Principles of Gas Detection: LEL, PID and NDIR Sensors and Applications

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Explosive or Flammable Atmospheres

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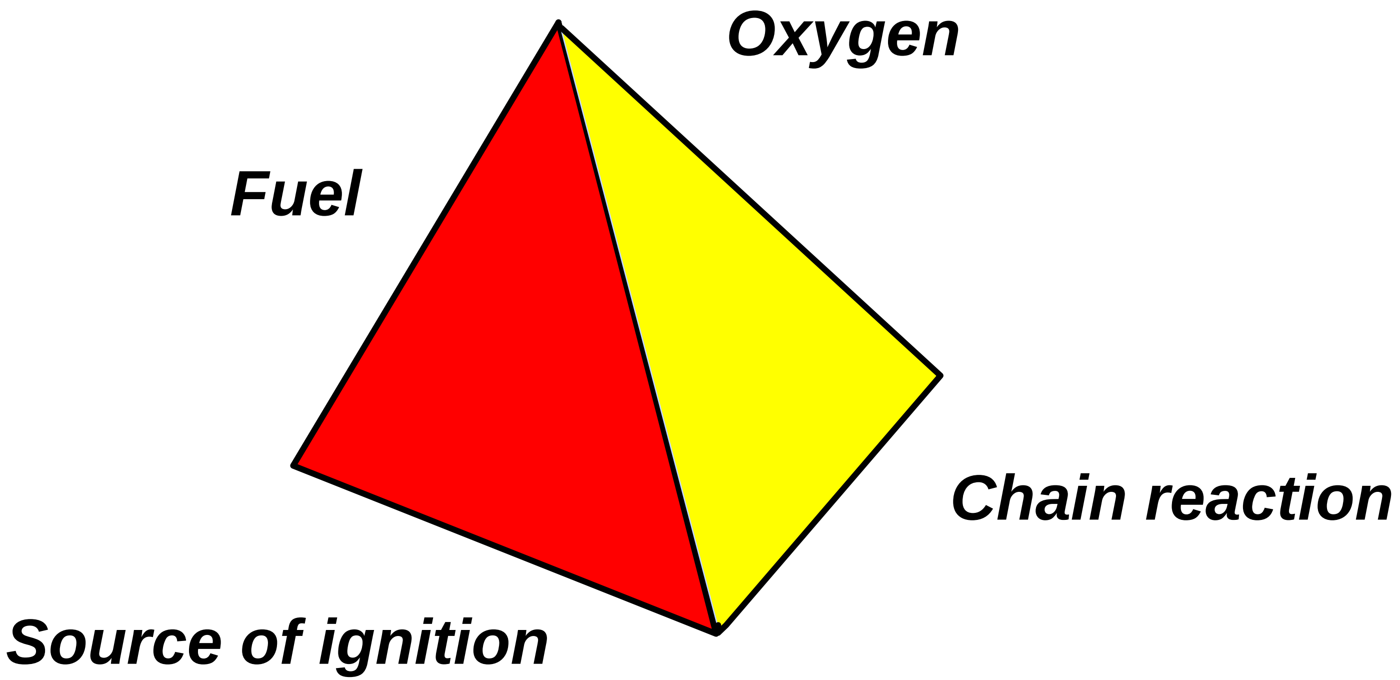
Oxygen
Fuel
Chain reaction
Source of ignition

Lower Explosive Limit (L.E.L.)

- ***Minimum concentration of a combustible gas or vapor in air which will ignite if a source of ignition is present***

Upper Explosive Limit (U.E.L.)

- *Most but not all combustible gases have an upper explosive limit*
    - *Maximum concentration in air which will support combustion*
    - *Concentrations which are above the U.E.L. are too “rich” to burn*

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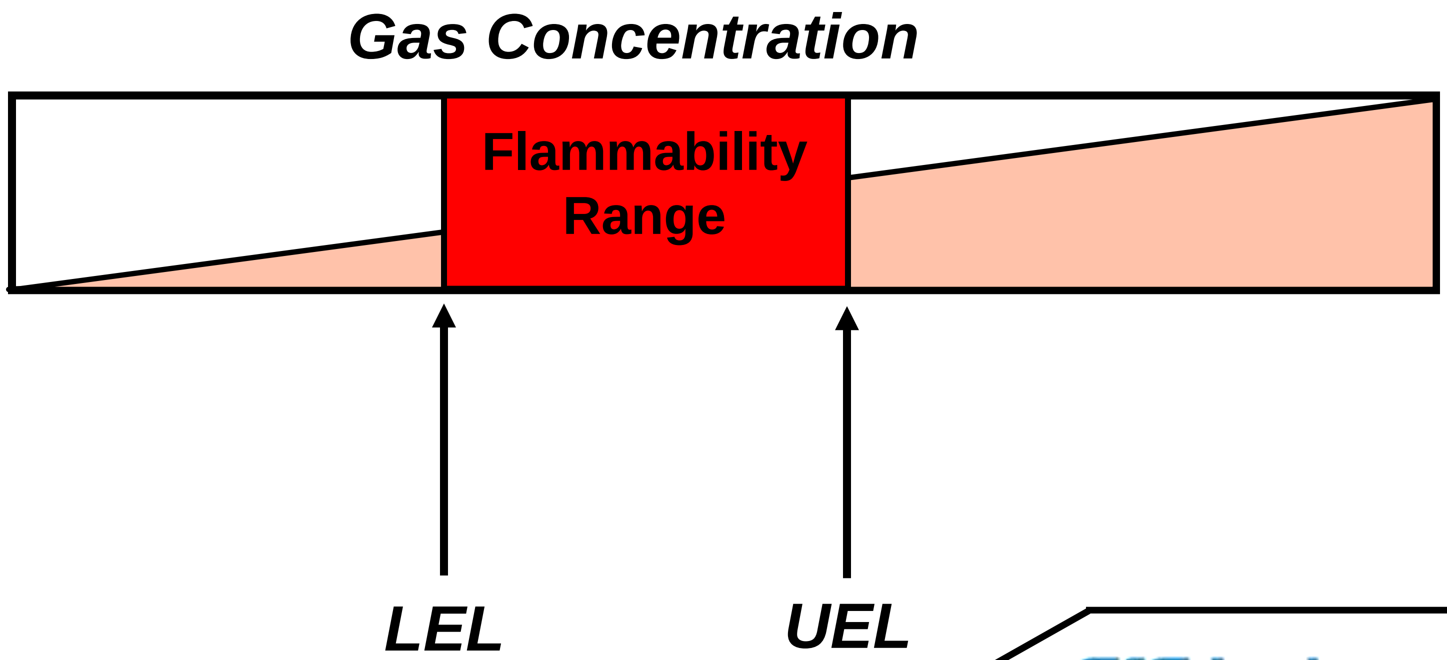
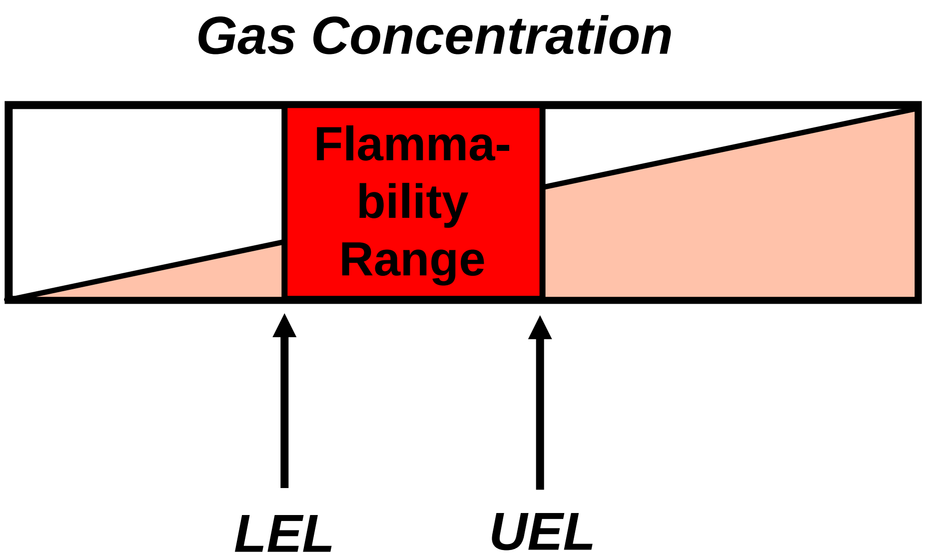
- ***The range between the L.E.L. and the U.E.L. of a combustible gas or liquid***
- ***Concentrations within the flammable range will burn or explode if a source of ignition is present***



Common 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

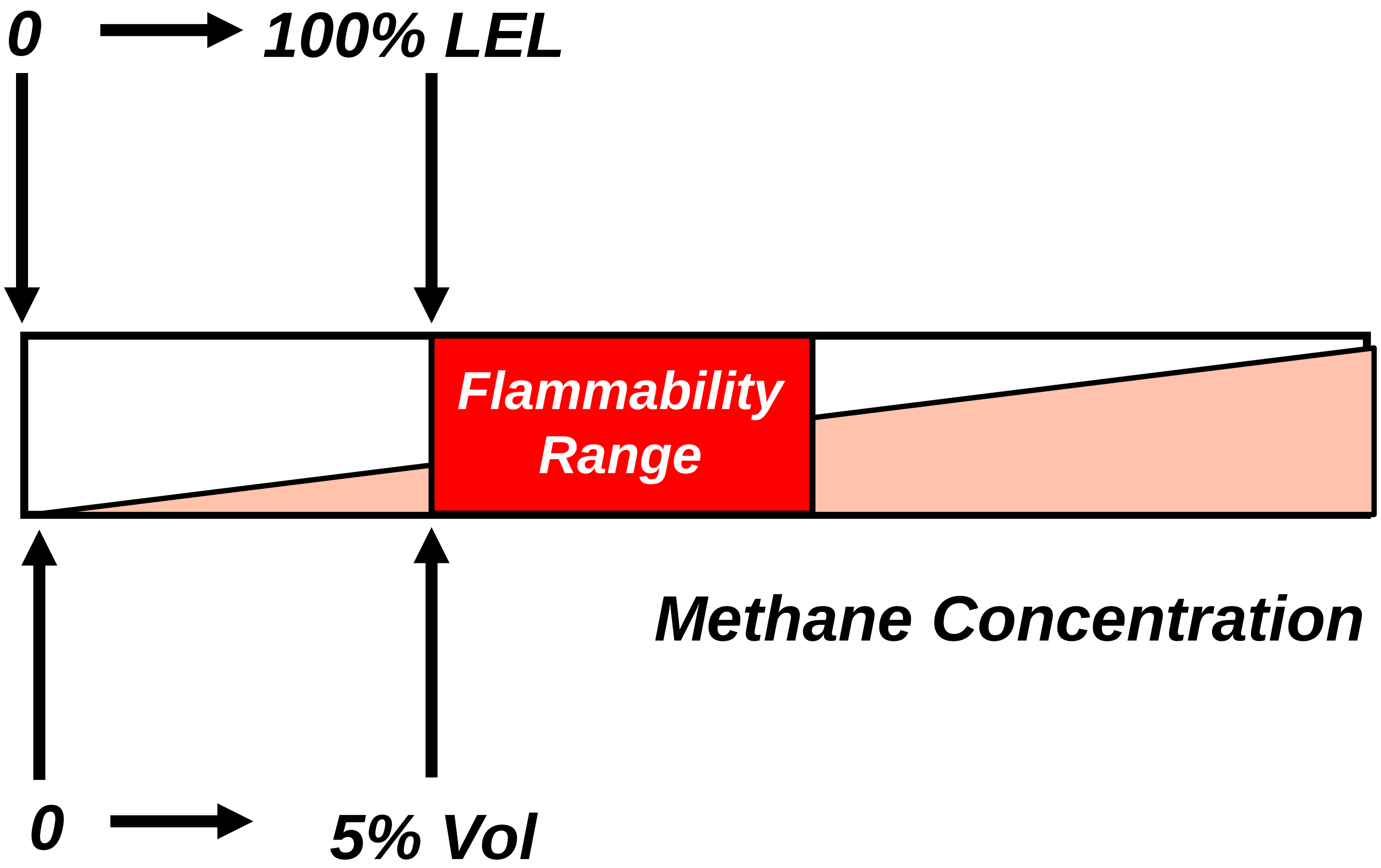
Over-Limit Protection

- *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*

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*

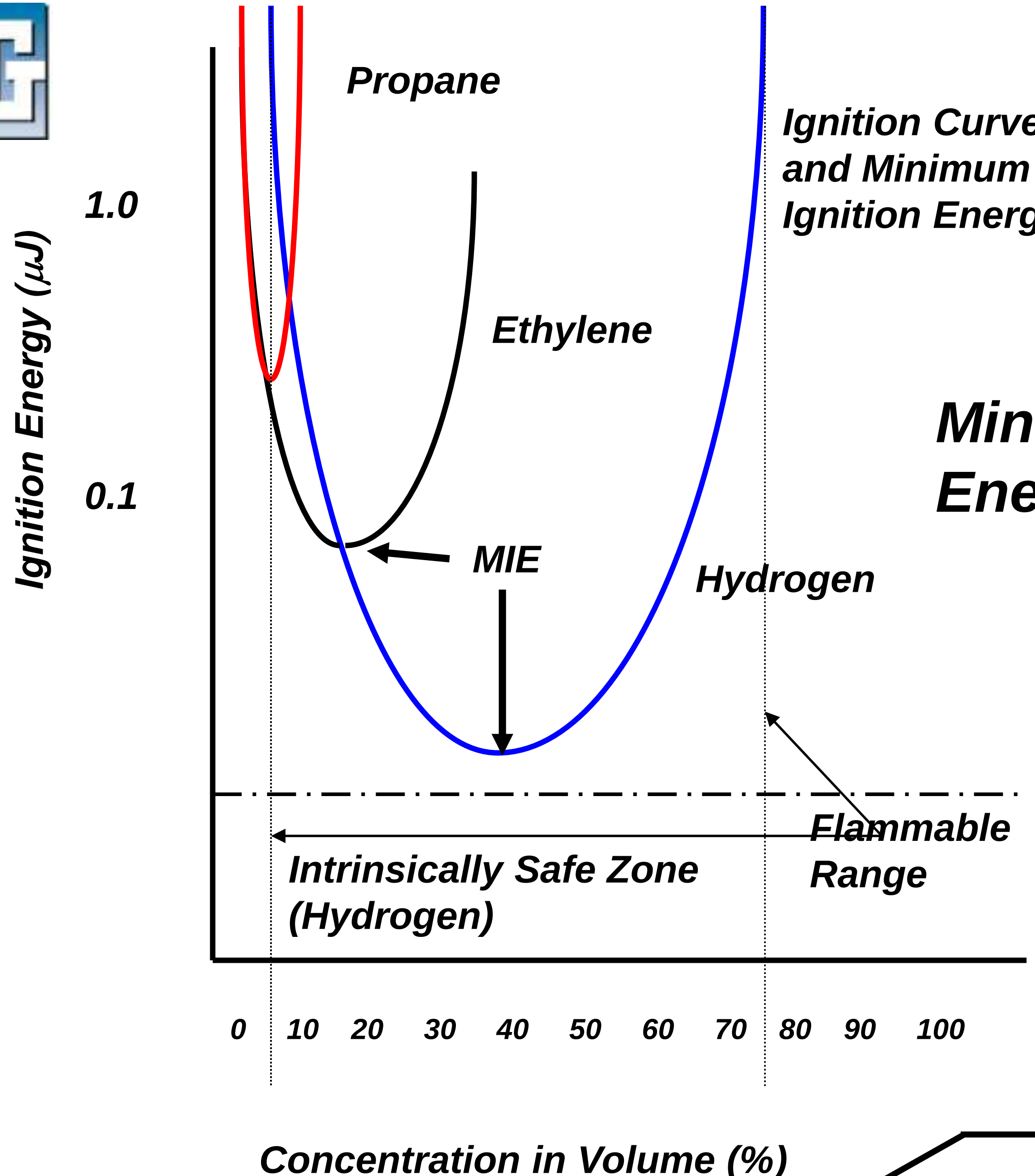
The Lower Explosion Limit (LEL) concentration for methane is 5.0% volume



