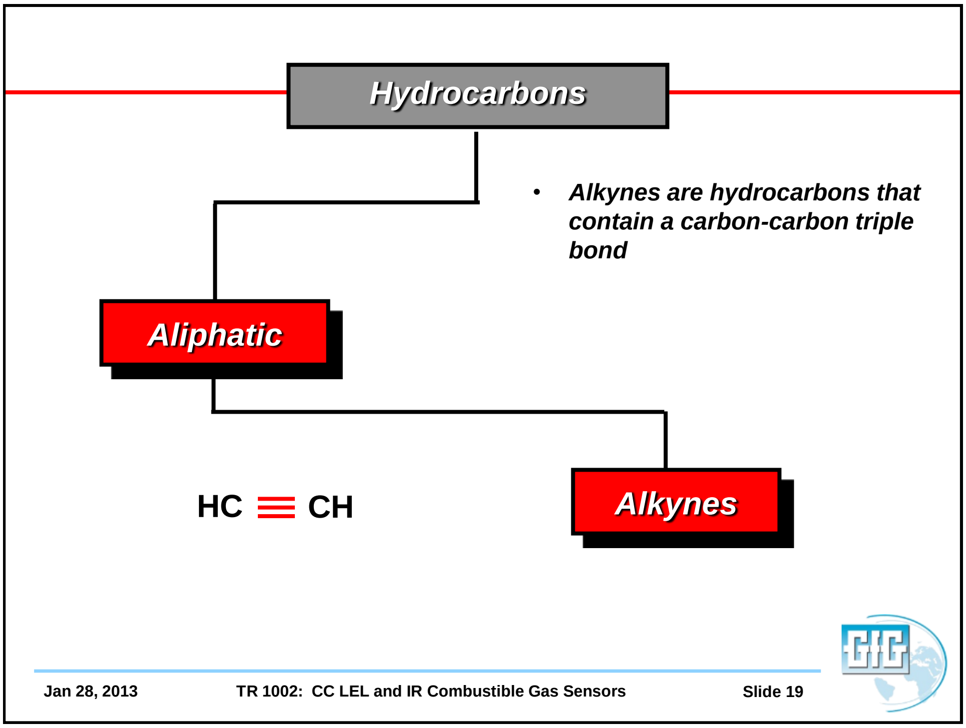
Hydrocarbons
Aliphatic
Alkynes
• Alkynes are hydrocarbons that contain a carbon-carbon triple bond
HC ≡ CH
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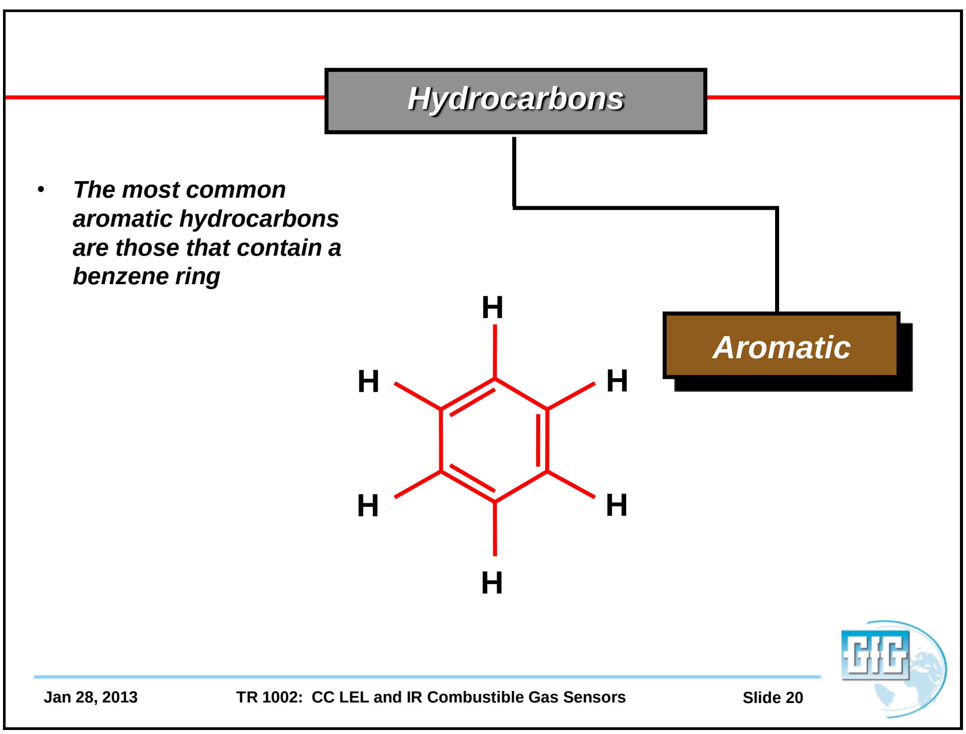
Hydrocarbons
Aromatic
• The most common aromatic hydrocarbons are those that contain a benzene ring
H
H
H
H
H
H
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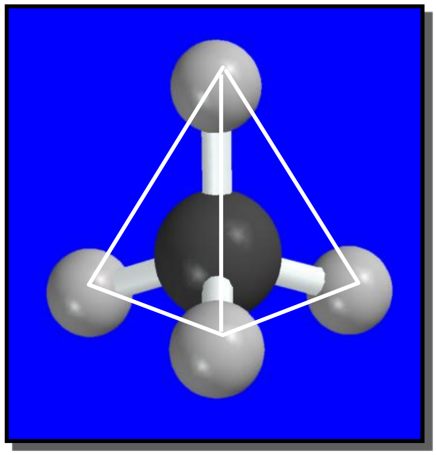
Chemical structure of Methane

- *Tetrahedral geometry*
- *Each H—C—H angle = 109.5°*

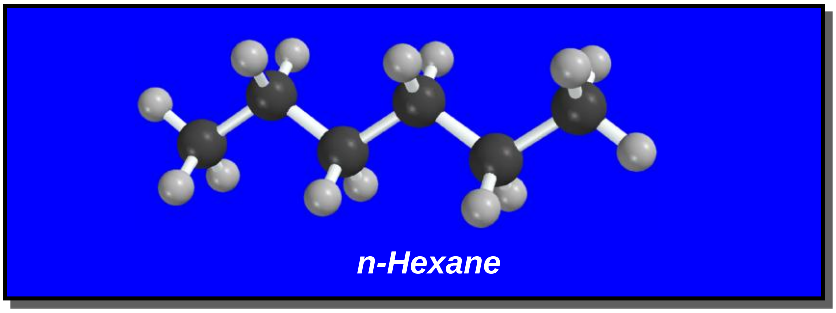


Names of Un-branched Alkanes

• *Methane*	CH_4	*1 Carbon*
• *Ethane*	CH_3CH_3	*2 Carbon*
• *Propane*	$CH_3CH_2CH_3$	*3 Carbon*
• *Butane*	$CH_3CH_2CH_2CH_3$	*4 Carbon*
• *Pentane*	$CH_3(CH_2)_3CH_3$	*5 Carbon*
• *Hexane*	$CH_3(CH_2)_4CH_3$	*6 Carbon*
• *Heptane*	$CH_3(CH_2)_5CH_3$	*7 Carbon*
• *Octane*	$CH_3(CH_2)_6CH_3$	*8 Carbon*
• *Nonane*	$CH_3(CH_2)_7CH_3$	*9 Carbon*
• *Decane*	$CH_3(CH_2)_8CH_3$	*10 Carbon*

Un-branched alkanes

- ***The most stable conformation of unbranched alkanes (designated "n")***



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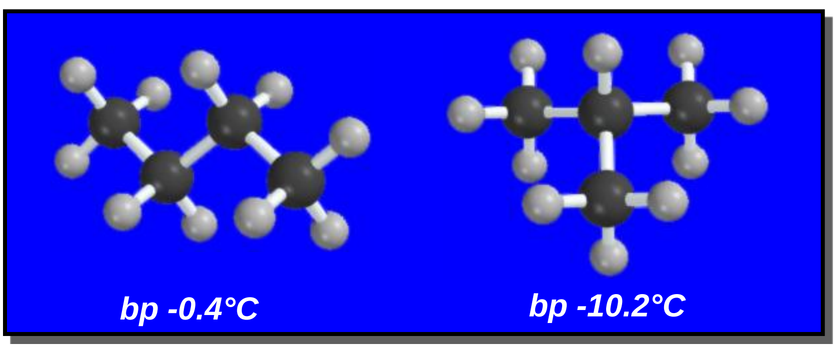
Isomeric Alkanes: Butanes C_4H_{10}

- ***n-Butane*** $CH_3CH_2CH_2CH_3$
- ***Isobutane*** $(CH_3)_3CH$



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Higher n-Alkanes

$CH_3CH_2CH_2CH_2CH_3$ *n-Pentane*

$CH_3CH_2CH_2CH_2CH_2CH_3$ *n-Hexane*

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ *n-Heptane*

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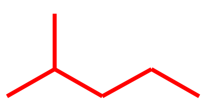
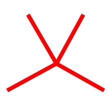
The C_5H_{12} Isomers

$CH_3CH_2CH_2CH_2CH_3$ *n-Pentane*



$(CH_3)_2CHCH_2CH_3$ *Isopentane*



$(CH_3)_4C$ *Neopentane*

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Petroleum Refining

- *Process of converting crude oil into high value products*
- *Most important refinery products are transportation fuels – gasoline, jet fuel, and diesel fuel*
- *Other important products include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt*

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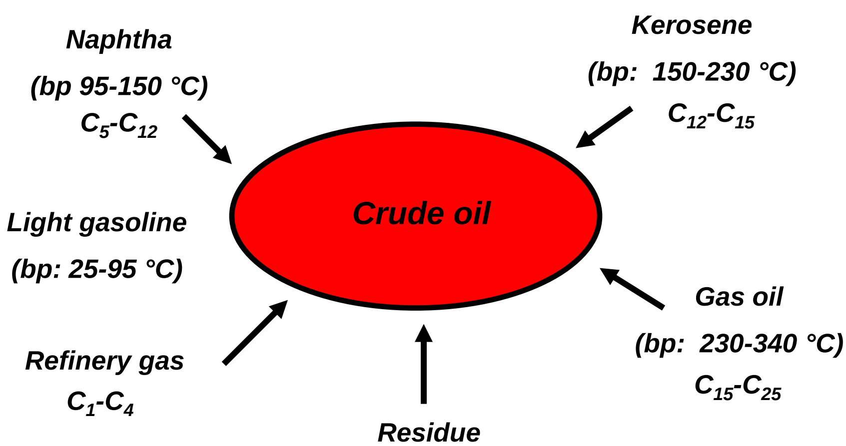
Crude Oil Constituents



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Petroleum Refining

- *Cracking*
  - *Converts high molecular weight hydrocarbons to more useful, low molecular weight ones*
- *Reforming*
  - *Increases branching of hydrocarbon chains*
  - *Branched hydrocarbons have better burning characteristics for automobile engines*

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Combustion of Alkanes

- *Heats of Combustion*
  - *All alkanes burn in air to give carbon dioxide and water*
  - *Heat of combustion is quantity of heat produced when one mole of a compound is burned to carbon dioxide and water*
    - *One mole = 6.02 x 10^{23} molecules of substance*
    - *Heats of combustion increase with increasing number of carbons*

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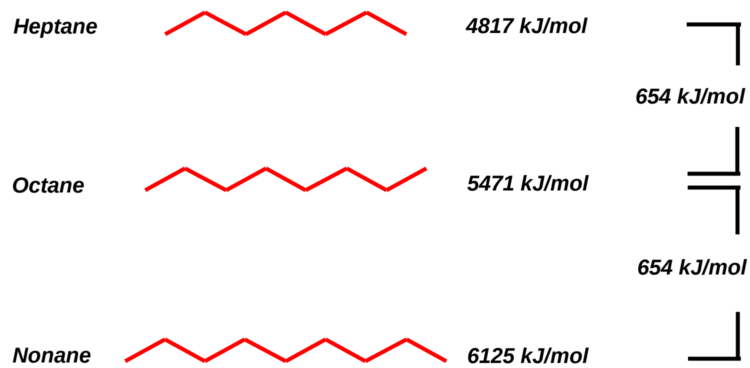
Heats of Combustion

- ***Each additional cH2 group increases the heat of combustion by 654kJ/mol:***



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:***

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

Minimum Ignition Energy

- ***MIE depends on type of gas and concentration***
- ***8.0% volume methane is "sweet spot" for stoichiometric combustion of methane***
- ***Although flammability range for CH_4 is 5 - 15%, concentration where it is easiest to ignite is 8% by volume***
- ***At 25° C, 1.0 atm, takes 0.3 mJ to initiate explosion chain reaction***
- ***Static electricity "zap" when insert key into ignition = 5.0 mJ***
- ***MIE for other combustible gases much lower***

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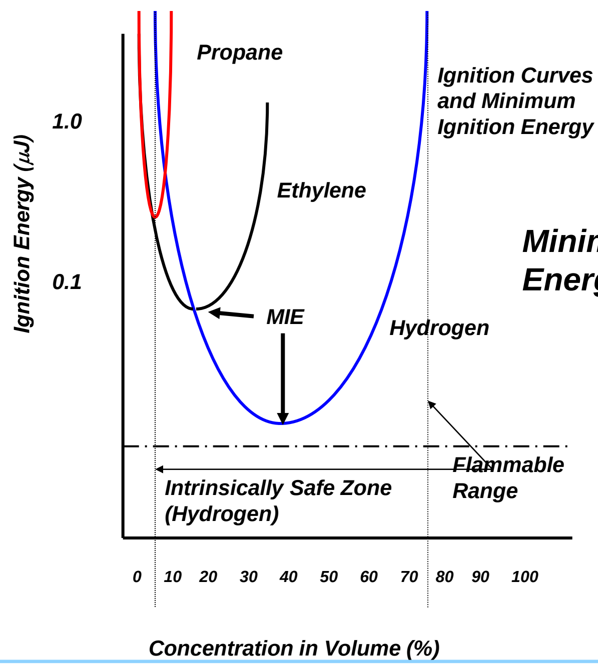