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*

Minimum Ignition Energy



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Vapors

- *Gaseous state of substances that are either liquids or solids at room temperatures*
  - *Gasoline evaporates*
  - *Dry ice (solid carbon dioxide) sublimates*

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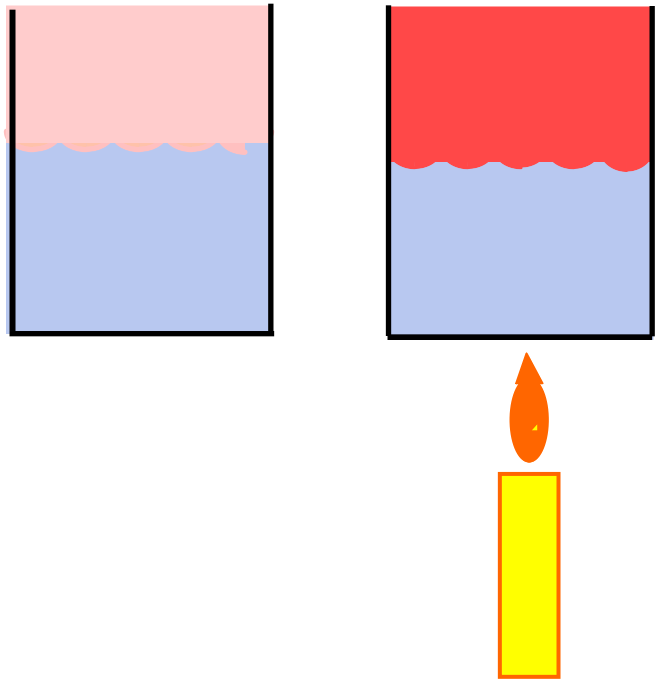
- *Increasing the temperature of the combustible liquid increases the amount of vapor produced*



Flashpoint

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

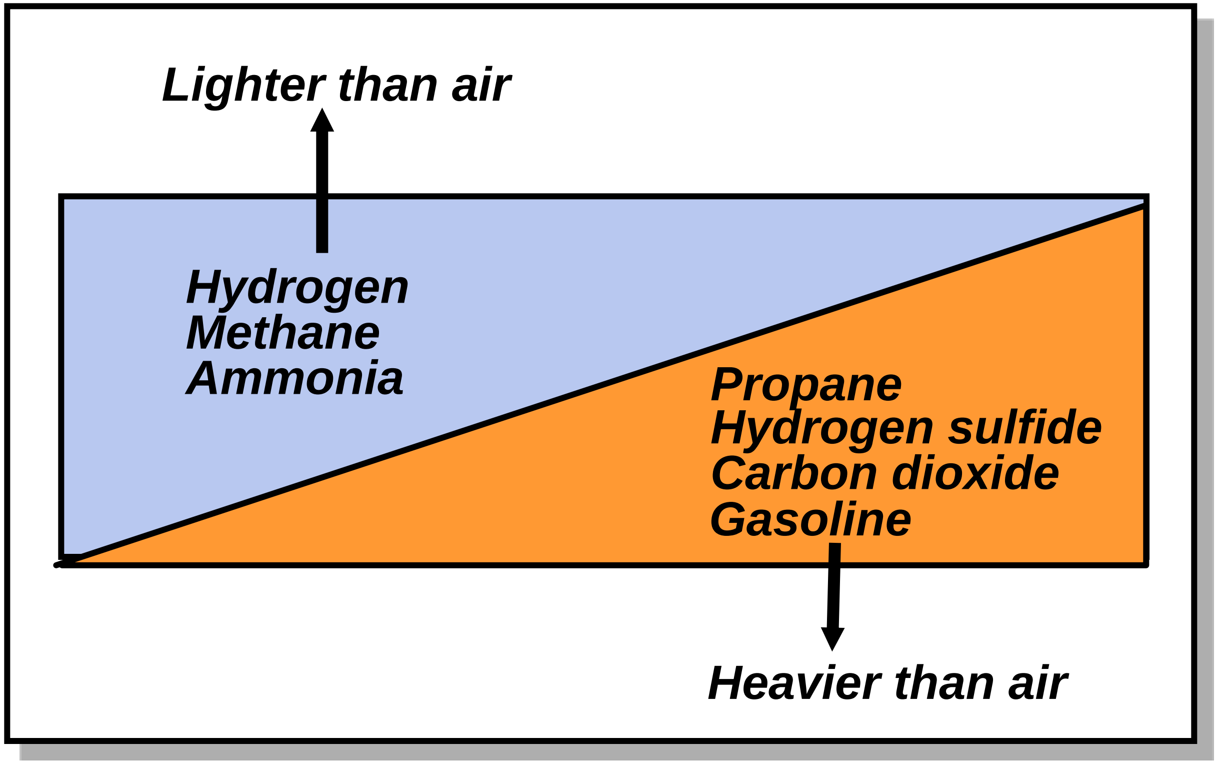
Flashpoints Vary

Common Flashpoints (degrees F)	
Gasoline (aviation grade)	- 50 (approx.)
Acetone	0
Methyl ethyl ketone	24
Ethanol (96 %)	62
Diesel oil	100 - 190

Flammable and combustible liquid classifications (OSHA 29 CFR 1910.106)

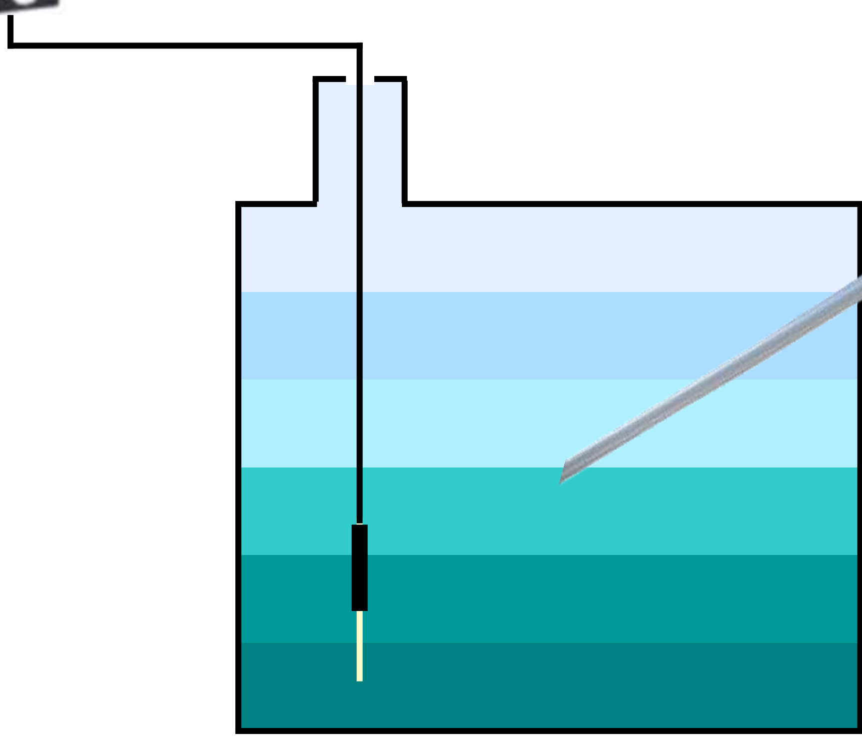
	Flash Point Temp °F	Boiling Point °F	Examples
Class IA flammable liquid	Below 73 °F	Below 100 °F	Methyl ethyl ether Pentane Petroleum ether
Class IB flammable liquid	Below 73 °F	Above 100 °F	Acetone Ethanol Gasoline Methanol
Class IC flammable liquid	At or above 73 °F	Below 100 °F	Styrene Turpentine 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		

- ***Measure of a vapor's weight compared to air***
- ***Gases lighter than air tend to rise; gases heavier than air tend to sink***



Stratification

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



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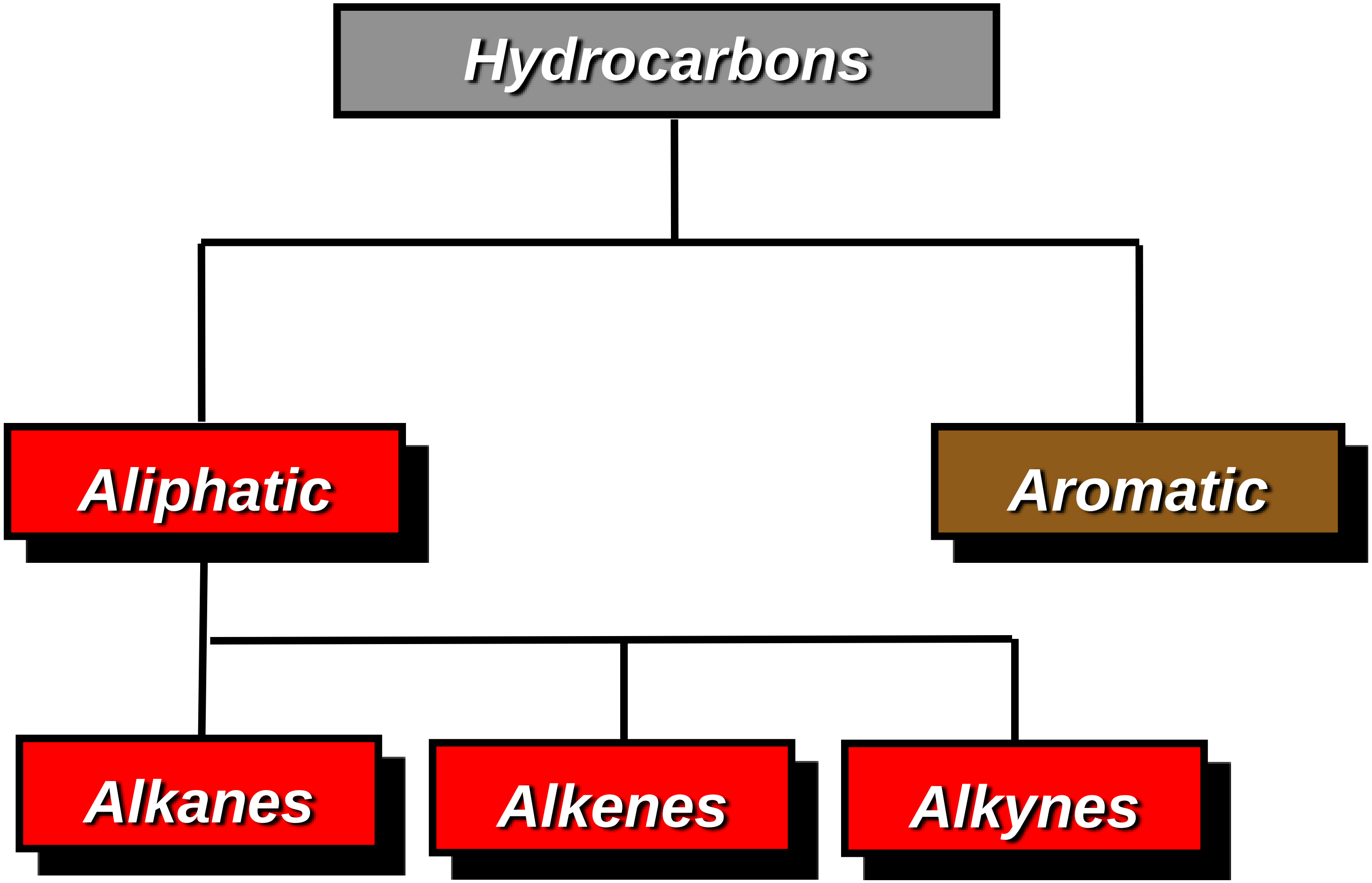
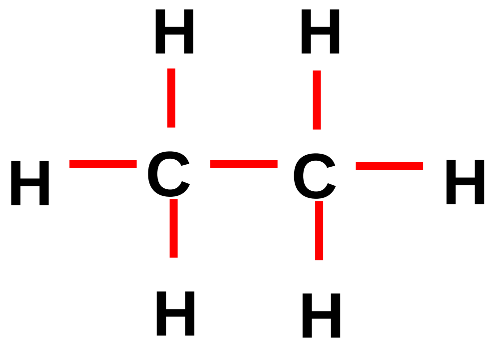
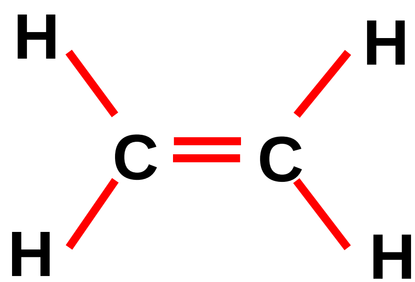