Minimum Ignition Energy

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Combustible sensor electrical safety and performance requirements

- *Important standards defining combustible sensor performance:*
  - *Canadian requirements: CSA 22.2*
  - *United States: UL 913*
  - *ATEX: EN50018*
  - *Harmonized IECEx: IEC60079-1*

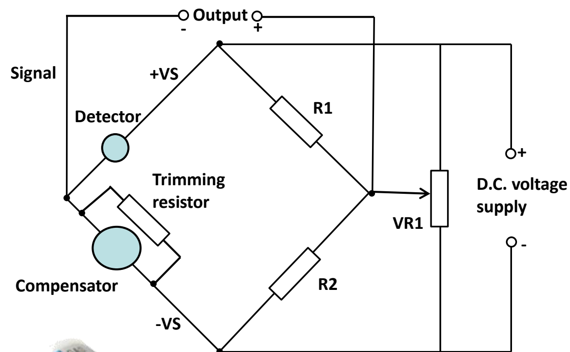
How combustible (percent LEL) gas detecting instruments detect gas

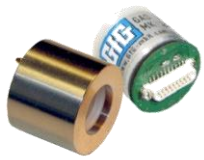
Catalytic "Hot Bead" Combustible Sensor

- ***Detects combustible gas by catalytic oxidation***
- ***When exposed to gas oxidation reaction causes bead to heat***
- ***Requires oxygen to detect gas!***

Catalytic "Hot Bead" Combustible Sensor

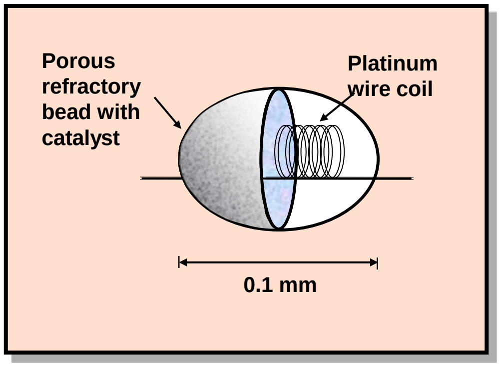
- ***Detects combustible gas by catalytic oxidation***
- ***When exposed to gas oxidation reaction causes the active (detector) bead to heat***
- ***Requires oxygen to detect gas!***





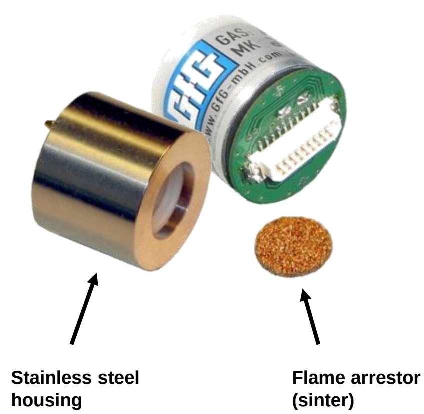
Combustible Gas Sensor

- *The catalyst in the LEL sensor bead can be harmed if it is exposed to certain substances*
- *LEL sensor poisons permanently reduce or destroy the sensor's response to gas*
- *The most common LEL sensor poisons are silicon containing vapors (like the silicones used in Armour All)*
- *Sensors which may have been exposed to a poison must be tested before further use*



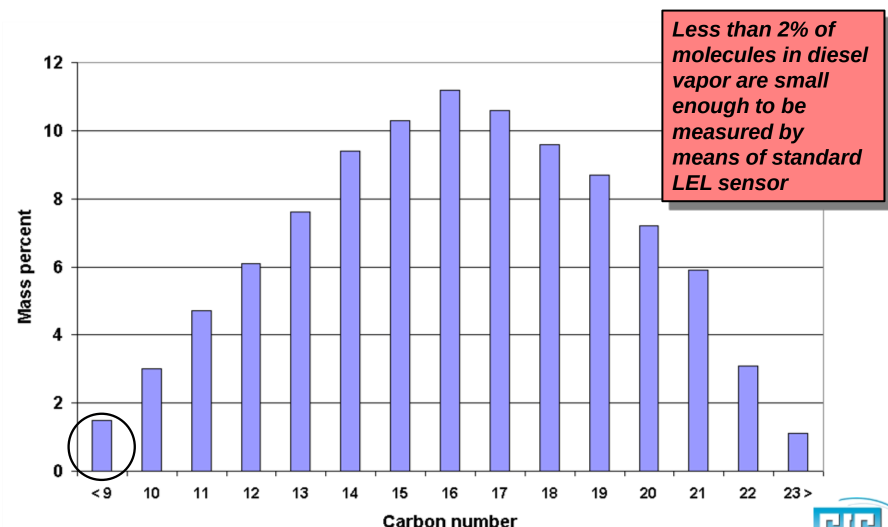
Traditional LEL sensors are "Flame proof" devices

- *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*
- *The flame arrestor can slow, reduce, or even prevent larger molecules from entering the sensor*
- *The larger the molecule, the slower it diffuses through the flame arrestor into the sensor*
- *The response of the sensor is so slow to molecules larger than nonane (C9) in size that they are effectively undetectable*



Catalytic Sensor Structure

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



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Flashpoint Temperature

- *Temperature at which a combustible liquid gives off enough vapor to form an ignitable mixture*

	Degrees F	Degrees C
Gasoline (aviation grade)	- 50 °F (approx.)	- 45 °C (approx.)
Acetone	0 °F	- 18 °C
Methyl ethyl ketone	24 °F	- 4 °C
Ethanol (96 %)	62 °F	17 °C
Diesel oil	100 - 190 °F	38 - 88 °C

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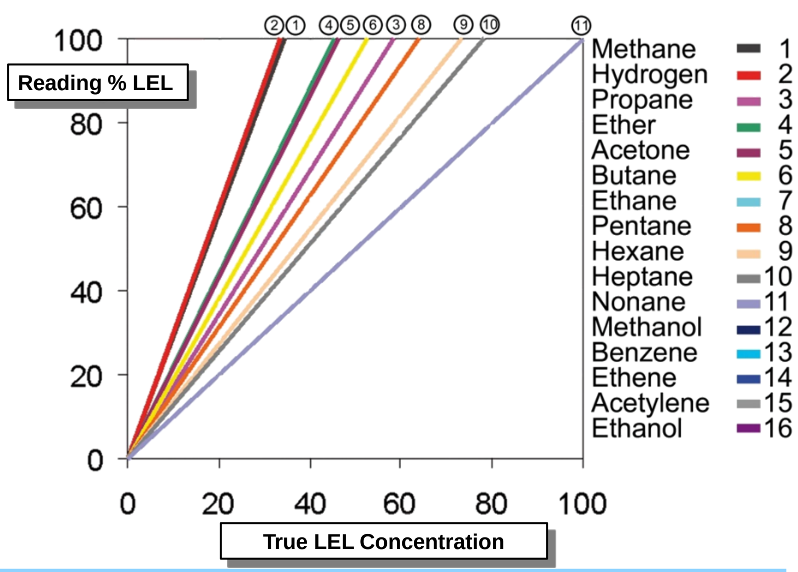
Flammable and combustible liquid classifications (OSHA 29 CFR 1910.106)

	Flash Point Temp °F	*Boiling Point °F*	*Examples*
Class IA flammable liquid	*Below 73 °F*	*Below 100 °F*	*Methyl ethyl ether Pentane Petroleum ether*
Class IB flammable liquid	*Below 73 °F*	*Above 100 °F*	*Acetone Ethanol Gasoline Methanol*
Class IC flammable liquid	*At or above 73 °F*	*Below 100 °F*	*Styrene Turpentine Xylene*
Class II combustible liquid	*At or above 100 °F*	*Below 140 °F*	*Fuel oil no. 44 (Diesel) Mineral spirits Kerosene*
Class IIIA combustible liquid	*At or above 140 °F*	*Below 200 °F*	*Aniline Carbolic acid Phenol Naphthalenes Pine oil*
Class IIIB combustible liquid	*At or above 200 °F*		

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

Catalytic pellistor combustible gas response curves



Correction Factors

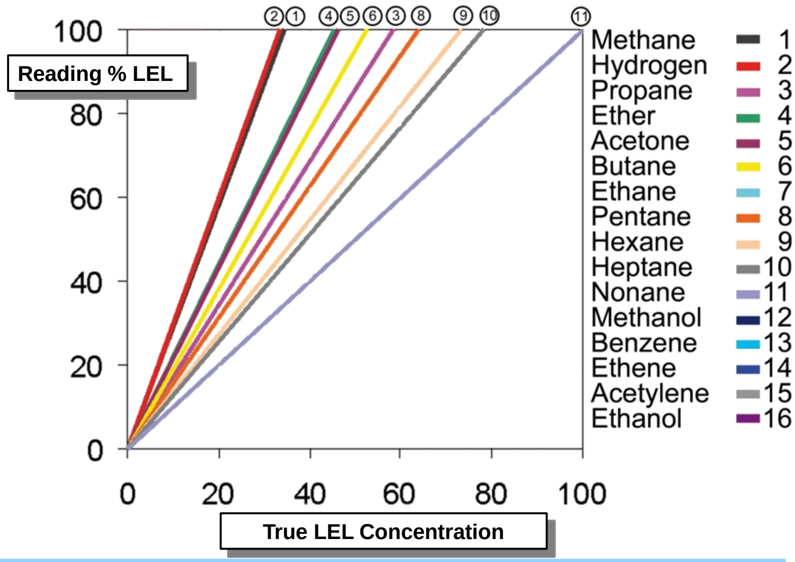
- *Correction factor is the reciprocal of the relative response*
- *The relative response of 4P-75 LEL sensor (methane scale) to ethanol is 0.8*
- *Multiplying the instrument reading by the correction factor for ethanol provides the true concentration*
- *Given a correction factor for ethanol of 1.25, 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*

Catalytic combustible LEL sensor correction factors

Correction factors for 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	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

Catalytic pellistor combustible gas response curves



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According to Preamble to OSHA 1910.146

- ***A combustible hazard exists whenever the combustible gas concentration exceeds 10% LEL***
- ***This is the general hazardous condition threshold, NOT the concentration that should always be used for the LEL alarm set-point***
- ***According to the original preamble to 1910.146, if Alternate Entry Procedures are used, the hazard condition threshold is 5% LEL***
- ***In some cases it may be necessary to use an even lower alarm setting to allow workers adequate time to escape***

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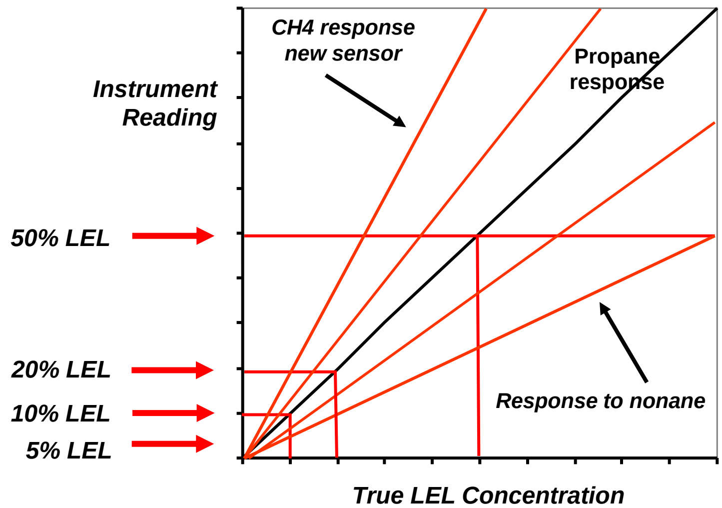
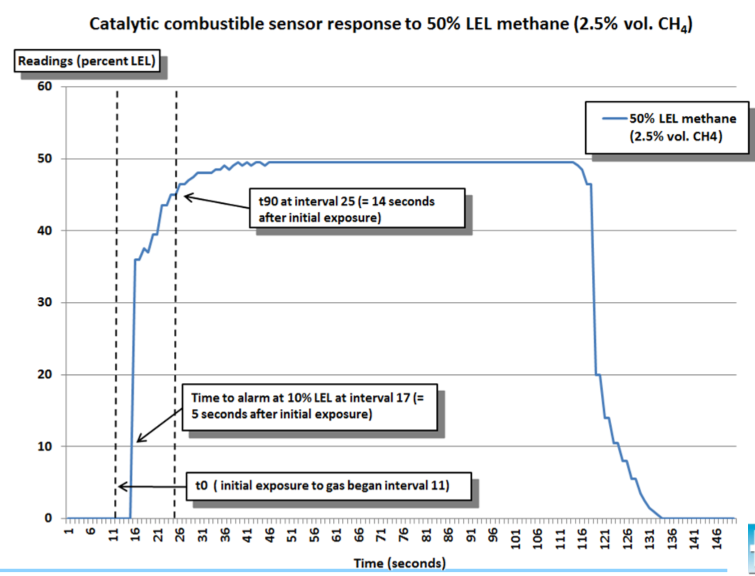
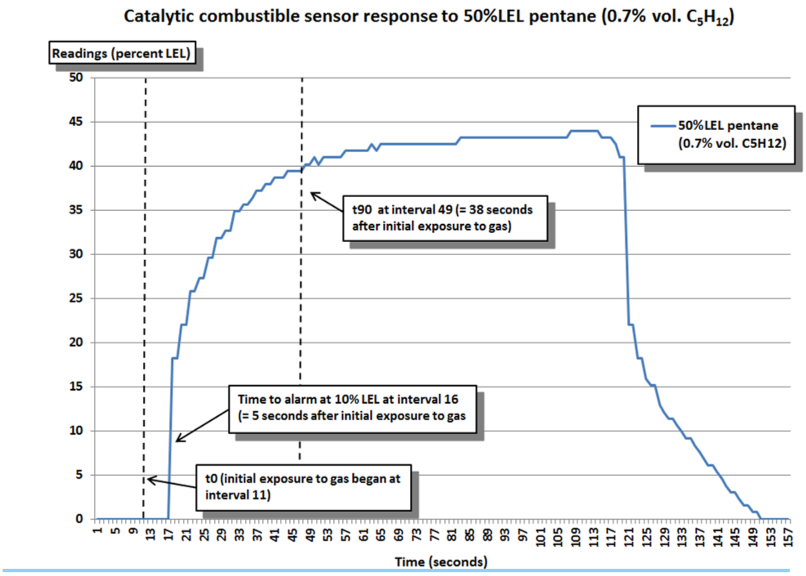
Using a lower alarm setting minimizes effect of relative response on readings