Hydrocarbons
Aliphatic
Aromatic
Alkanes
Alkenes
Alkynes

- ***Alkanes:***



- ***Alkenes:***



- ***Alkynes:*** $HC \equiv CH$

Increasingly reactive (less stable)

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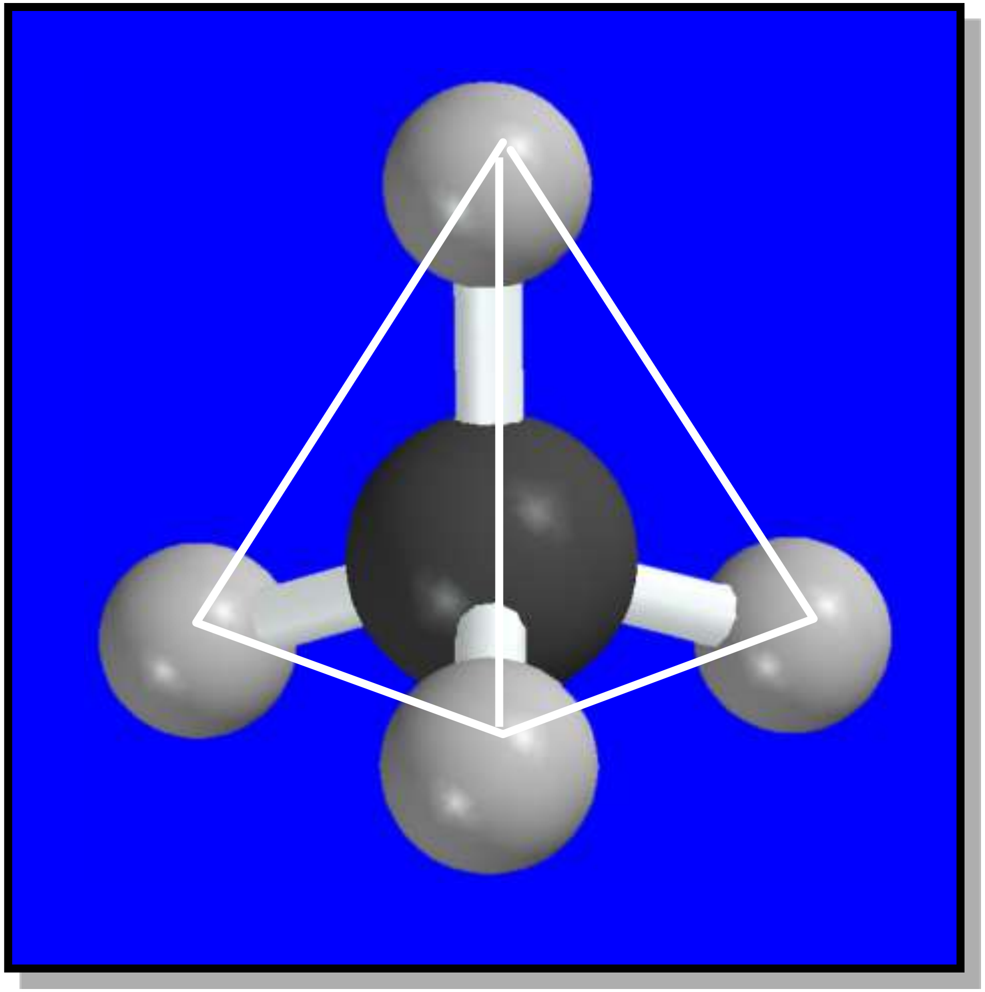
Chemical structure of Methane

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



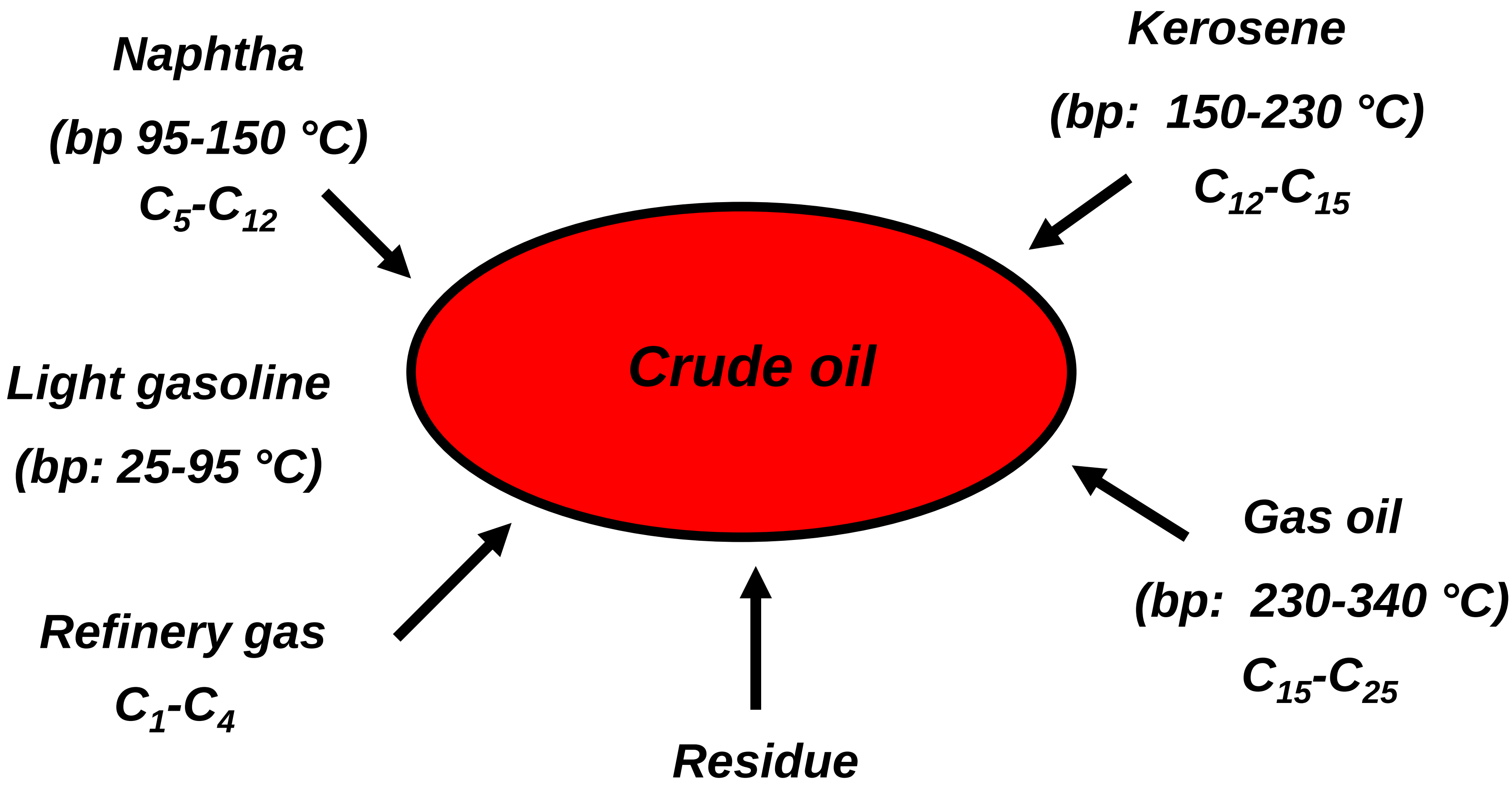
Names of Unbranched Alkanes

• 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

Petroleum Refining

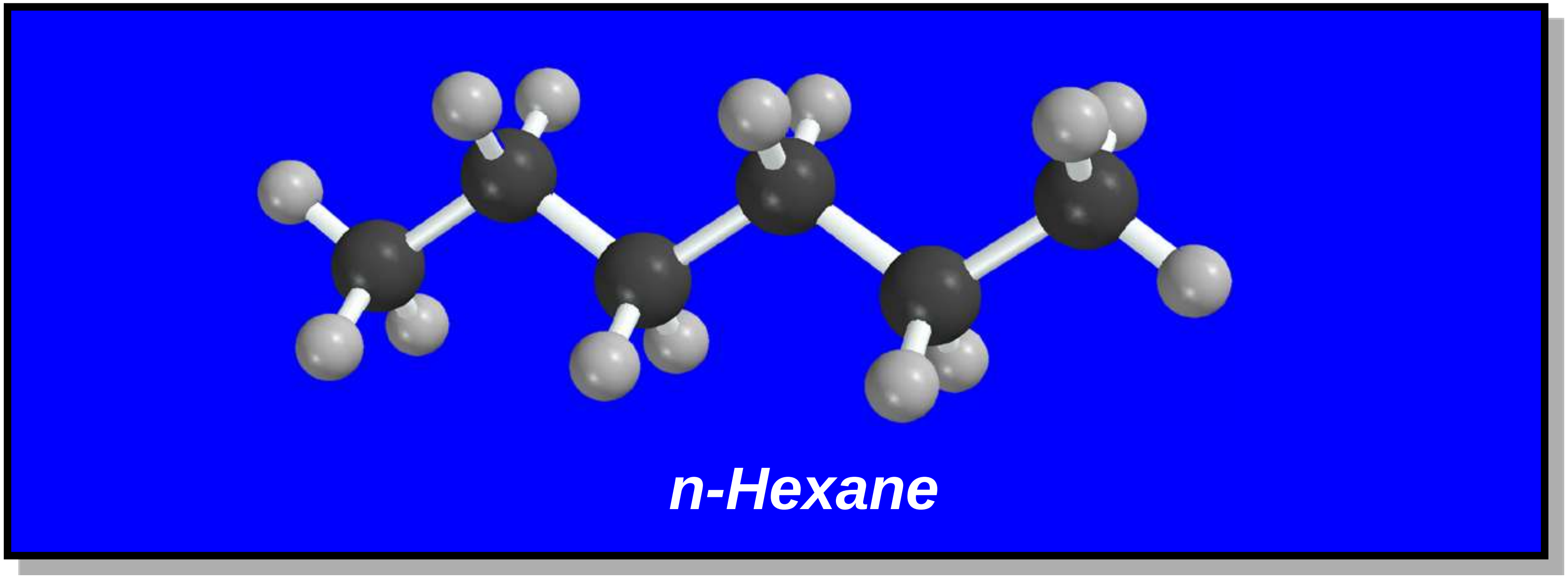
- ***Process of converting crude oil into high value products***
- ***Most important refinery products are transportation fuels – gasoline, jet fuel, and diesel fuel***
- ***Other important products include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt***

Crude Oil Constituents



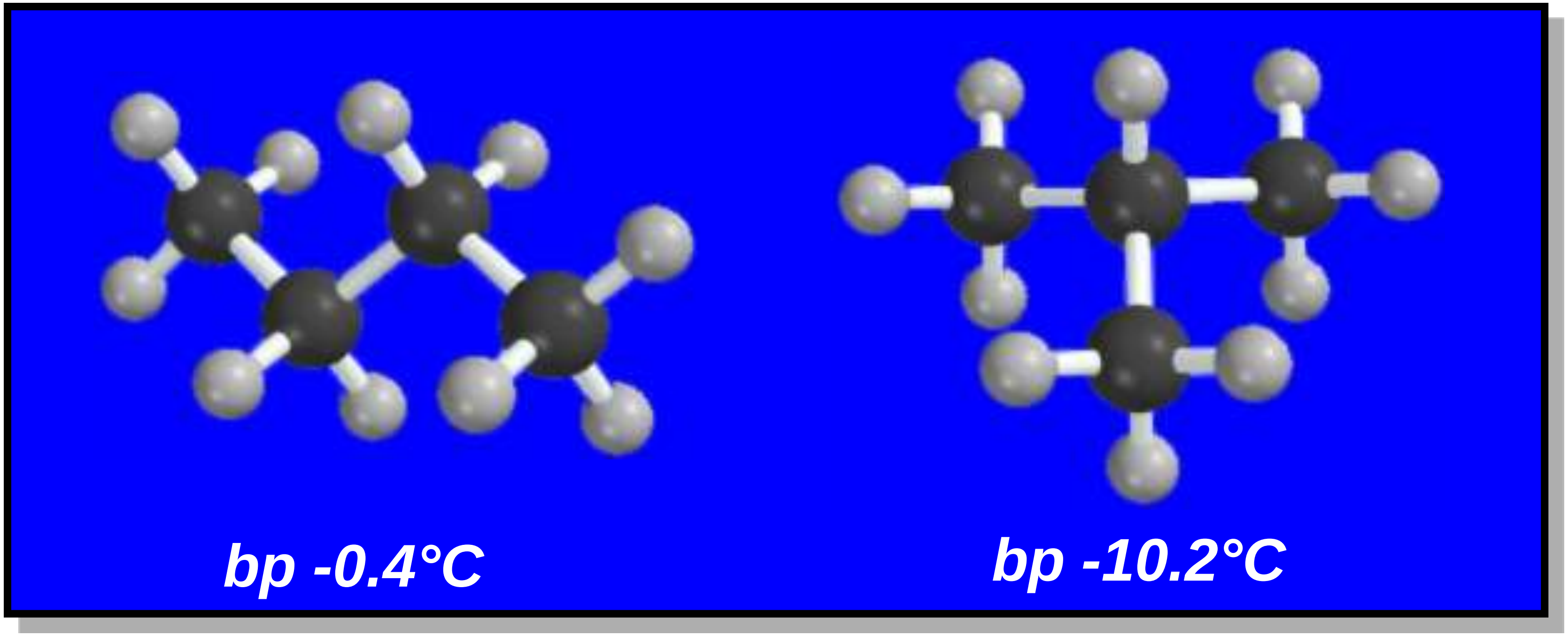
- *Cracking*
  - *Converts high molecular weight hydrocarbons to more useful, low molecular weight ones*
- *Reforming*
  - *Increases branching of hydrocarbon chains*
  - *Branched hydrocarbons have better burning characteristics for automobile engines*