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



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



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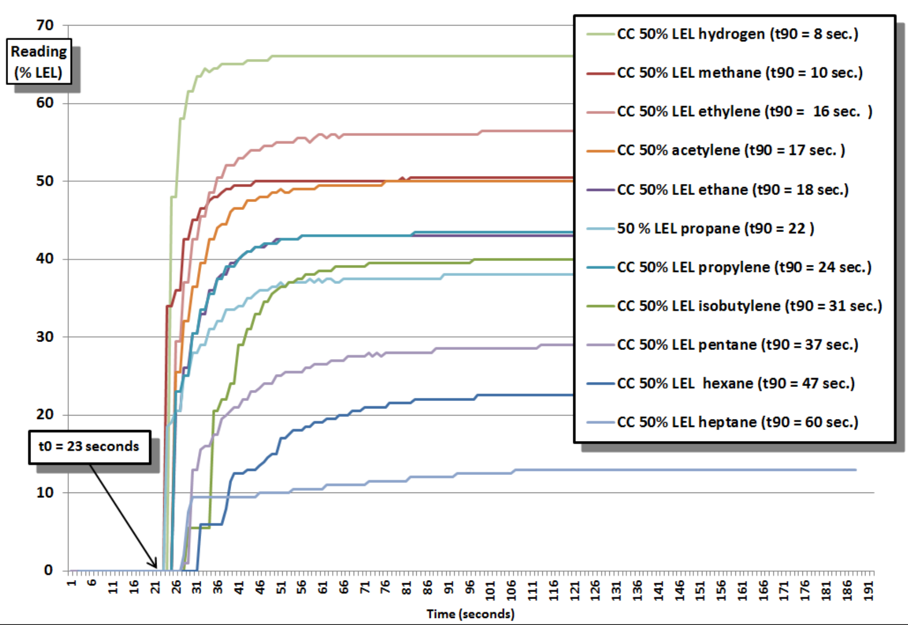
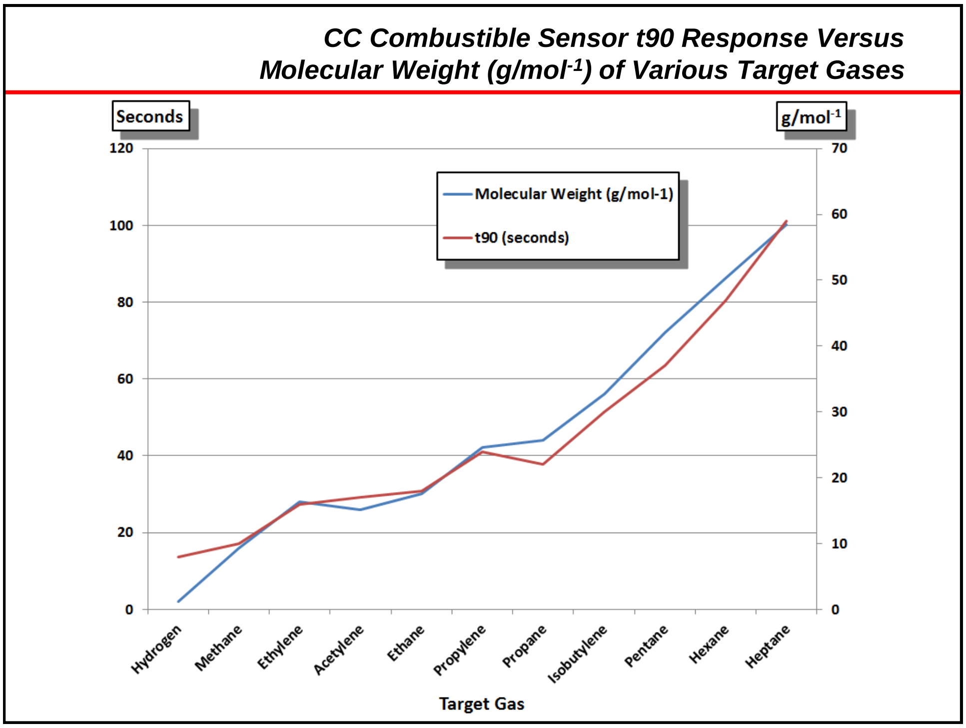
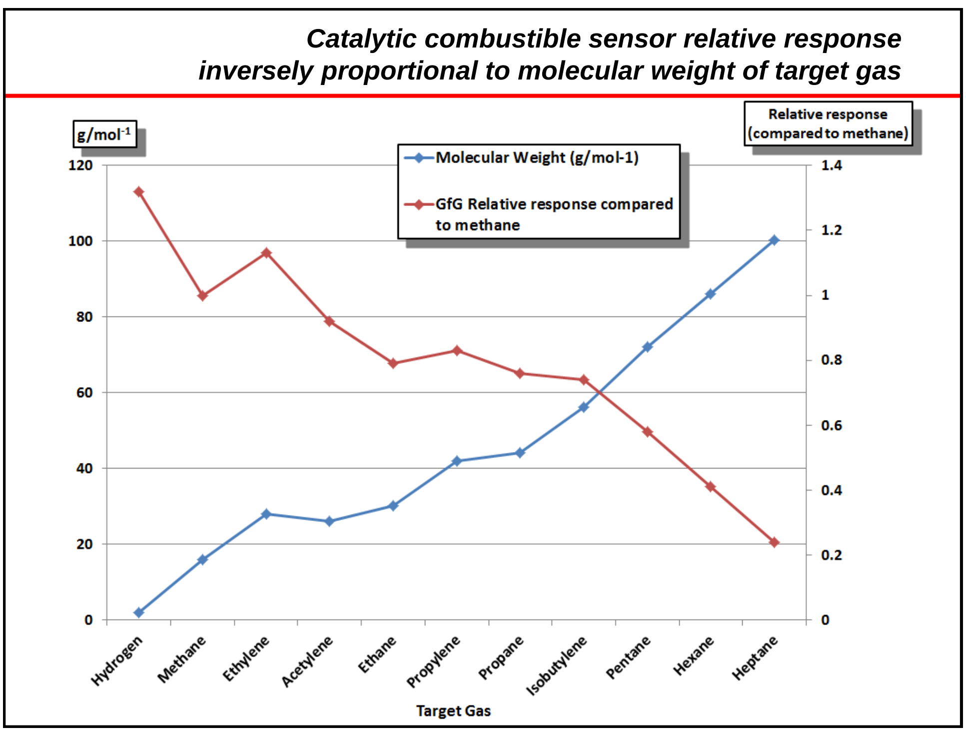
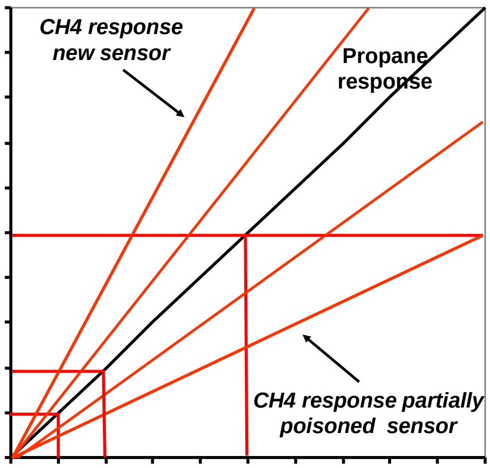
Catalytic combustible sensor exposed to various gases

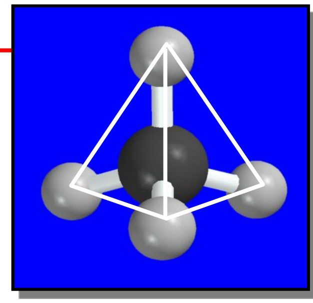



CC Combustible Sensor t90 Response Versus
Molecular Weight (g/mol-1) of Various Target Gases
Seconds
g/mol-1
Molecular Weight (g/mol-1)
t90 (seconds)
Hydrogen
Methane
Ethylene
Acetylene
Ethane
Propylene
Propane
Isobutylene
Pentane
Hexane
Heptane
Target Gas


Catalytic combustible sensor relative response
inversely proportional to molecular weight of target gas
g/mol-1
Relative response
(compared to methane)
Molecular Weight (g/mol-1)
GfG Relative response compared
to methane
Hydrogen
Methane
Ethylene
Acetylene
Ethane
Propylene
Propane
Isobutylene
Pentane
Hexane
Heptane
Target Gas

Response to methane over life of sensor





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

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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

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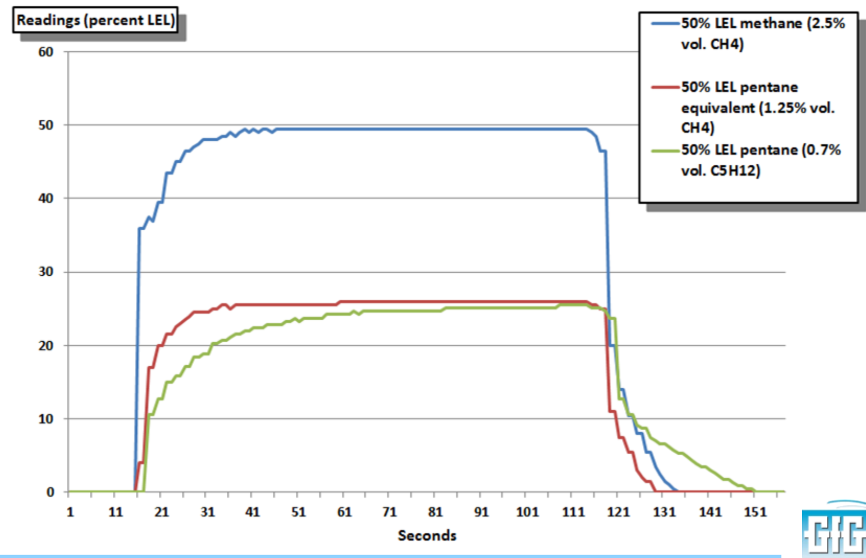
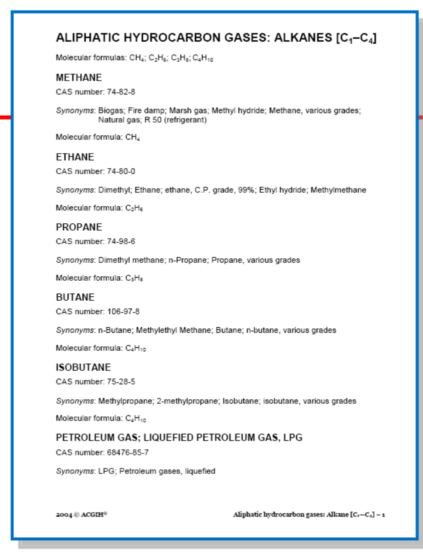
CC LEL sensor response to 50% LEL methane (2.5% vol. CH_4), 50% LEL pentane (7.0% vol. C_5H_{12}) and 50% LEL "pentane equivalent" (1.25% vol. CH_4)



C1 – C4 Aliphatic Hydrocarbon Gases

- ***TLV® officially adopted in 2004***
- ***Specifies toxic exposure limit (8 hour TWA) for methane, ethane, propane and butane of 1,000 ppm***
- ***Has the force of law in many jurisdictions in the United States and Canada***



ALIPHATIC HYDROCARBON GASES: ALKANES [C_1–C_4]

Molecular formulas: CH_4; C_2H_6; C_3H_8; C_4H_{10}

METHANE

CAS number: 74-82-8

Synonyms: Biogas; Fire damp; Marsh gas; Methyl hydride; Methane, various grades; Natural gas; R 50 (refrigerant)

Molecular formula: CH_4

ETHANE

CAS number: 74-80-0

Synonyms: Dimethyl; Ethane; ethane, C.P. grade, 99%; Ethyl hydride; Methylmethane

Molecular formula: C_2H_6

PROPANE

CAS number: 74-98-6

Synonyms: Dimethyl methane; n-Propane; Propane, various grades

Molecular formula: C_3H_8

BUTANE

CAS number: 106-97-8

Synonyms: n-Butane; Methylethyl Methane; Butane; n-butane, various grades

Molecular formula: C_4H_{10}

ISOBUTANE

CAS number: 75-28-5

Synonyms: Methylpropane; 2-methylpropane; Isobutane; isobutane, various grades

Molecular formula: C_4H_{10}

PETROLEUM GAS; LIQUEFIED PETROLEUM GAS, LPG

CAS number: 68476-85-7

Synonyms: LPG; Petroleum gases, liquefied

2004 © ACGIH® Aliphatic hydrocarbon gases: Alkane [C_1—C_4] – 1

Flammability Ranges and Toxic Exposure Limits for C1 – C5 Alkanes

Flammability Ranges and Toxic Exposure Limits for C1 – C5 Alkanes

Gas	Response of sensor (calibrated to CH_4) when exposed to 1% LEL of listed gas	Response of sensor (calibrated to C_5H_{12}) when exposed to 1% LEL of listed gas	LEL (%VOL)	TLV (8 hr. TWA)		LEL reading of pentane calibrated instrument when exposed to TLV concentration of gas	True ppm concentration of listed gas when alarm activated at 4% LEL (pentane scale)
				in ppm	in % LEL		
Methane	1.0	2.0	5.0	1000	2%	4.0%	1000 ppm methane
Ethane	0.75	1.5	3.0	1000	3.34%	5.0%	850 ppm ethane
Propane	0.65	1.3	2.1	1000	4.76%	6.2%	670 ppm propane
Butane	0.6	1.2	1.8	1000	5.56%	6.7%	595 ppm butane
Pentane	0.5	1.0	1.5	600	4%	4.0%	600 ppm pentane

C1 – C4 Monitoring Strategy

- *Choosing a pentane level of sensitivity and 4% LEL alarm setting ensures C1 – C4 TLV concentration is never exceeded*
- *For methane the alarm is activated at exactly at the 1,000 PPM limit*
- *For ethane, propane and butane the alarm is activated before the concentration reaches the 1,000 ppm limit*
- *The 4% alarm activated by:*
  - *Approximately 1,000 ppm methane*
  - *Approximately 816 ppm ethane*
  - *Approximately 667 ppm propane*
  - *Approximately 635 ppm butane*
- *An added bonus: At 4% the alarm is also activated at the TLV for pentane (600 ppm)*

Limitations of catalytic pellistor LEL sensors

- ***Flame arrestor limits molecules larger than nine carbons (nonane) from entering sensor***
- ***Even when molecules are able to diffuse into sensor: the larger the molecule the lower the relative response***
- ***Easily poisoned***
- ***Exposure to high concentration combustible gas damaging to sensor***

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Combustible sensor limitations

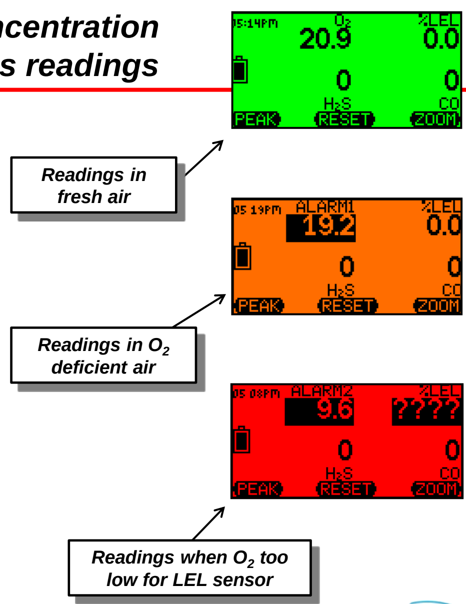
Contaminant	*LEL (Vol %)*	*Flashpoint Temp (ºF)*	*OSHA PEL*	*NIOSH REL*	*TLV*	*5% LEL in PPM*
Acetone	*2.5%*	*-4ºF (-20 ºC)*	*1,000 PPM TWA*	*250 PPM TWA*	*500 PPM TWA; 750 PPM STEL*	*1250 PPM*
Diesel (No.2) vapor	*0.6%*	*125ºF (51.7ºC)*	*None Listed*	*None Listed*	*15 PPM*	*300 PPM*
Ethanol	*3.3%*	*55ºF (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*

Over-Limit Protection

- *LEL sensor only designed to detect 0-100% LEL concentration of flammable gas*
- *If O2 concentration less than 10% O2, LEL sensor will not read properly*
- *Also, sensor may 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)*
- *CSA 22.2 stipulates latched "OL" alarm cannot be set higher than 60% LEL*

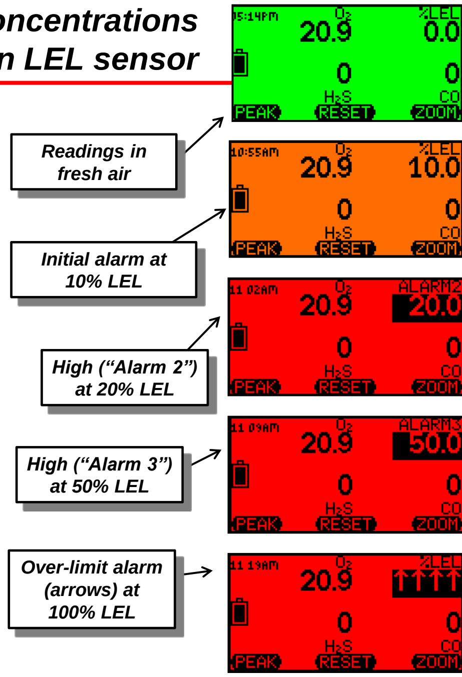
Effects of O_2 concentration on combustible gas readings

- *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*

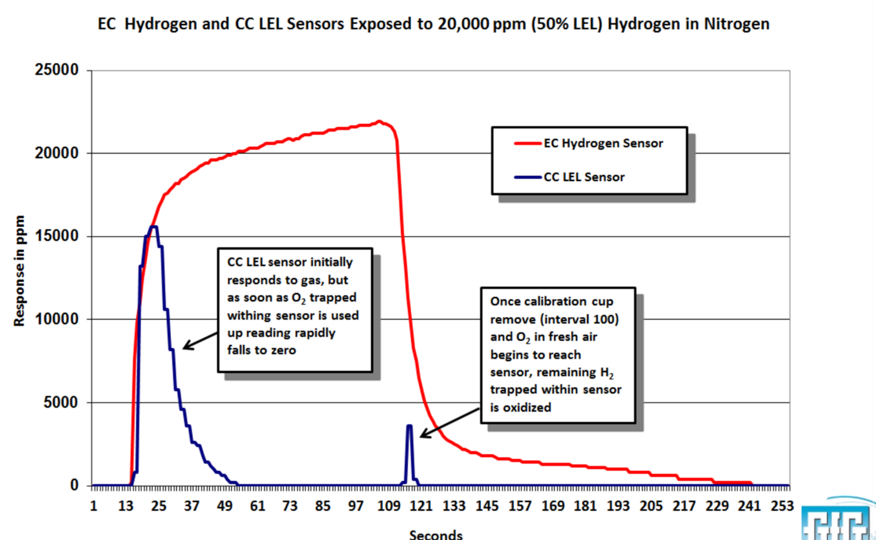


Effects of high concentrations of gas on LEL sensor

- *When doing atmospheric testing we are only concerned with the LEL. 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*



Response of electrochemical and LEL sensor to 20,000 ppm hydrogen in nitrogen



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Combustible sensor poisons

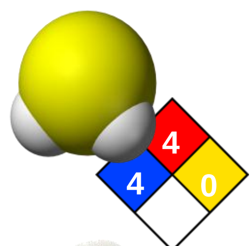
- *Combustible sensor poisons:*
  - *Silicones (by far the most virulent poison)*
  - *Hydrogen sulfide*

> ***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.)*

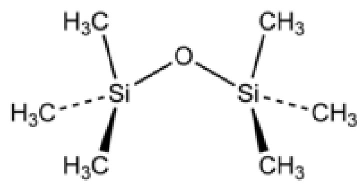
Effects of H_2S on combustible gas sensors

- *H_2S affects sensor as inhibitor AND as poison*
  - *Some byproducts of oxidation of H2S left as 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*
- *H_2S 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*

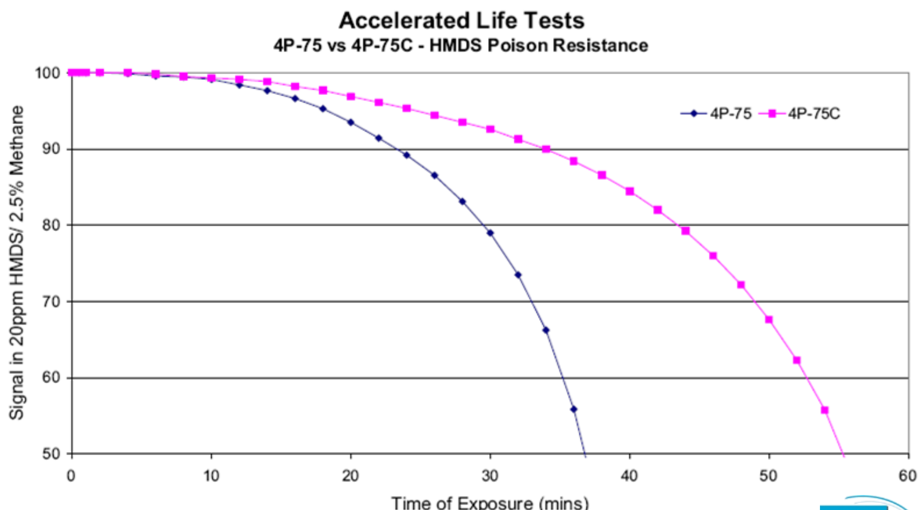


“Silicone resistant” vs. “standard” pellistor type LEL sensors

- ***"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 (should not be used on C8 – C9 hydrocarbons)***

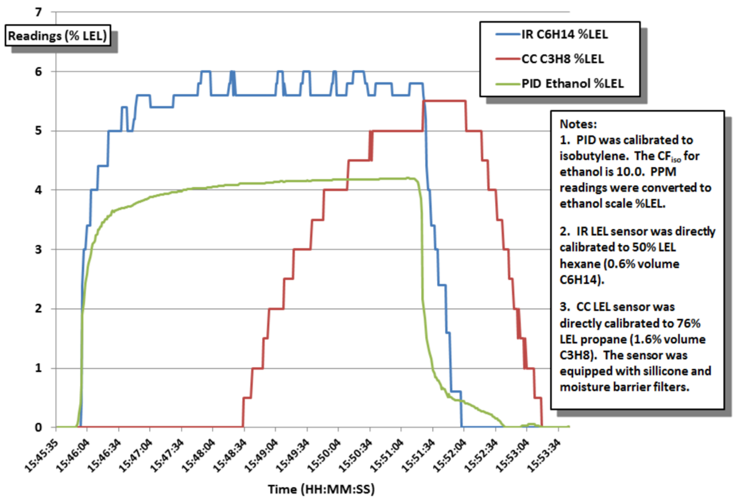


Effects of hexamethyldisiloxane (HMDS) on pellistor sensor



Effects of silicone filter on LEL sensor performance

Response of IR LEL, CC LEL (with sillicone filter) and PID sensors to 5% LEL (2,150 ppm) ethanol in air



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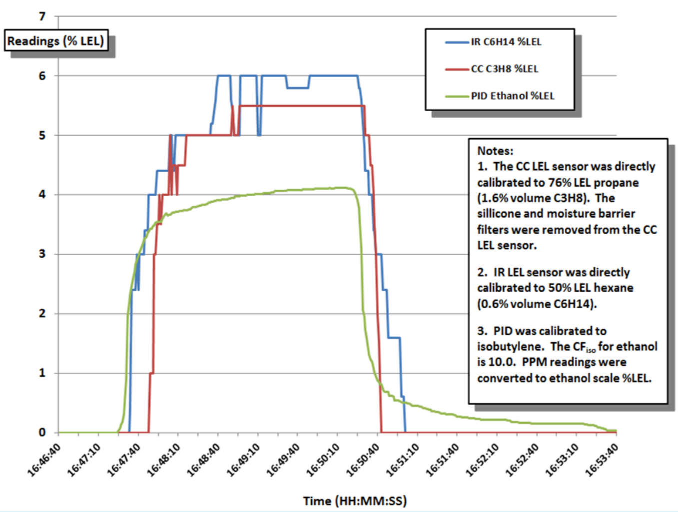
Effects of silicone filter on LEL sensor performance

Response of IR LEL, CC LEL (no sillicone filter) and PID sensors to 5% LEL (1,650 ppm) ethanol in air



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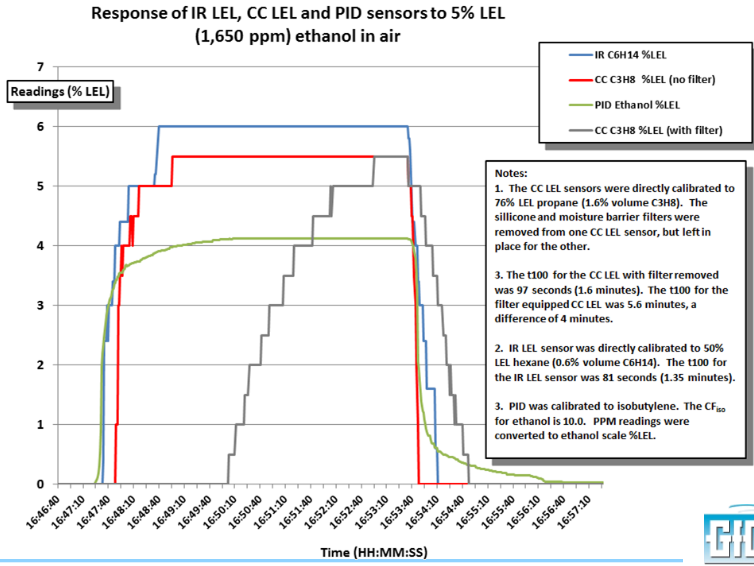
Effects of silicone filter on LEL sensor performance