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



Isomeric Alkanes: Butanes C_4H_{10}

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



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How combustible (percent LEL) gas detecting instruments detect gas

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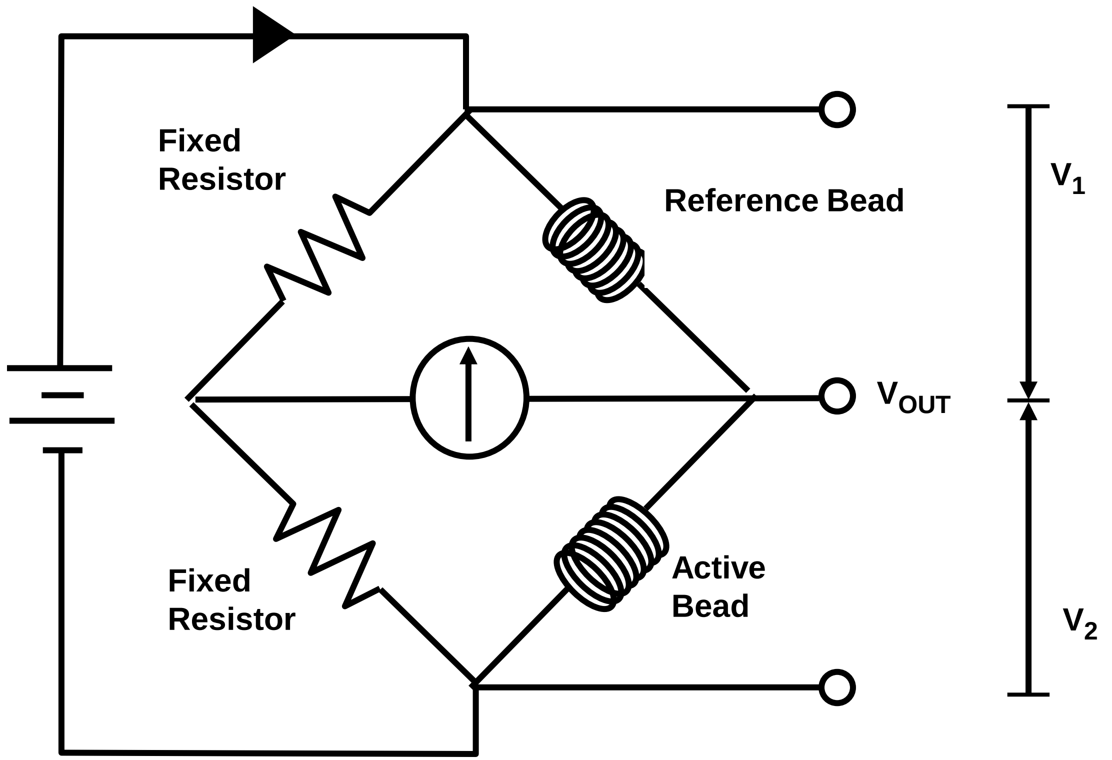
Catalytic “Hot Bead” Combustible Sensor

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

Simplified Balanced Wheatstone Bridge



Catalytic "Hot Bead" Combustible Sensor

- ***Detects combustible gas by catalytic oxidation***
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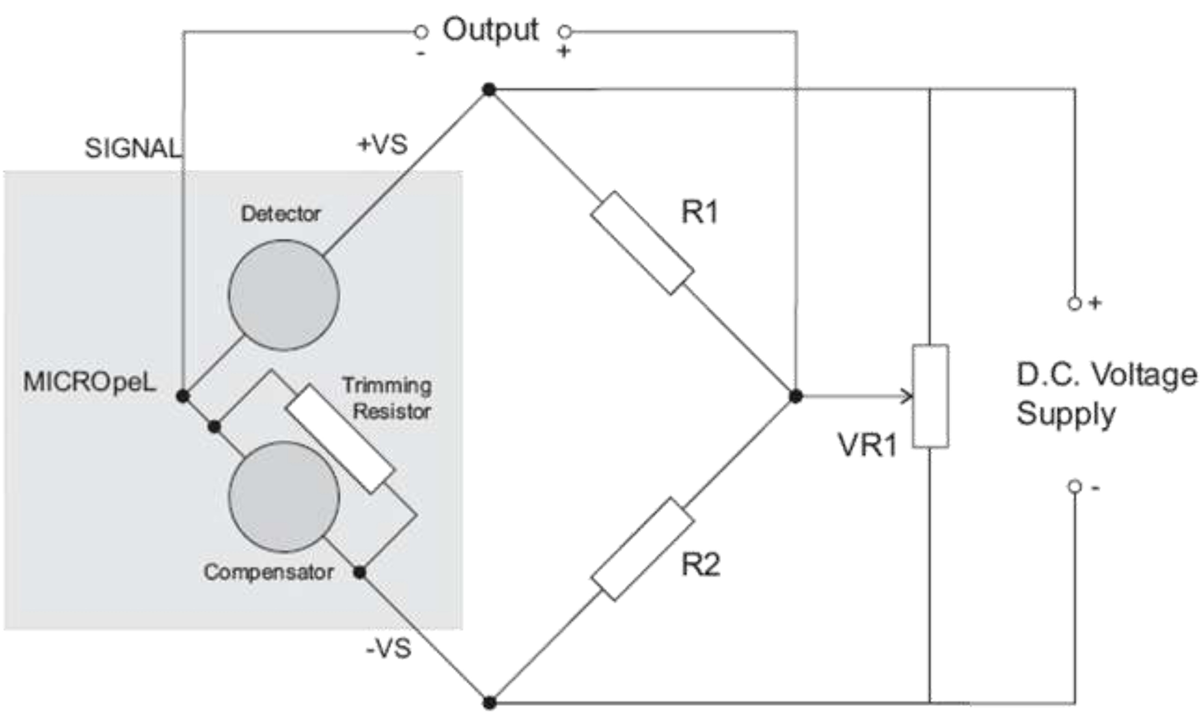
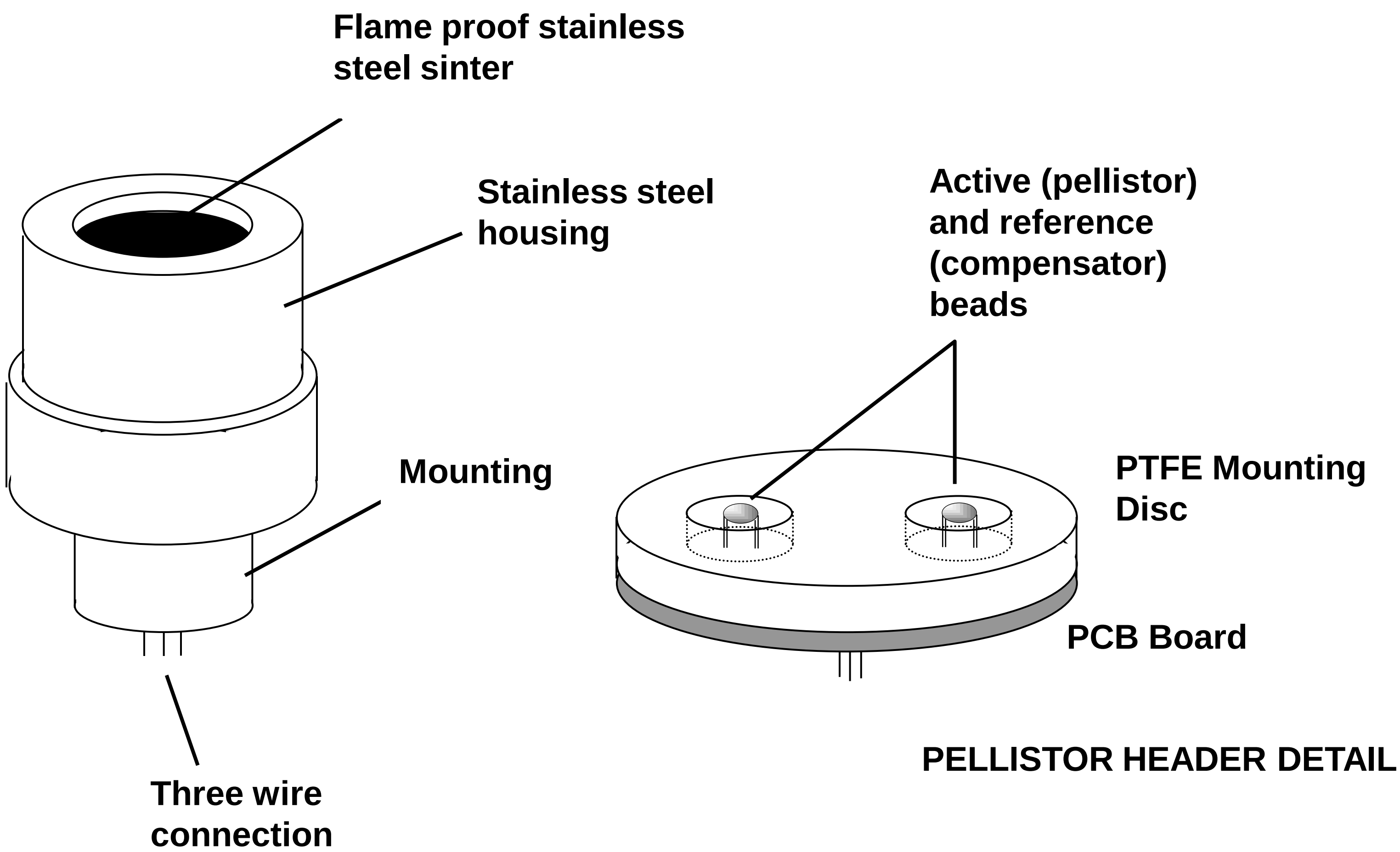
- ***Requires oxygen to detect gas!***