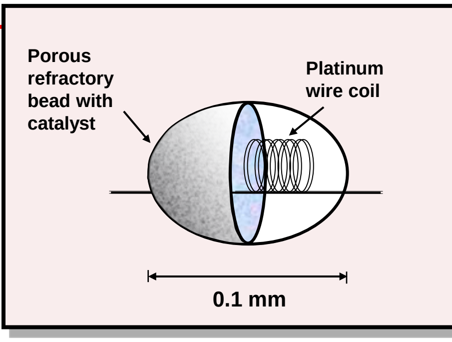


Miniaturized Intrinsically Safe Pellistor LEL Sensors

- ***"MicroPel" sensor operated at lower power (providing longer operation time per charge)***
- ***Can be Classified as Intrinsically Safe (versus "Flame Proof" classification carried by traditional pellistor sensors)***
- ***Faster response to gas due to elimination of T6 stainless steel flame arrestor (sinter)***
- ***Unmatched active bead and compensator require longer stabilization time***
- ***Because sensor runs at 3.0 versus 3.3 V, less able to "cook off" poisons and inhibitors***

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 working temperature (≈ 600°C)*

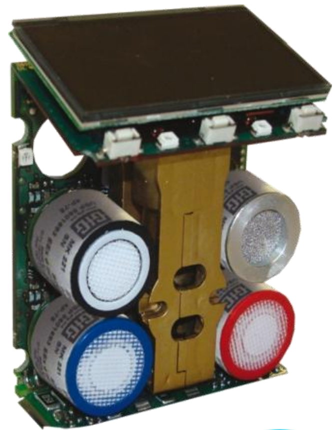


Combustible sensor advice

- *Whatever the brand, allow enough time for full stabilization prior to performing fresh air zero*
  - *DO NOT PERFORM AUTO ZERO AS PART OF AUTOMATIC START-UP SEQUENCE*
- *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 whether the sensor has disproportionately lost sensitivity to methane*

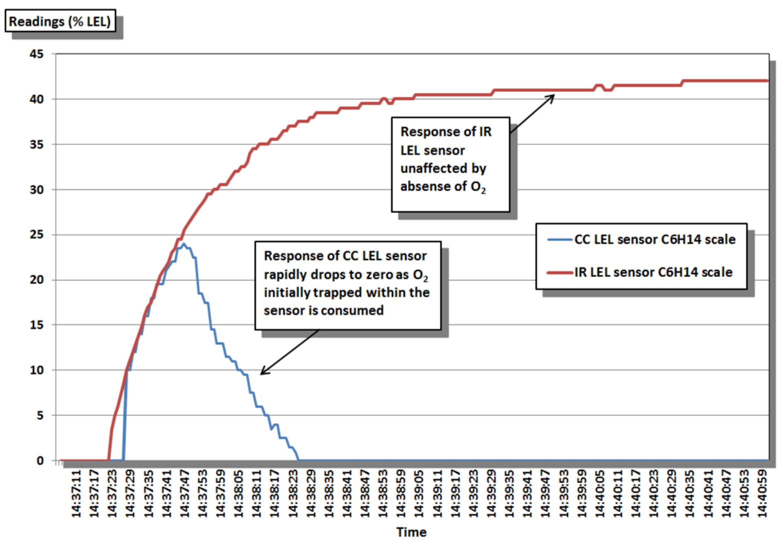
High Range Catalytic LEL Combustible Sensor Limitations

- *Even with protective circuitry that protects bead at concentrations above 100% LEL, no direct display of gas concentration*
- *Techniques for high range combustible gas measurement:*
  - *Dilution fittings*
  - *Thermal conductivity sensors*
  - *Calculation by means of oxygen displacement*
- ***Using infrared (NDIR) sensor to measure combustible gas avoids all of these issues!***



IR LEL sensor performance unaffected by the absence of oxygen

IR and CC LEL sensors exposed to 44% LEL hexane (0.48% vol. C_6H_{14})



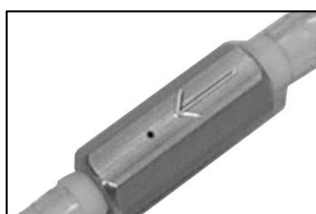
Dilution Fitting

- *Mixes the gas sample with an equal volume of fresh air*
- *Allows use of standard catalytic bead sensor to obtain readings from oxygen deficient atmospheres*
- *As long as O_2 concentration in sample exceeds 10%, the combustible gas sensor has enough oxygen to read accurately*

> ***Be Careful!***
>
> ***Anything that changes the ratio of fresh air introduced into the sample will change the results.***
>
> ***The instrument must be calibrated with the complete sample draw system in place.***
>
> ***The dilution ratio can be affected by filter loading, changing the length of sample tubing, variations in the flow rate of pump, changes in the settings of the dilution fitting and other factors.***

Dilution Fitting Limitations

- ***Remember that the amount of combustible gas in the sample is also diluted!***
- ***Combustible and toxic gas readings must be doubled to obtain true concentrations***
  - ***That means if a reading of 20 % LEL is obtained while the dilution orifice is being used, the true concentration is actually 40 % LEL!***



Examples of dilution fittings

Dilution Fitting Correction factors

- *If dilution adapter non-adjustable, may be necessary to calculate correction factor if dilution ratio varies from 50/50*
- *Correction factor is reciprocal of percentage of difference between actual reading and expected value with adapter in place*
- *Example:*
  - *When sensor exposed to 50% LEL gas, expected reading with adapter in place is 25% LEL*
  - *If actual reading is 20% LEL, the correction factor would be calculated as:*

    1 / (20% / 25%) = 1.25
  - *Multiplying actual reading by correction factor provides corrected reading with adapter in place:*

    20% X 1.25 = 25%
  - *Remember, need to double reading (multiply by 2) for true LEL concentration.*

    (20% X 1.25) X 2 = 50% LEL

Dilution Adapter Readings for O_2

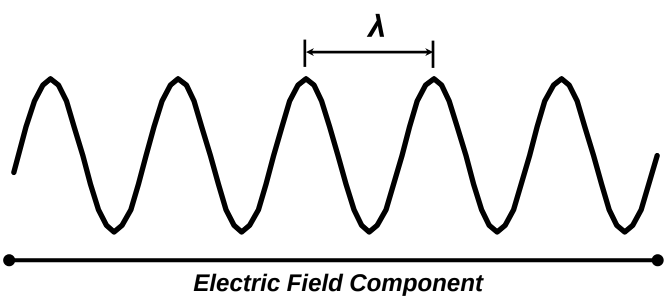
- *Many applications require oxygen to be measured at same time as combustible gas readings are obtained from low oxygen environment.*
- *Remove the adapter or block the dilution pore BEFORE taking readings for oxygen*
- *If the adapter is left in place, or the dilution pore is unblocked, the sample will be diluted with fresh air containing 20.9% oxygen*
- *Make sure to allow time for sensor readings to stabilize fully after removing the adapter or blocking the dilution pore BEFORE recording the readings*

Non-dispersive infrared (NDIR) sensors

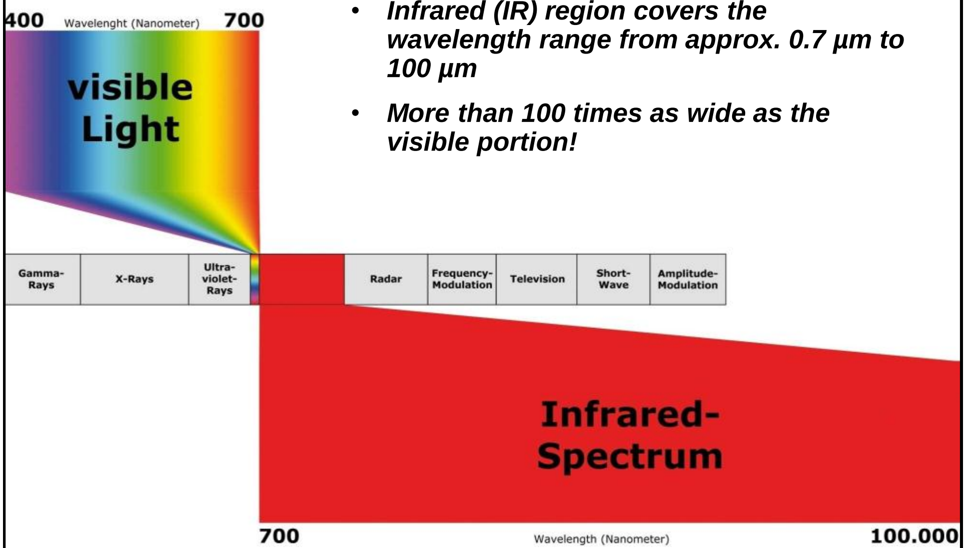
- *Many gases absorb infrared light at a unique wavelength (color)*
- *In NDIR sensors the amount of IR light absorbed is proportional to the amount of target gas present*
- *The longer the optical path through the sensor the better the resolution*

Properties of Light

- *Light is an electromagnetic field that oscillates as it travels through space:*

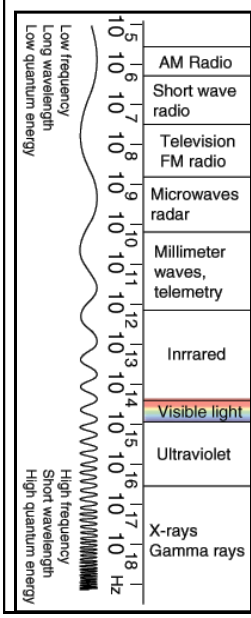


Electromagnetic radiation spectrum



- *Infrared (IR) region covers the wavelength range from approx. 0.7 µm to 100 µm*
- *More than 100 times as wide as the visible portion!*

Electromagnetic Spectrum



	Wavelength (m)	Frequency (Hz)	Energy (J)
Radio	> 1 x 10^{-1}	< 3 x 10^{9}	< 2 x 10^{-24}
Micro-wave	1 x 10^{-3} - 1 x 10^{-1}	3 x 10^{9} - 3 x 10^{11}	2 x 10^{-24}- 2 x 10^{-22}
Infrared	7 x 10^{-7} - 1 x 10^{-3}	3 x 10^{11} - 4 x 10^{14}	2 x 10^{-22} - 3 x 10^{-19}
Optical	4 x 10^{-7} - 7 x 10^{-7}	4 x 10^{14} - 7.5 x 10^{14}	3 x 10^{-19} - 5 x 10^{-19}
UV	1 x 10^{-8} - 4 x 10^{-7}	7.5 x 10^{14} - 3 x 10^{16}	5 x 10^{-19} - 2 x 10^{-17}
X-ray	1 x 10^{-11} - 1 x 10^{-8}	3 x 10^{16} - 3 x 10^{19}	2 x 10^{-17} - 2 x 10^{-14}
Gamma-ray	< 1 x 10^{-11}	> 3 x 10^{19}	> 2 x 10^{-14}

Non-dispersive Infrared Gas Detectors

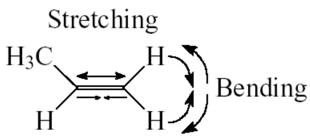
- *Measure wavelength-dependent absorption by polyatomic, asymmetric molecules*
- *IR absorption has advantages of high sensitivity, low cross-sensitivity, long life, and resistance to contamination*
- *IR absorption employed in both very high-performance laboratory analyzers and in very low-performance systems (e.g. inexpensive, non-intrinsically safe hand-held CO2 detectors)*

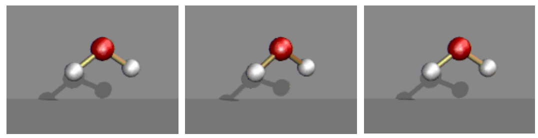
Infrared Detectors

- *Chemical bonds absorb infrared radiation*
- *For infrared energy to be absorbed (that is, for vibrational energy to be transferred to the molecule), the frequency must match the frequency of the mode of vibration*
- *Thus, specific molecules absorb infrared radiation at precise frequencies*

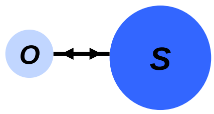
Energy Absorbed by "Bond Stretching" and "Bending" Vibration

- *Must have a COVALENT CHEMICAL BOND*





Symmetric Stretch | *Asymmetric Stretch* | *Bend*



Nonlinear Molecules

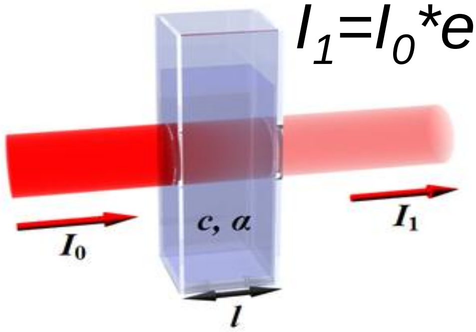
Linear molecules: SO

Infrared Detectors

- *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*

Beer-Lambert Law

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



Size (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

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 H_2 DO NOT absorb IR
  - Also IR-transparent:
    - N_2
    - O_2
    - F_2
    - Cl_2
    - Hg_2
    - Ar

Wavelength vs wavenumber (cm^{-1})

- ***Wavenumber is the number of waves per unit distance***
- ***Wavenumber is reciprocal of wavelength***
- ***In spectroscopy, wave number is usually expressed in reciprocal centimeters, as 100,000 cm^{-1} (100,000 per centimeter)***
- ***Example: The absorbance peak for CO is = 4.6 µm***

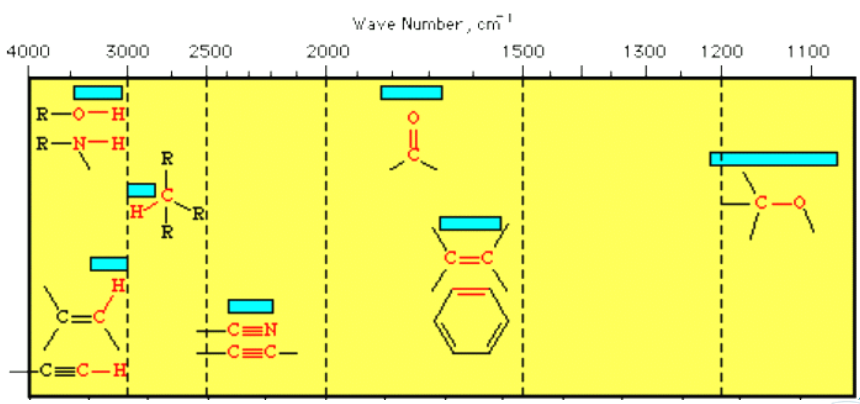
  4.6 µm = .00046 cm

  1 divided by .0046 cm = 2174 cm^{-1}

  Wavenumber = 2174 cm^{-1}

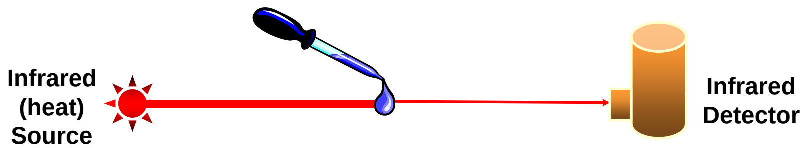
Infrared Spectroscopy

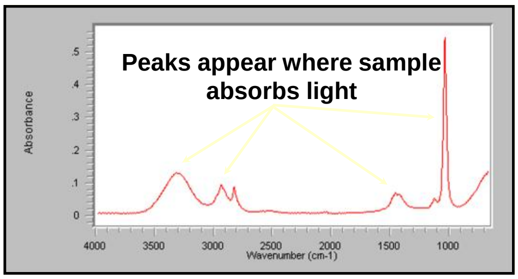
- ***Geometry of molecule and absorbance of light by specific bonds gives rise to a characteristic IR absorbance "fingerprint" of molecule***



Infrared Spectrum

- *A spectrum is a graph of how much infrared light is absorbed by molecules at each wavenumber of infrared light*





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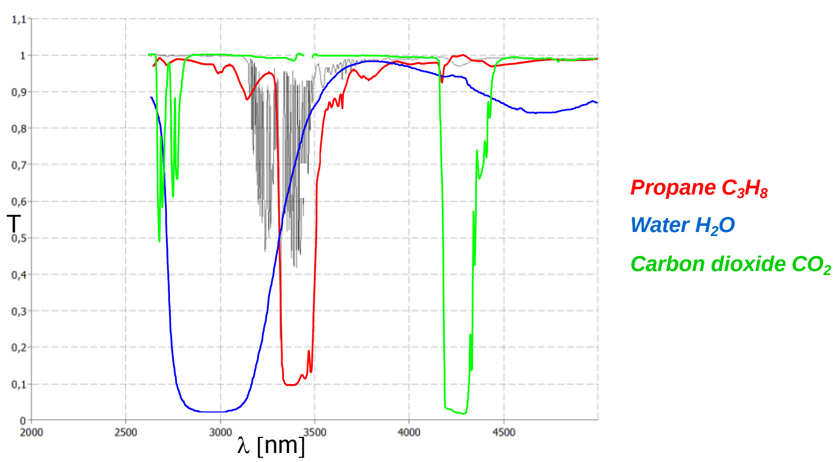
Infrared absorption spectra for several gases



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Double wavelength NDIR sensors

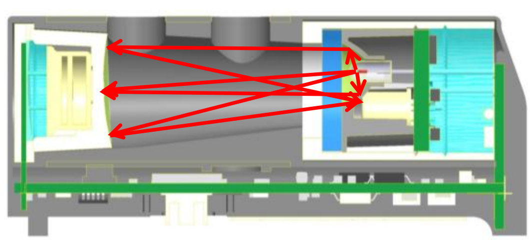
- *Commonly used in many portable instruments*

GfG IR sensor (Note longer pathlength)

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

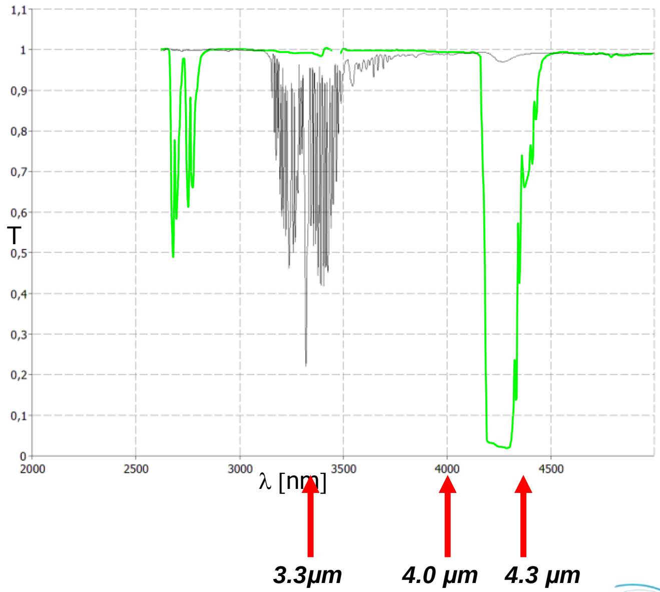
Light path through NDIR sensor

- *Optical path can be longer than it looks from the outside of sensor*
- *Optimal pathlength may be different for different gases*



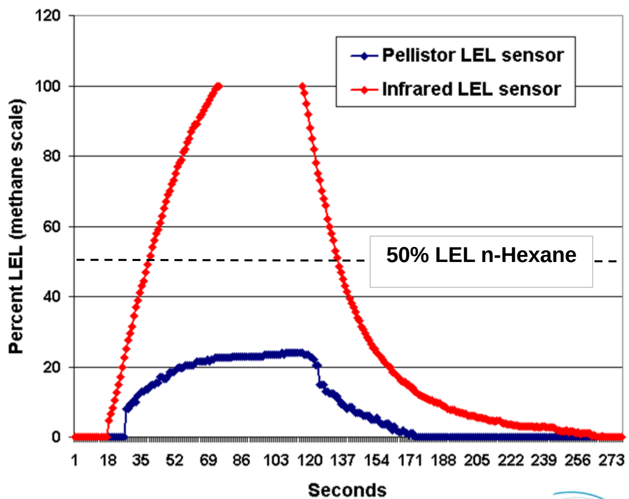
Wavelengths typically used for NDIR measurement

- ***LEL: 3.3 µm***
- ***CO_2: 4.3µm***
- ***Ref: 4.0µm***



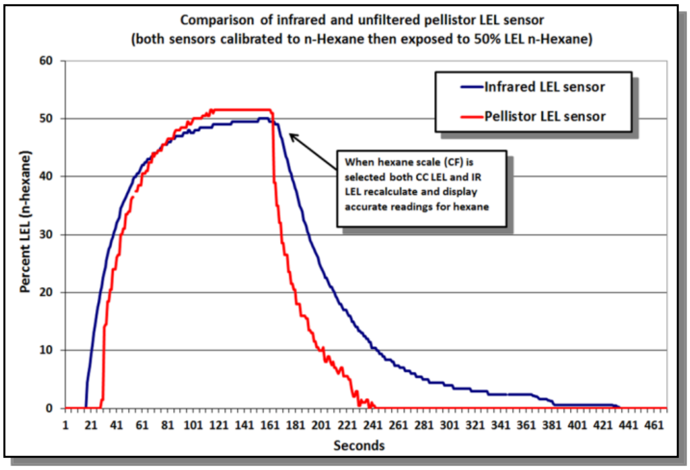
Relative response of pellistor and infrared sensors to n-Hexane

- ***Both sensors were calibrated to 50% LEL methane***
- ***Uncorrected readings for the pellistor LEL sensor much lower than the true concentration***
- ***Uncorrected readings for the IR sensor more than twice as high as the true concentration***



Response of calibrated pellistor and IR 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)*



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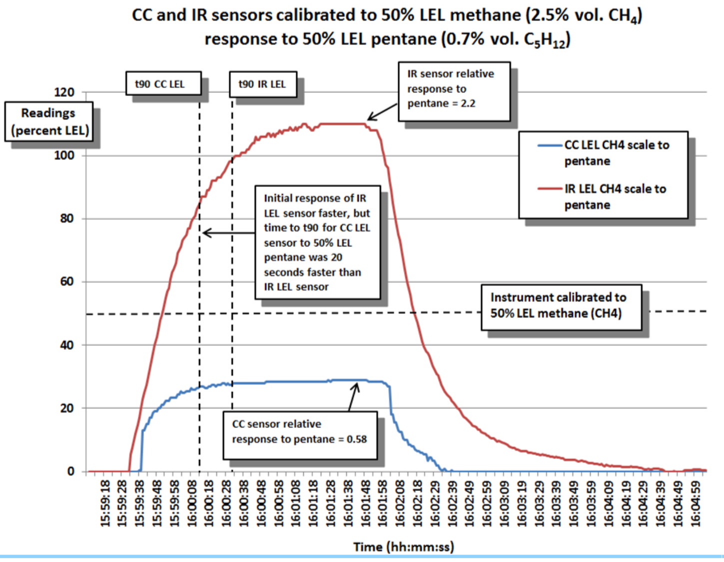
Relative response of pellistor and infrared sensors to n-Pentane



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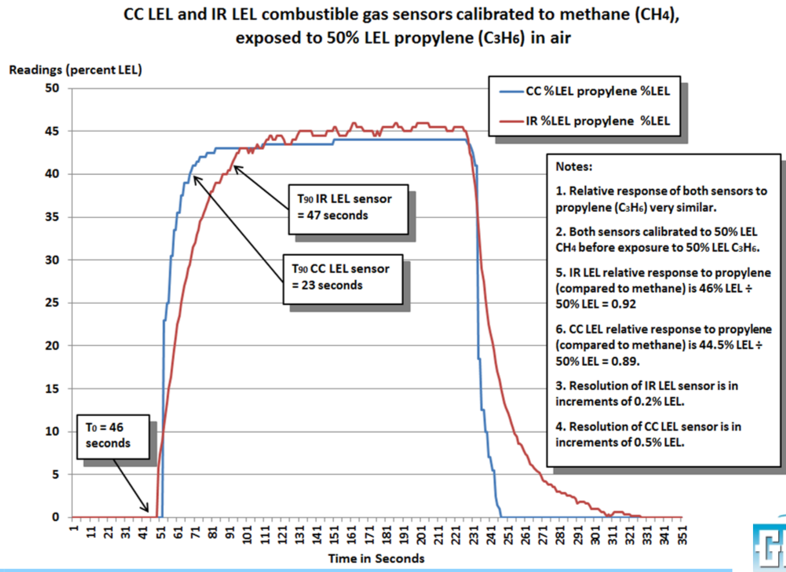
Relative response of pellistor and infrared sensors to propylene (C_3H_6) in air



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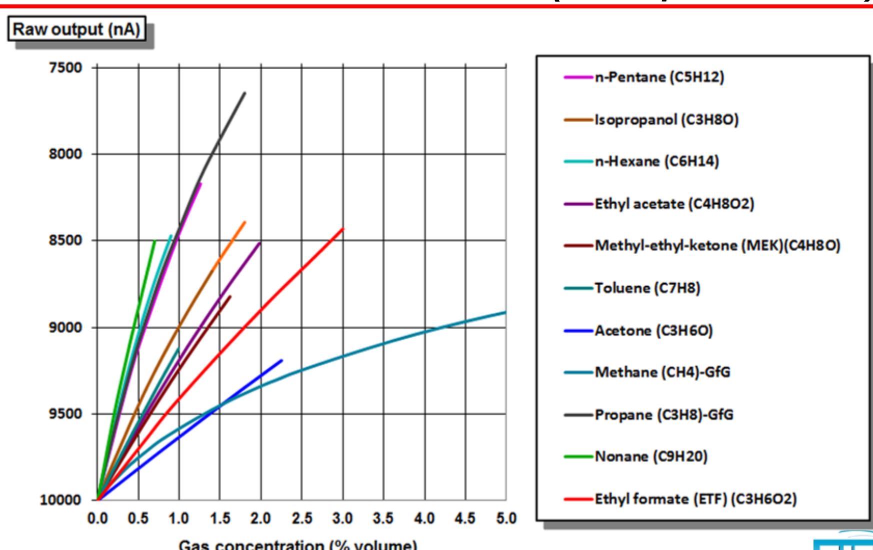
NDIR LEL sensor raw transmittance curves (λ=3.33µm / L=44mm)



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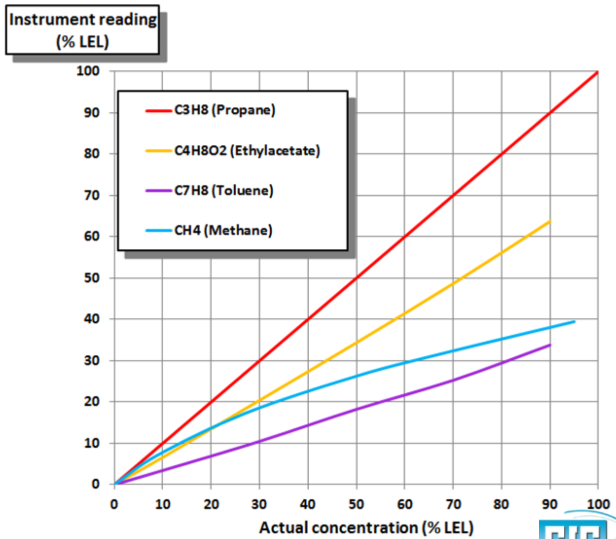
Response of NDIR LEL sensor (3.33 µm, 44 mm path) to various target gases