Combustible sensors detect gas by catalytic combustion



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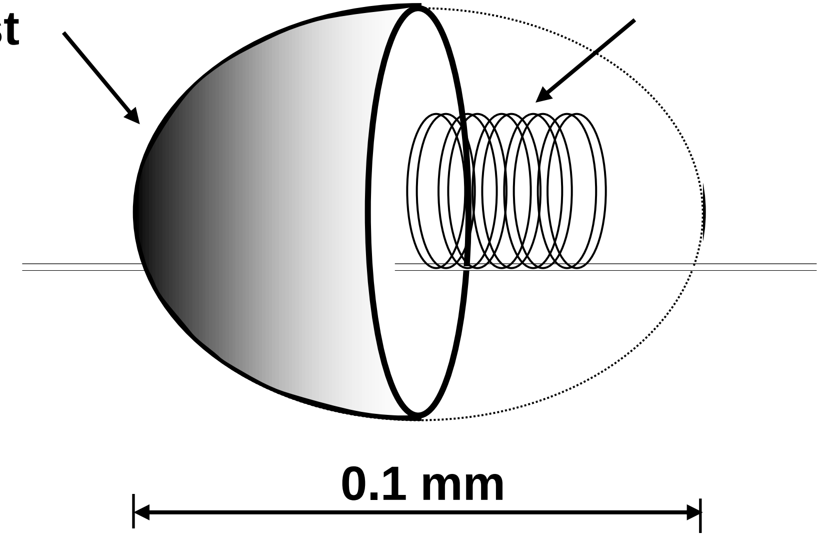
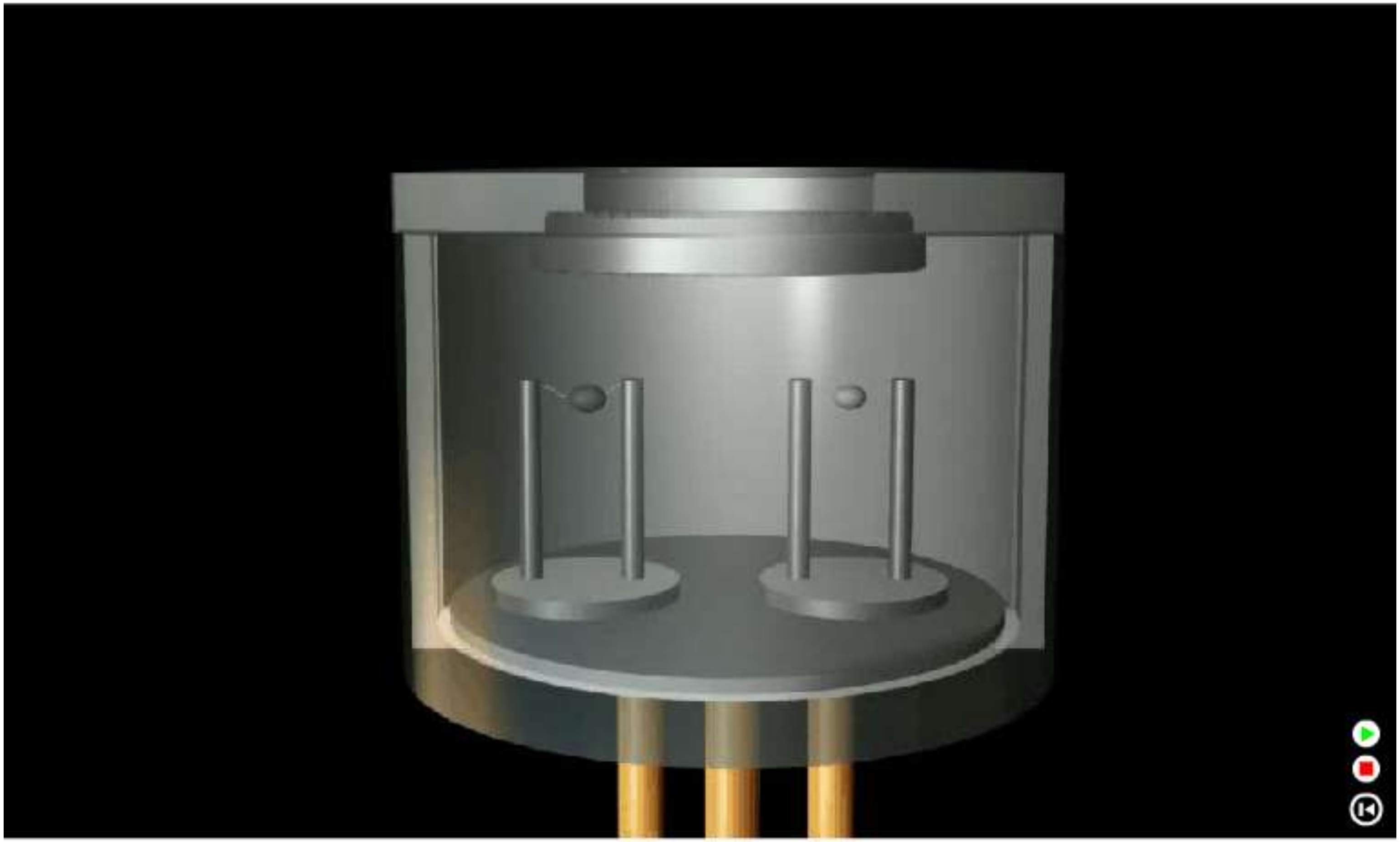
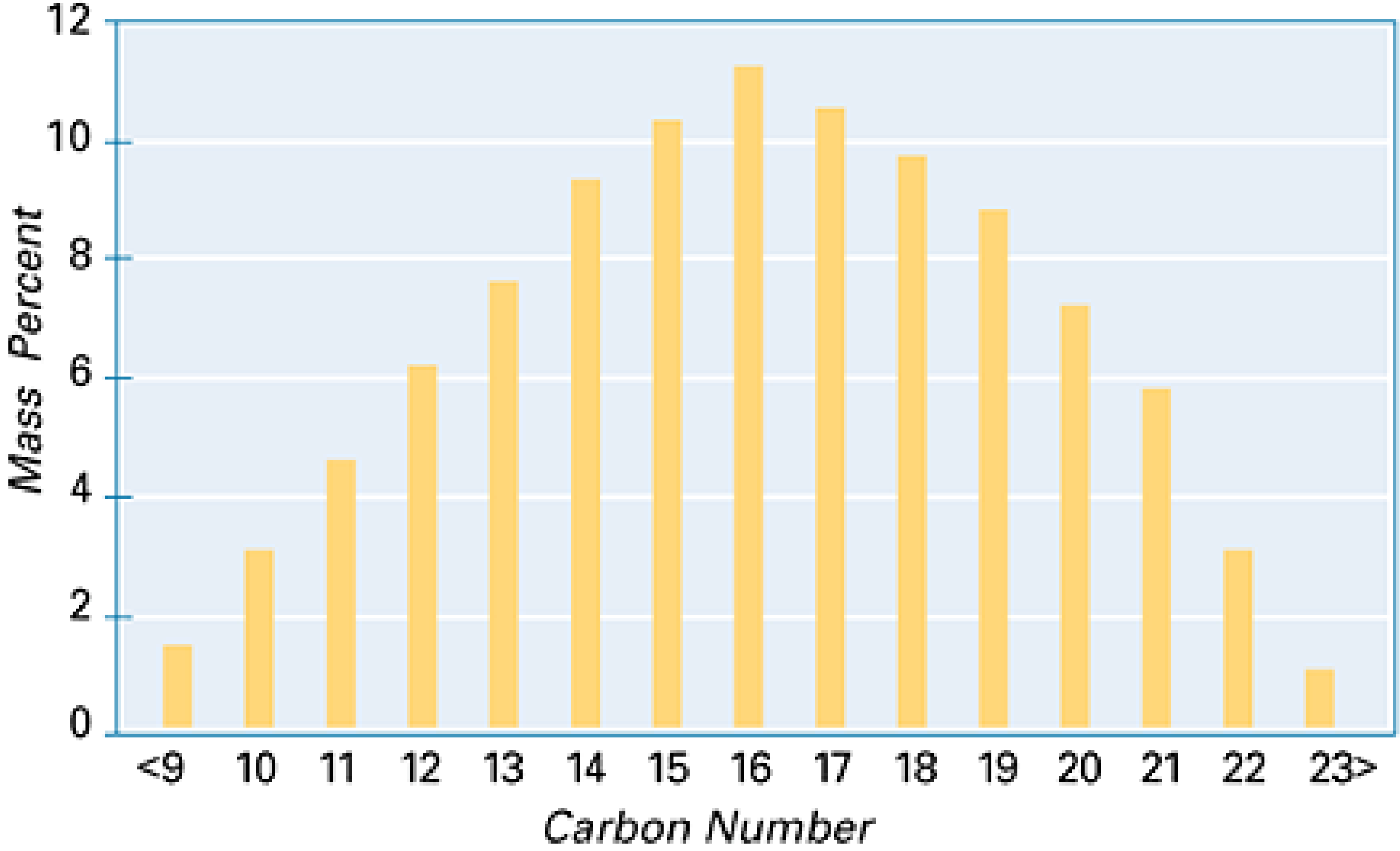

Porous
refractory bead
with catalyst
Platinum wire
coil
0.1 mm

Catalytic Sensor Structure



Typical Carbon Number distribution in No. 2 Diesel Fuel



LEL Sensor
Relative Response

Relative Response of a Flammable/Combustible Sensor

Combustible gas / vapor	Relative response when sensor is calibrated on pentane	Relative response when sensor is calibrated on propane	Relative response when sensor is calibrated on methane
Hydrogen	2.2	1.7	1.1
Methane	2.0	1.5	1.0
Propane	1.3	1.0	0.65
n-Butane	1.2	0.9	0.6
n-Pentane	1.0	0.75	0.5
n-Hexane	0.9	0.7	0.45
n-Octane	0.8	0.6	0.4
Methanol	2.3	1.75	1.15
Ethanol	1.6	1.2	0.8
Isopropyl Alcohol	1.4	1.05	0.7
Acetone	1.4	1.05	0.7
Ammonia	2.6	2.0	1.3
Toluene	0.7	0.5	0.35
Gasoline (Unleaded)	1.2	0.9	0.6

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Correction Factors

- *The correction factor is the reciprocal of the relative response*
- *Consider a detector calibrated on methane, then used to monitor ethanol*
- *When calibrated on methane, the sensor shows a relative response to ethanol of 0.8*
- *In other words, the readings will be 20% lower than actual*
- *The correction factor would be calculated as: 1 / 0.8 = 1.25*

LEL Sensor Correction Factors

Correction Factor of a Flammable/Combustible Sensor

Combustible gas / vapor	Correction factor when sensor is calibrated on pentane	Correction factor when sensor is calibrated on propane	Correction factor when sensor is calibrated on methane
Hydrogen	0.45	0.59	0.9
Methane	0.5	0.67	1.0
Propane	0.77	1.0	1.54
n-Butane	0.83	1.12	1.67
n-Pentane	1.0	1.34	2.0
n-Hexane	1.11	1.43	2.23
n-Octane	1.25	1.67	2.5
Methanol	0.44	0.57	0.87
Ethanol	0.63	0.84	1.25
Isopropyl Alcohol	0.71	0.95	1.43
Acetone	0.71	0.95	1.43
Ammonia	0.39	0.5	0.77
Toluene	1.43	2.0	2.86
Gasoline (Unleaded)	0.84	1.12	1.67

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Correction Factors

- ***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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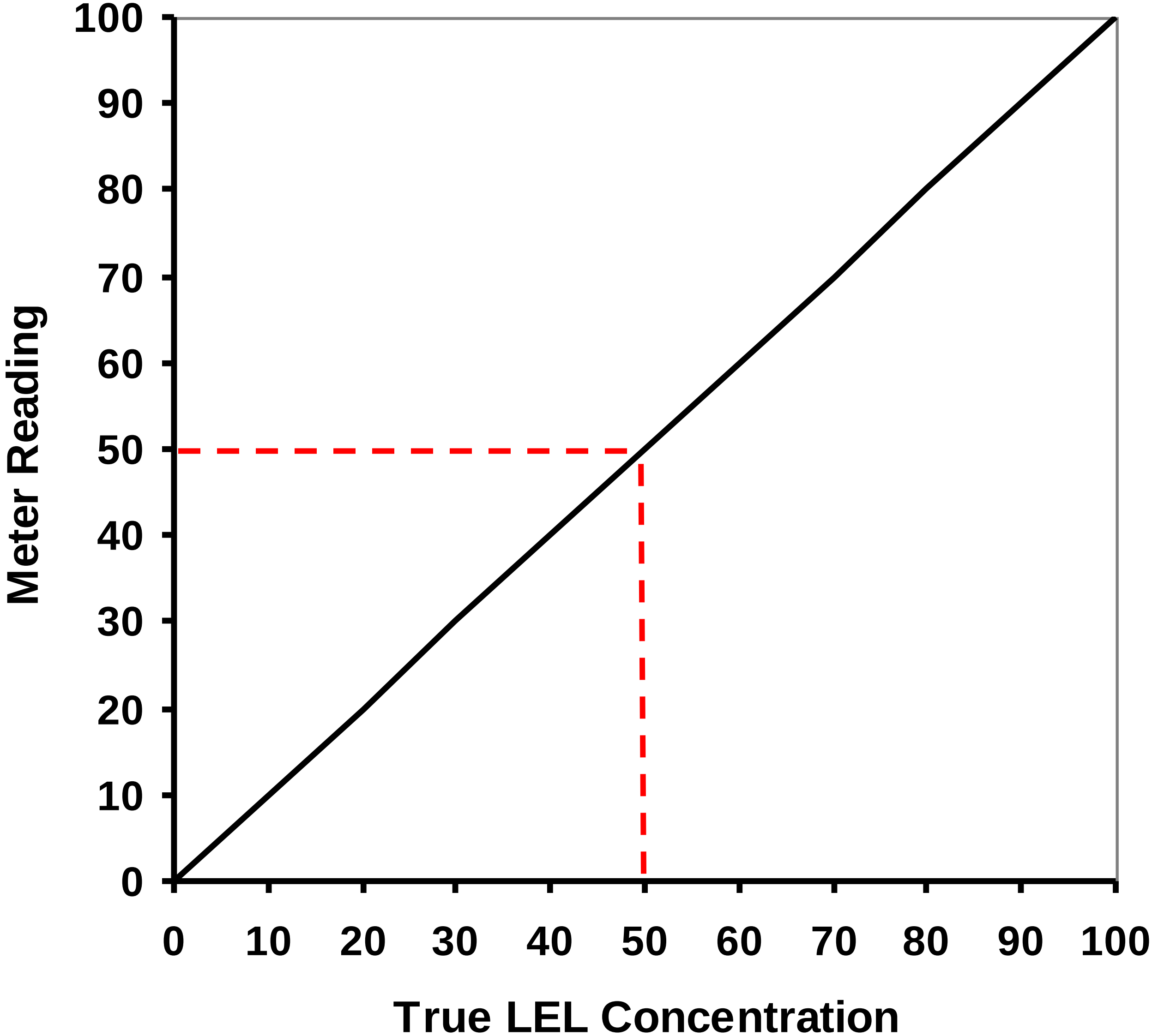
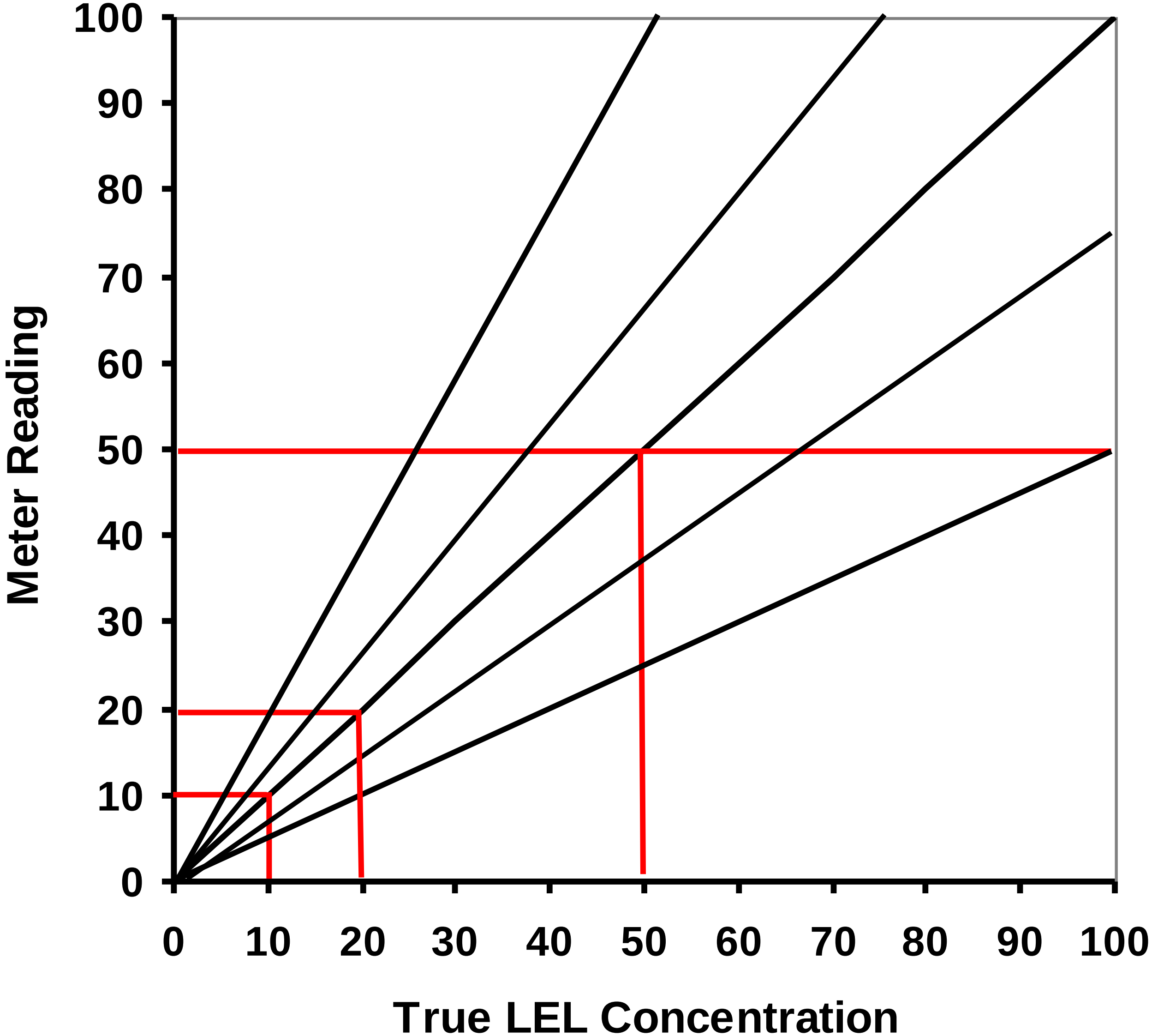
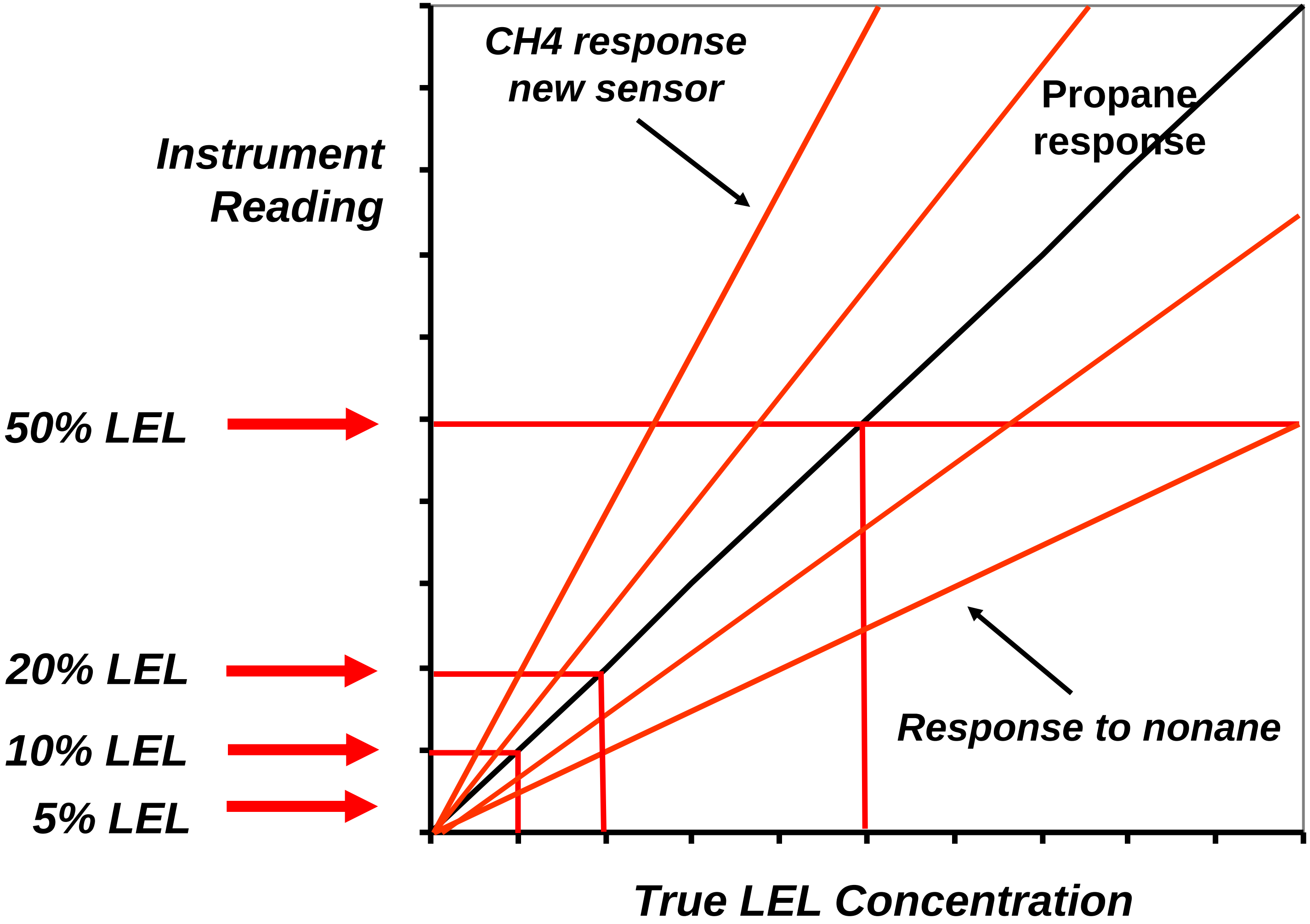
Linear Response Curve (Calibration Standard)



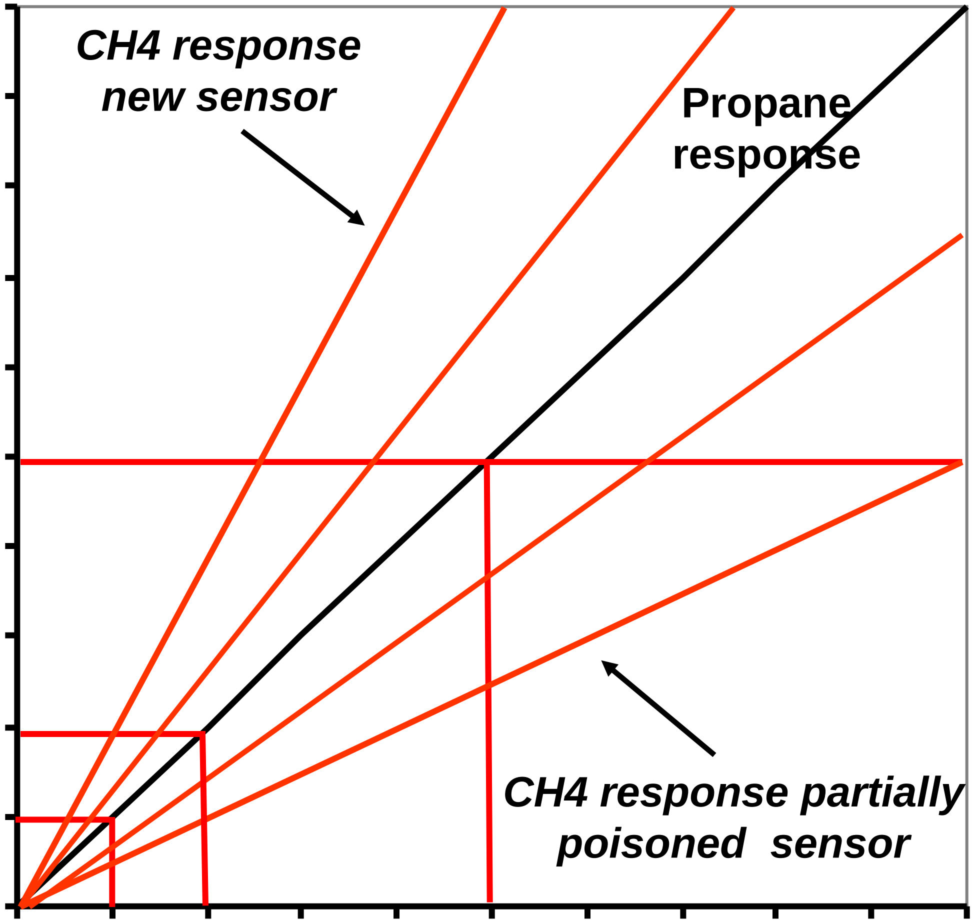
Relative Response Curves

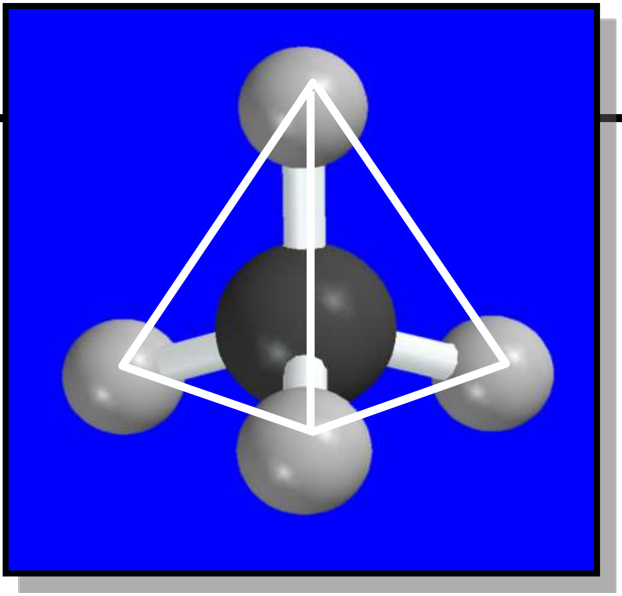


Using a lower alarm setting minimizes effect of relative response on readings



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

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

Complying with the TLV® Exposure Limit for C1 – C4 Hydrocarbon Gases

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

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C1 – C4 Strategy at USA Oil Industry Facilities

- *Fortunately, compliance with the C1 – C4 exposure limit is relatively easy for most oil industry instrument users*
- *Most refinery instruments are already calibrated to a pentane level of sensitivity*
- *Most refinery instruments have the combustible (percent LEL) alarm set at 5% LEL*
- *All they need to do is change the alarm setting from 5% to 4% LEL*
- *The following slides provide an explanation of why this alarm setting strategy ensures compliance with the new TLV®*

How to comply C1 – C4 exposure limit

- ***Fortunately, compliance with the C1 – C4 exposure limit is relatively easy for most instrument users***
- ***Make sure the LEL sensor is calibrated to a pentane level of sensitivity***
- ***Change the alarm setting from 10% to 4% LEL***

Flammability Ranges and Toxic Exposure Limits for C1 – C5 Alkanes

Gas	Response of sensor (calibrated to CH4) when exposed to 1% LEL of listed gas	Response of sensor (calibrated to C5H12) 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	1000	2 %	4.0 %	1000 ppm methane
Ethane	0.75	1.5	3	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 <u>before</u> 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)***

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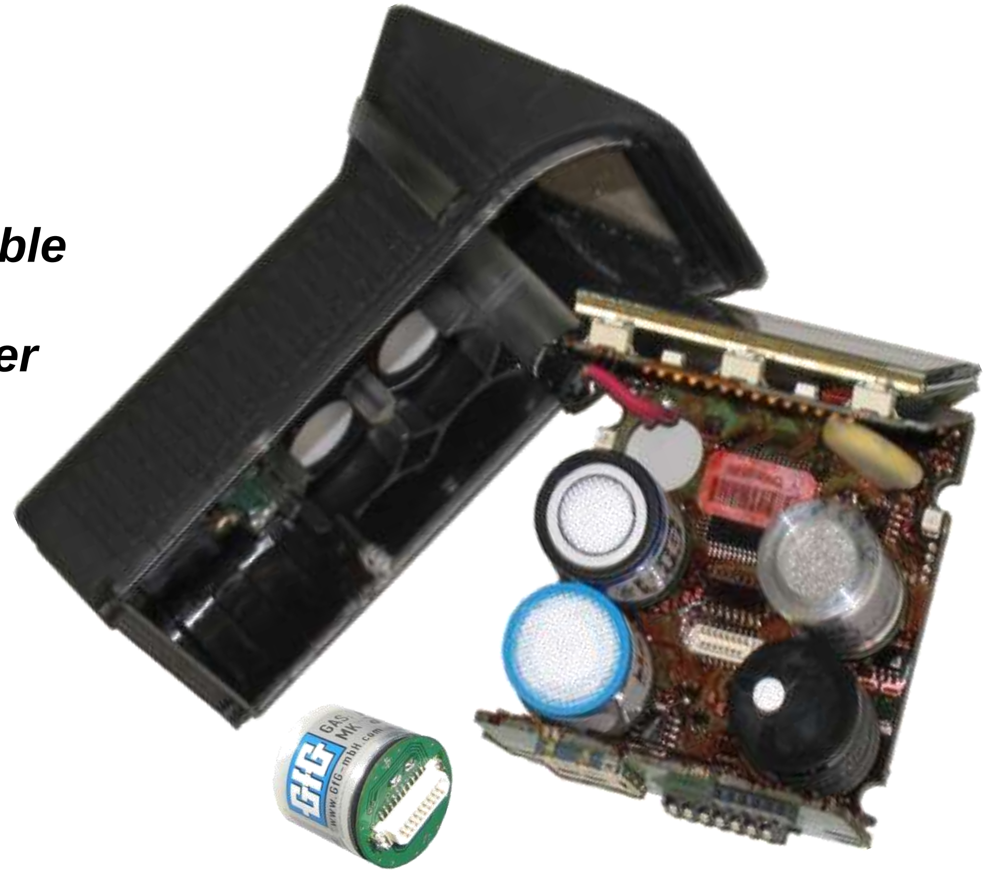
Limitations of catalytic pellistor LEL sensors

- ***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***
- ***Requires oxygen to detect gas!***

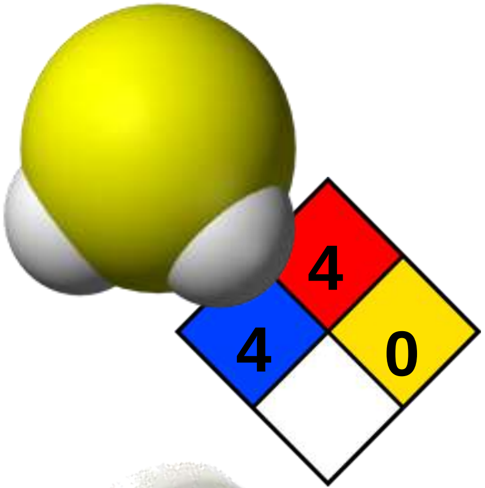


Combustible sensor poisons

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

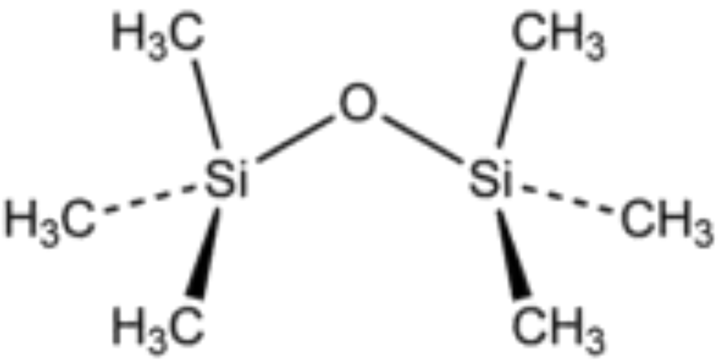
Effects of H2S on combustible gas sensors

- 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.