- *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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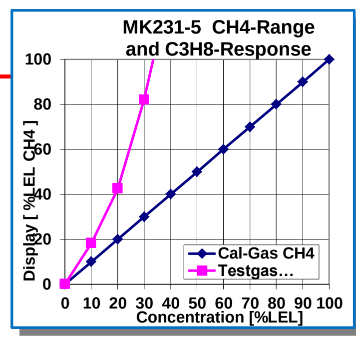
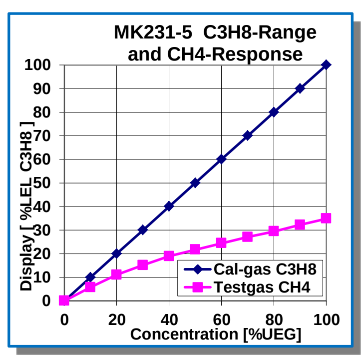
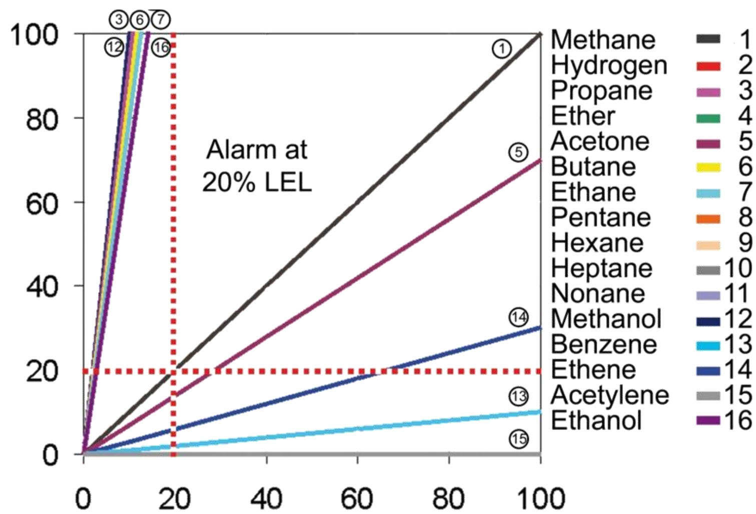
NDIR sensor performance

- *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*





Linearized NDIR combustible gas response curves



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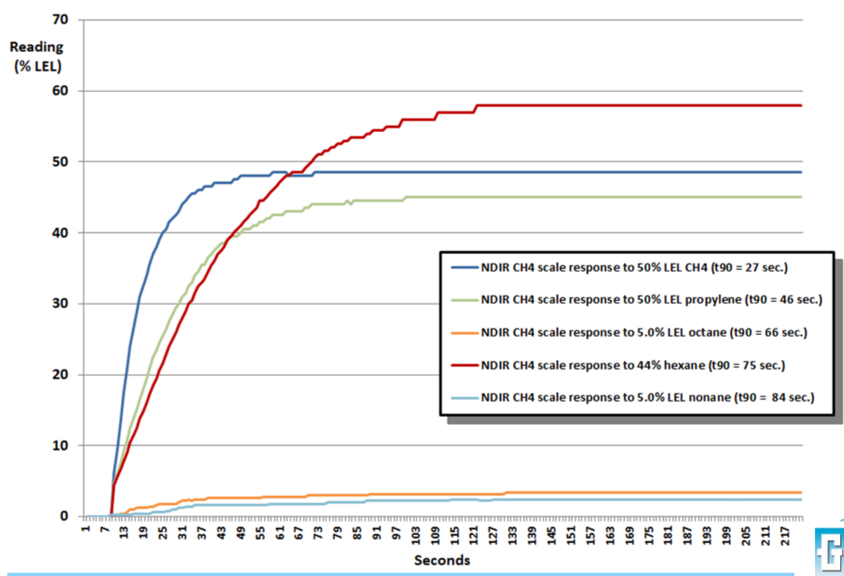
IR LEL (CH_4 scale) response to various combustible gases



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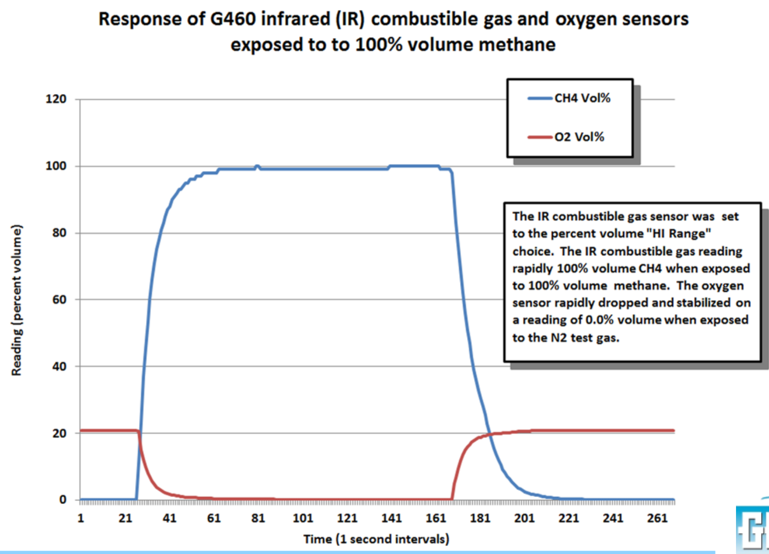
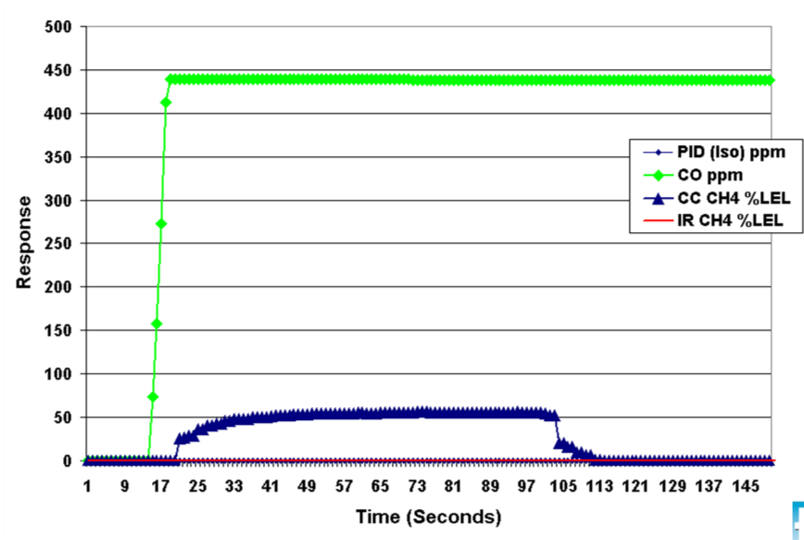
IR combustible sensors can be used for high range measurement up to 100% volume gas



Choosing the best sensor configuration

- *Multi-sensor instruments can include up to seven channels of real-time measurement*
- *Available sensors for combustible gas and VOC measurement::*
  - *CC %LEL*
  - *IR %LEL*
  - *IR %Vol*
  - *Thermal Conductivity %Vol*
  - *Electrochemical toxic*
  - *PID*

PID, CC LEL, IR LEL and CO sensors exposed to 50% LEL acetylene (1.25% volume)



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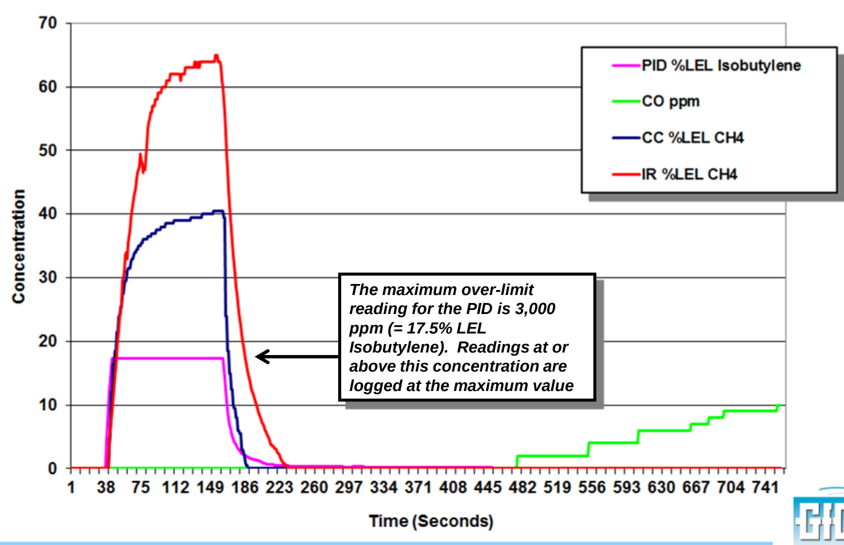
PID, CC LEL, IR LEL and CO sensors exposed to 50% LEL isobutylene (9,000 ppm)



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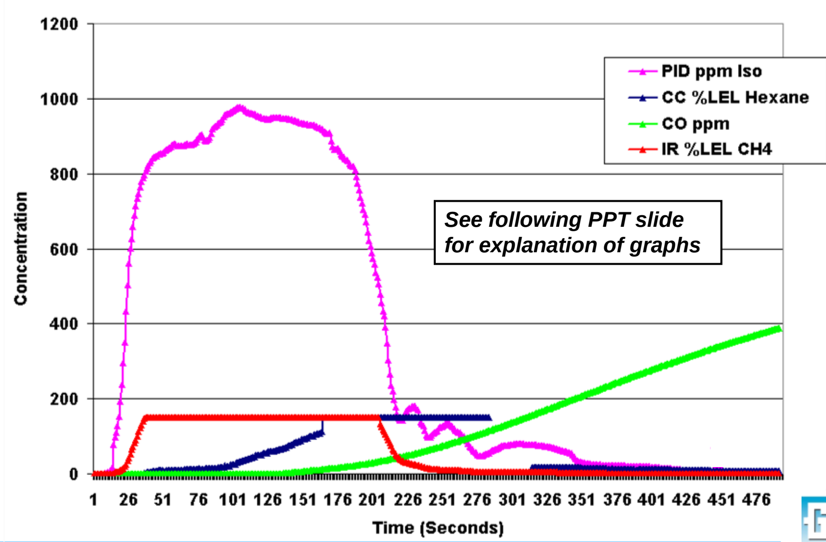
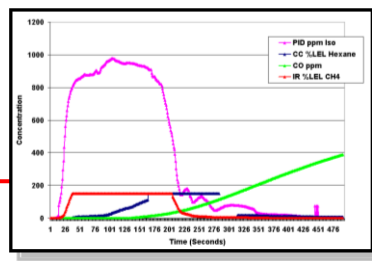
PID, CC LEL, IR LEL and CO sensors exposed to denatured alcohols vapor

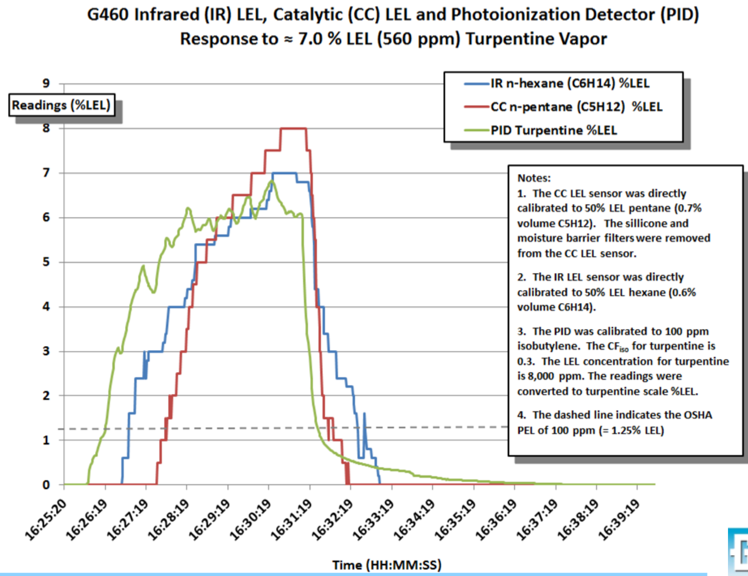


Explanation of response curves in previous slide: PID, CC LEL, IR LEL and CO sensors exposed to denatured alcohols vapor

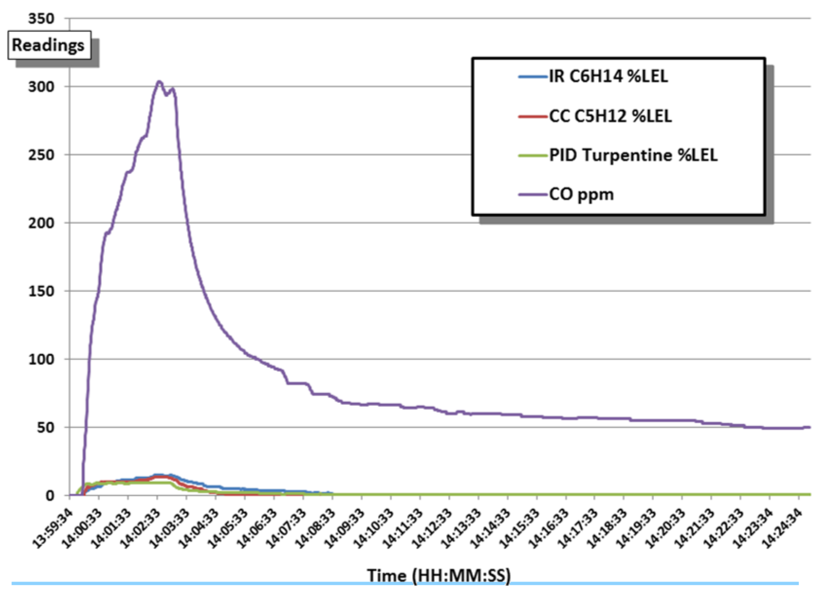


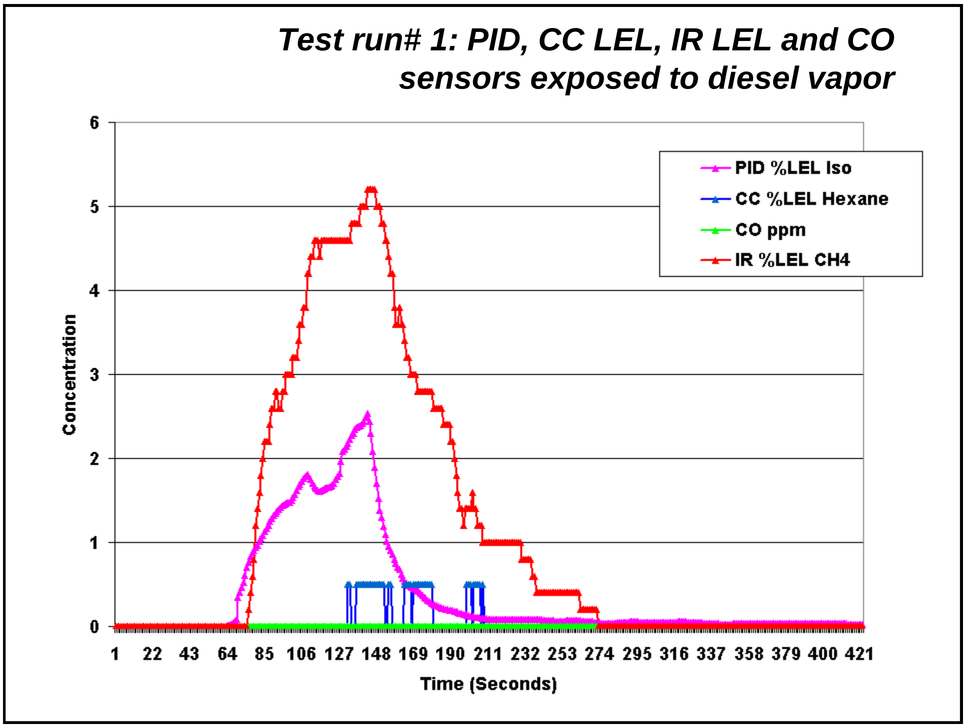
- *IR %LEL response curve (Red):*
  - *Sensor responds very rapidly to alcohol vapor*
  - *Maximum full-range reading for G460 IR LEL sensor is 150% LEL*
  - *Readings at or above this concentration logged at the maximum value*
  - *IR sensor resumes logging concentration when readings drop below 150% LEL*
- *Catalytic %LEL response curve (Dark Blue):*
  - *CC LEL sensor responds much more slowly than the IR LEL sensor*
  - *At 150% LEL instrument "latches" the over-limit alarm, and cuts power to the active bead to avoid damage to the sensor*
  - *Readings at or above this concentration logged at the maximum value*
  - *CC %LEL sensor must be manually reset to return to normal operation*
  - *Graph shows 43 second warm-up period after manually resetting the sensor*
- *CO sensor response curve (Green):*
  - *CO sensor did not begin to show readings until after exposure to alcohol was ended*
  - *CO readings eventually climbed reached the 500 ppm "over limit" concentration*
  - *Took over four hours for CO sensor to recover and stabilize at fresh-air value*

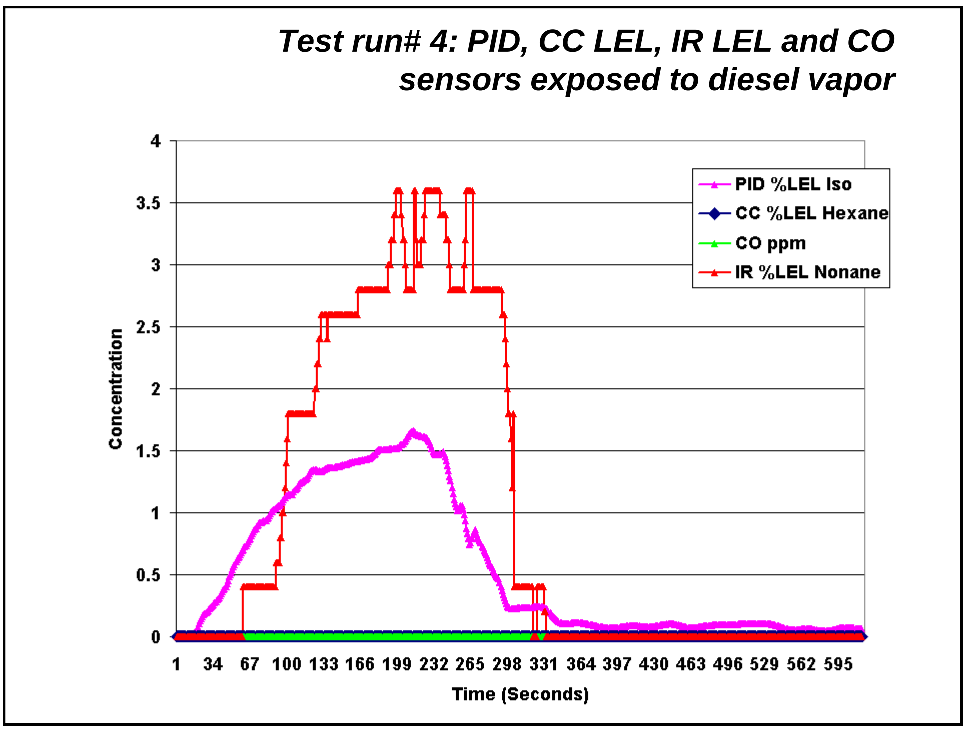
Response of IR LEL, CC LEL and PID to 7% LEL (560 ppm) turpentine vapor



Response of IR LEL, CC LEL, PID and CO sensors to 15% LEL turpentine vapor

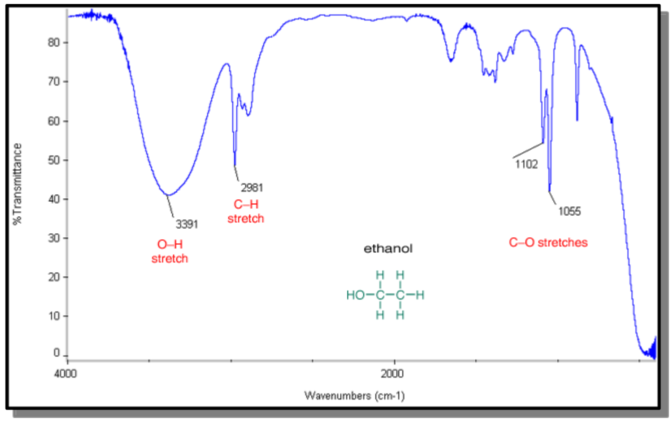



Test run# 1: PID, CC LEL, IR LEL and CO sensors exposed to diesel vapor
PID %LEL Iso
CC %LEL Hexane
CO ppm
IR %LEL CH4
Concentration
Time (Seconds)
0
1
2
3
4
5
6
1 22 43 64 85 106 127 148 169 190 211 232 253 274 295 316 337 358 379 400 421

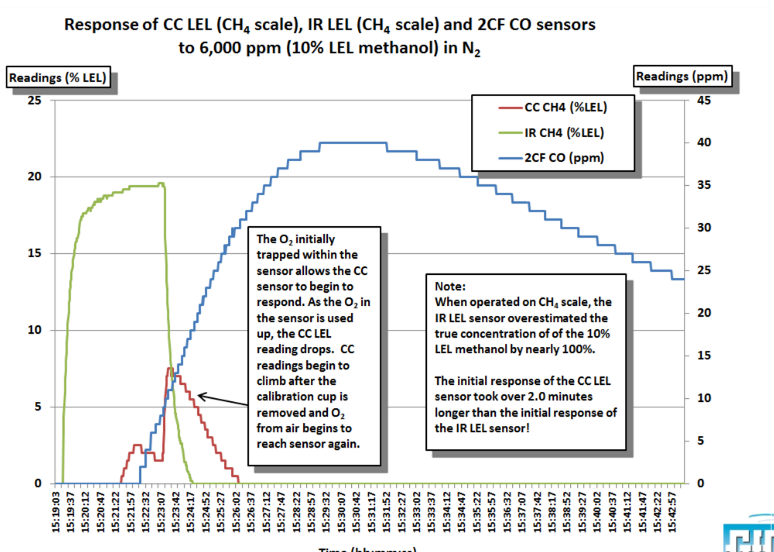

Test run# 4: PID, CC LEL, IR LEL and CO sensors exposed to diesel vapor
PID %LEL Iso
CC %LEL Hexane
CO ppm
IR %LEL Nonane
Concentration
Time (Seconds)
0
0.5
1
1.5
2
2.5
3
3.5
4
1 34 67 100 133 166 199 232 265 298 331 364 397 430 463 496 529 562 595

Infrared LEL sensor excellent for methanol and other alcohols

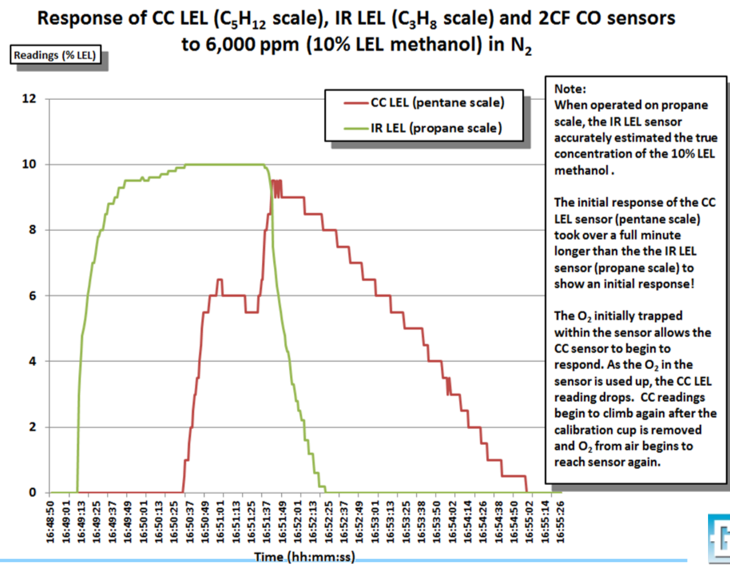
- ***Measurement near 3.34µm picks up both C-H stretch and O-H stretch***



Infrared LEL and CC LEL response to methanol on CH_4 scale



Infrared LEL (C_3H_8 scale) and CC LEL (C_5H_{12} scale) response to methanol



Selection matrix for Sensors for measurement of combustible gas and VOCs

	Able to detect LEL range C1 – C5 hydro-carbon gases (methane, ethane, propane, butane, pentane and natural gas)	Able to detect LEL range C6 – C9 hydro-carbon gases (hexane, heptane, octane, nonane)	Able to accurately detect LEL range heavy fuel vapors (e.g. diesel, jet fuel, kerosene, etc.)	Able to detect heavy fuel vapors in low ppm range (e.g. diesel, jet fuel, kerosene, etc.)	Able to use in low oxygen atmospheres	Vulnerable to sensor poisons (e.g. silicones, phosphine, tetraethyl lead, H2S, etc.)	Able to use for high range combustible gas measurement (100% LEL and higher)	Able to measure H2
Standard Pellistor type LEL sensor	Yes	Yes	No	No	No	Yes	No	Yes
NDIR combustible gas sensor	Yes	Yes	Yes	Yes*	Yes	No	Yes	No
PID (with standard 10.6 eV lamp)	No	Yes**	Yes**	Yes	Yes	No	No	No
Electrochemical H2 sensor	No	No	No	No	Yes	No	No	Yes
Thermal Conductivity Sensor	Yes	Yes	No	No	Yes***	No****	Yes	Yes

*Examples of possible sensor configurations optimized for specific applications**

	Confined space monitoring for municipal, water and wastewater	Confined space monitoring for shipyards	High range CH_4 from "sour" (high H_2S) natural gas wells	Typical oil refinery Instrument	Instrument used to measure O_2 and % LEL gas in inerted vessels	Landfill monitor
Type of hydrocarbon and / or VOC being measured	%LEL CH_2, 02, CO and H_2S	Heavy fuel and VOC (diesel, bunker, JP-8, solvents), natural gas and H_2	%LEL and high-range %Vol. CH_4	%LEL C1 – C9 gases, ppm range VOC, %LEL H_2, CO and H_2S	%LEL C1 – C9 in low O_2 atmosphere, ppm range VOC, CO and H_2S	%LEL and high-range %Vol. CH_4 and O_2
Standard Pellistor type LEL sensor	Yes	No	No	Yes	No	No
NDIR combustible gas sensor	No	Yes	Yes	No	Yes	Yes
PID (with standard 10.6 eV lamp)	No	Yes	No	Yes	No	No
Electrochemical H2 sensor	No	No	No	No	No	No
Electrochemical CO	Yes	Yes	No	Yes	Yes	Yes
Electrochemical H_2S	Yes	Yes	Yes	Yes	Yes	Yes
Oxygen sensor	Yes	Yes	Yes	Yes	Yes	Yes

**** Note that the listed sensor configurations represent possible solutions for specific applications. The presence of additional conditions or requirements may change the optimal sensor configuration.***

Questions?