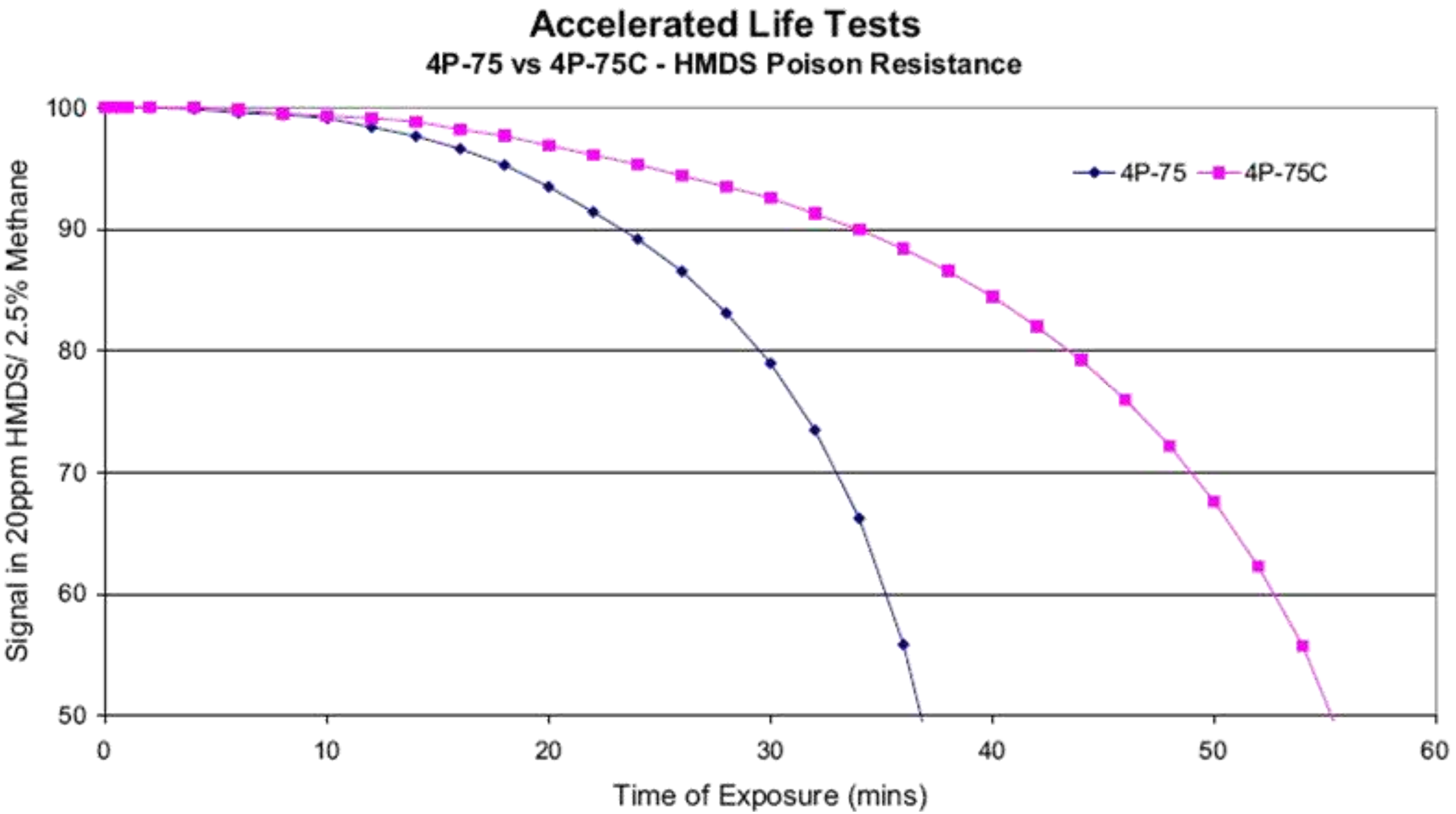
“Silicone resistant” vs. “standard” pellistor type LEL sensors

- ***"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***



GfG Instrumentation

Effects of hexamethyldisiloxane (HMDS) on pellistor sensor



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***

GfG Instrumentation

Low-power pellistor advice

- *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*

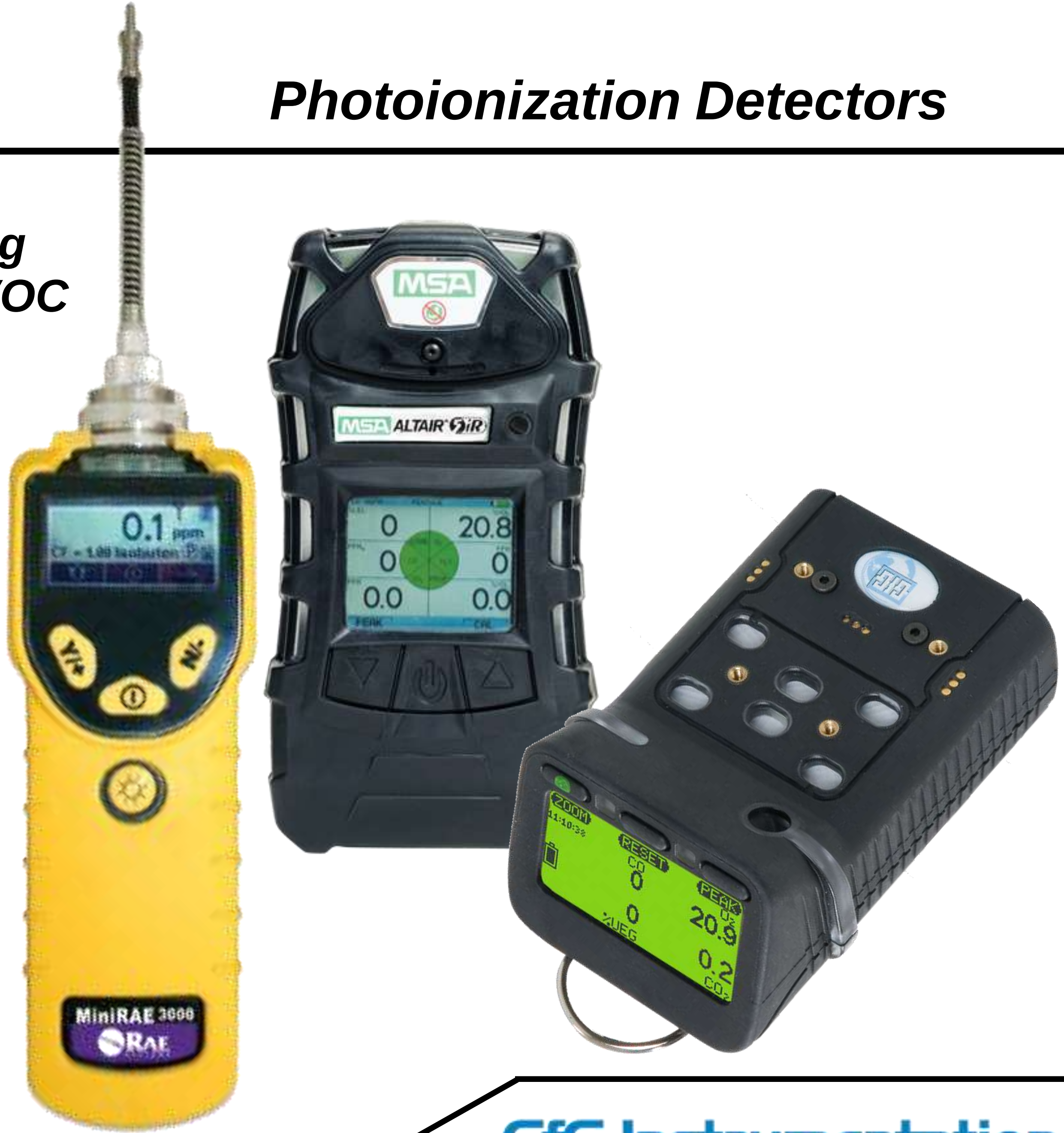
GfG Instrumentation

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 is a MUCH better solution!!***

Photoionization Detectors

- ***Used for measuring solvent, fuel and VOC vapors in the workplace environment***



GfG Instrumentation

Photoionization Detectors

- ***Used for measuring solvent, fuel and VOC vapors in the workplace environment***

GfG Instrumentation

Volatile organic compounds (VOCs)

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

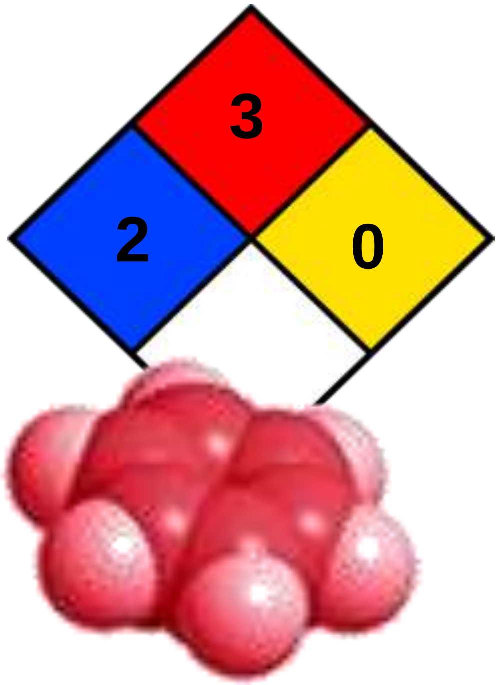
Volatile organic compounds (VOCs)

- *Solvent, fuel and other VOC vapors common in many workplace environments*
- *Most have surprisingly low occupational exposure limits*
- *Long before you reach a concentration sufficient to register on a combustible gas indicator, you will have easily exceeded the toxic exposure limits for most VOC contaminants*
- *PID equipped instruments generally the best choice for measurement of VOCs at exposure limit concentrations*

GfG Instrumentation

VOC Toxicity

- *VOCs present multiple potential threats in the workplace environment*
- *Heavier than air, flammable and toxic*
- *Increased awareness of toxicity is leading to lowered exposure limits*
- *This leads in turn to increased need for direct measurement of VOCs at exposure limit concentrations*



VOC Exposure Symptoms

- ***Symptoms may not become manifest for years***
  - ***Respiratory tract irritation (acute or chronic)***
  - ***Dizziness, headaches (acute or chronic)***
  - ***Long-term neurological: diminished cognition, memory, reaction time, hand-eye and foot-eye coordination***
  - ***Mood disorders: depression, irritability, and fatigue***
  - ***Peripheral neurotoxicity: tremors and diminished fine and gross motor movements***
  - ***Kidney damage and immunological problems, including increased cancer rates***
    - ***Benzene, (toxic VOC found in gasoline, diesel, jet fuel and other chemical products), linked to chemically induced leukemia, aplastic anemia and multiple myeloma (a cancer of the lymphatic system)***

VOC Exposure Limits

- *Several recently revised VOC exposure limits, including TLVs for diesel vapor, hexane, toluene, kerosene and gasoline*
- *Because safety procedures for many international corporations are tied to the most conservative published standard, TLVs® receive much attention*
- *Diesel TLV specifies 8-hour TWA for total diesel hydrocarbons (vapor and aerosol) = 100 mg/m3*
- *Equivalent to approximately 15 parts-per-million diesel vapor*
- *For diesel vapor, 1.0% LEL is equivalent to 60 PPM*
- *Even if LEL instrument properly calibrated for diesel – which may not be possible – reading of only 1.0% LEL would exceed the TLV® for diesel by 600 percent!*

VOCs and Flammability

- *Most VOC vapors flammable at surprisingly low concentrations*
  - *For hexane and toluene 100% LEL = 1.1% (11,000 PPM)*
  - *By comparison, LEL concentration for methane = 5% (50,000 PPM)*
- *Tendency in past has been to measure them by means of percent LEL combustible gas instruments*
- *Combustible gas instrument alarms usually set to 5% or 10% LEL*
- *Unfortunately, most VOC vapors are also toxic, with exposure limit values much lower than the 5% or 10% LEL*
- *Toxic exposure exceeded long before LEL alarm concentration reached*

Toxic VOC Example: Hexane

- *Most standards reference an 8-hour TWA for hexane of 50 PPM calculated as an 8-hour TWA*
- *The LEL concentration for hexane = 1.1% (11,000 PPM)*
- *If combustible sensor alarm is set at 10% LEL, with a properly calibrated instrument, it would take a concentration of:*

  0.10 X 11,000 ppm = 1,100 ppm to trigger an alarm

- *Even if alarm set to 5% LEL, it still would still require a concentration of 550 PPM to trigger the alarm*

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
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

LEL vs. PID Sensors

- ***Catalytic LEL and PID sensors are complementary detection techniques***
- ***Catalytic LEL sensors excellent for methane, propane, and other common combustible gases that are NOT detectable by PID***
- ***PIDs detect large VOC and hydrocarbon molecules that are undetectable by hot-bead sensors***
- ***Best approach is to use multi-sensor instrument that includes both types of sensors***

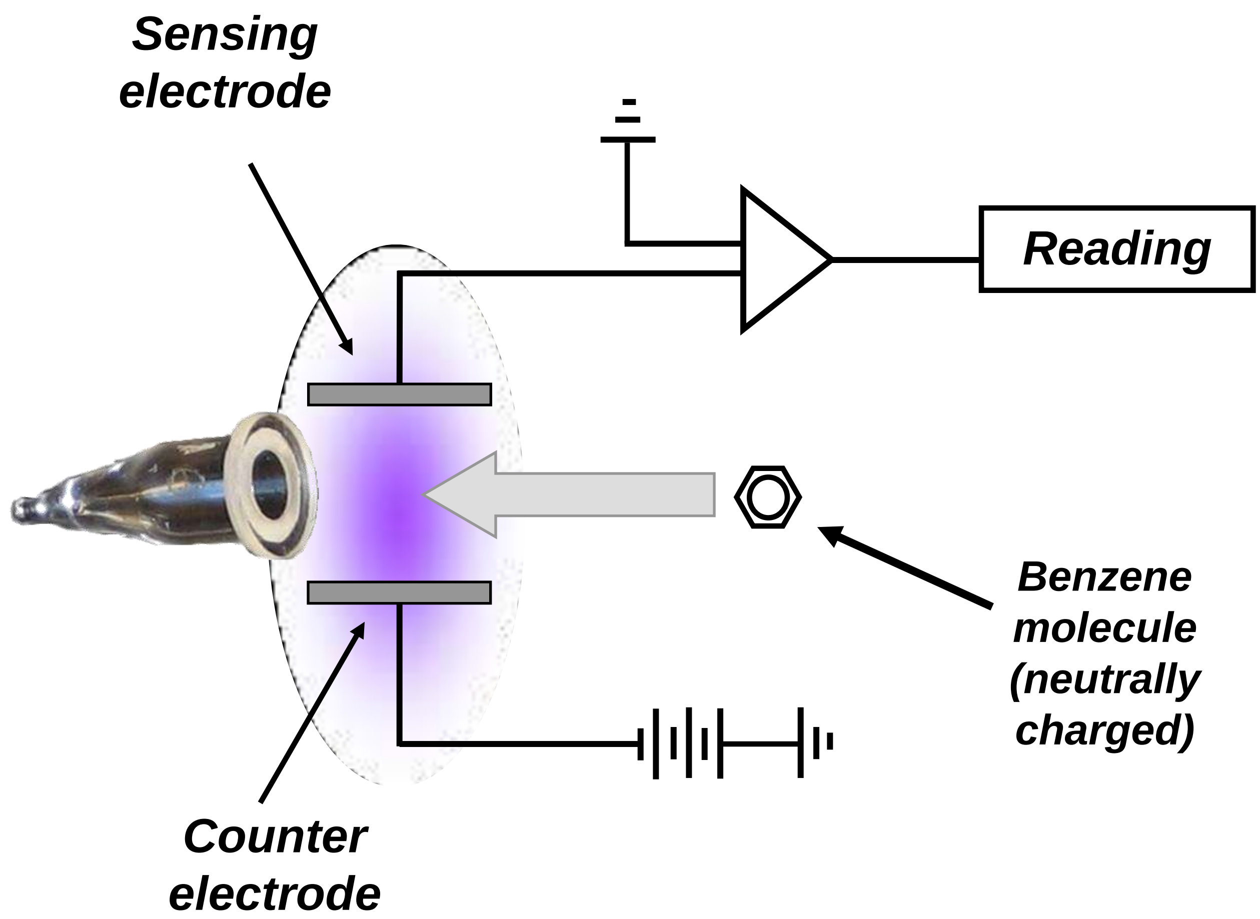
PID - Operating Principle

- *PIDs use ultraviolet light as source of energy to remove an electron from neutrally charged target molecules creating electrically charged fragments (ions)*
- *This produces a flow of electrical current proportional to the concentration of contaminant*
- *The amount of energy needed to remove an electron from a particular molecule is the ionization potential (or IP)*
- *The energy must be greater than the IP in order for an ionization detector to be able to detect a particular substance*

Operation of PID lamp, sensing and counter electrodes

Detection sequence:

1. Neutrally charged molecule diffuses into glow zone

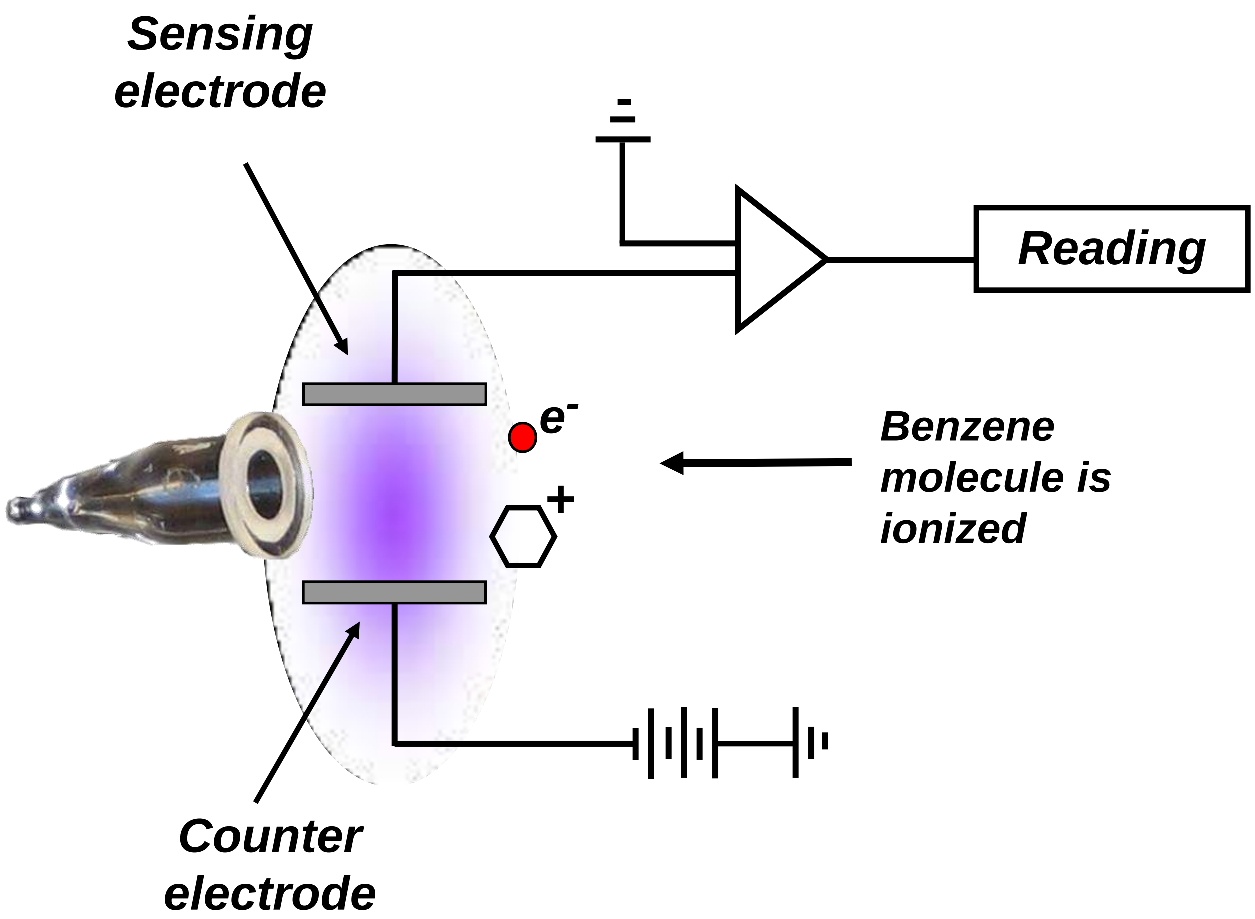


GfG Instrumentation

Operation of PID lamp, sensing and counter electrodes

Detection sequence:

2. *Molecule is ionized*

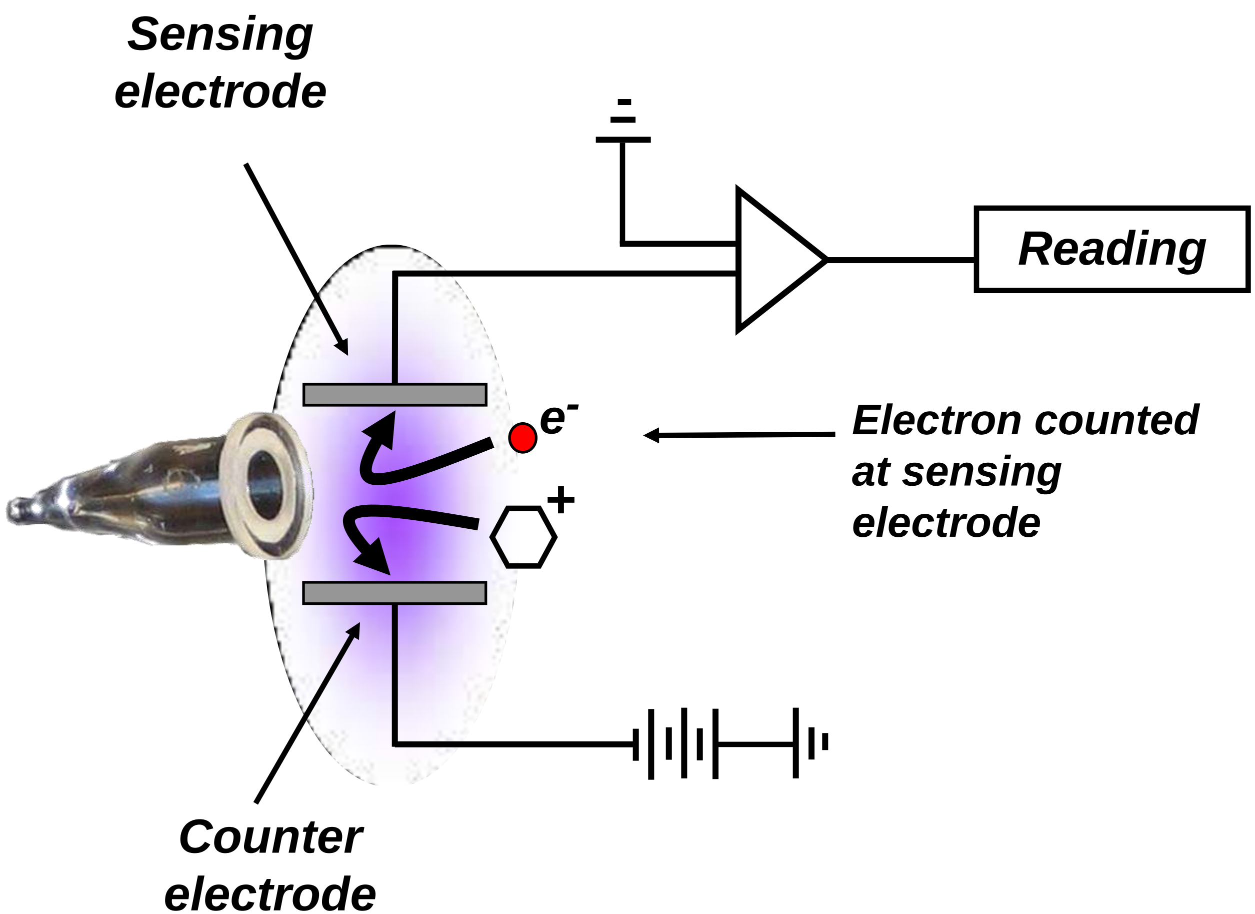


GfG Instrumentation

Operation of PID lamp, sensing and counter electrodes

Detection sequence:

3. Free electron is electrostatically accelerated to positively charged sensing electrode where it is counted

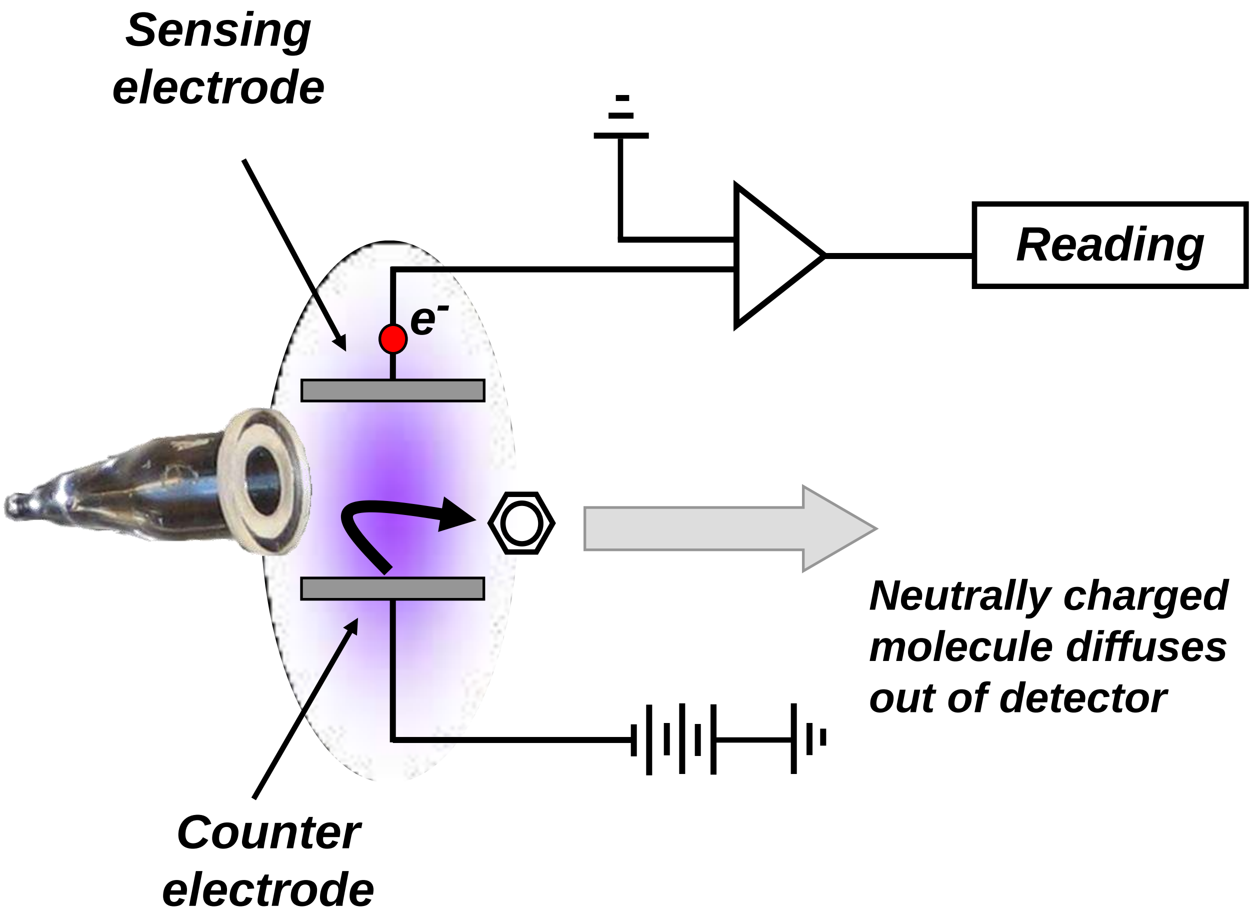


GfG Instrumentation

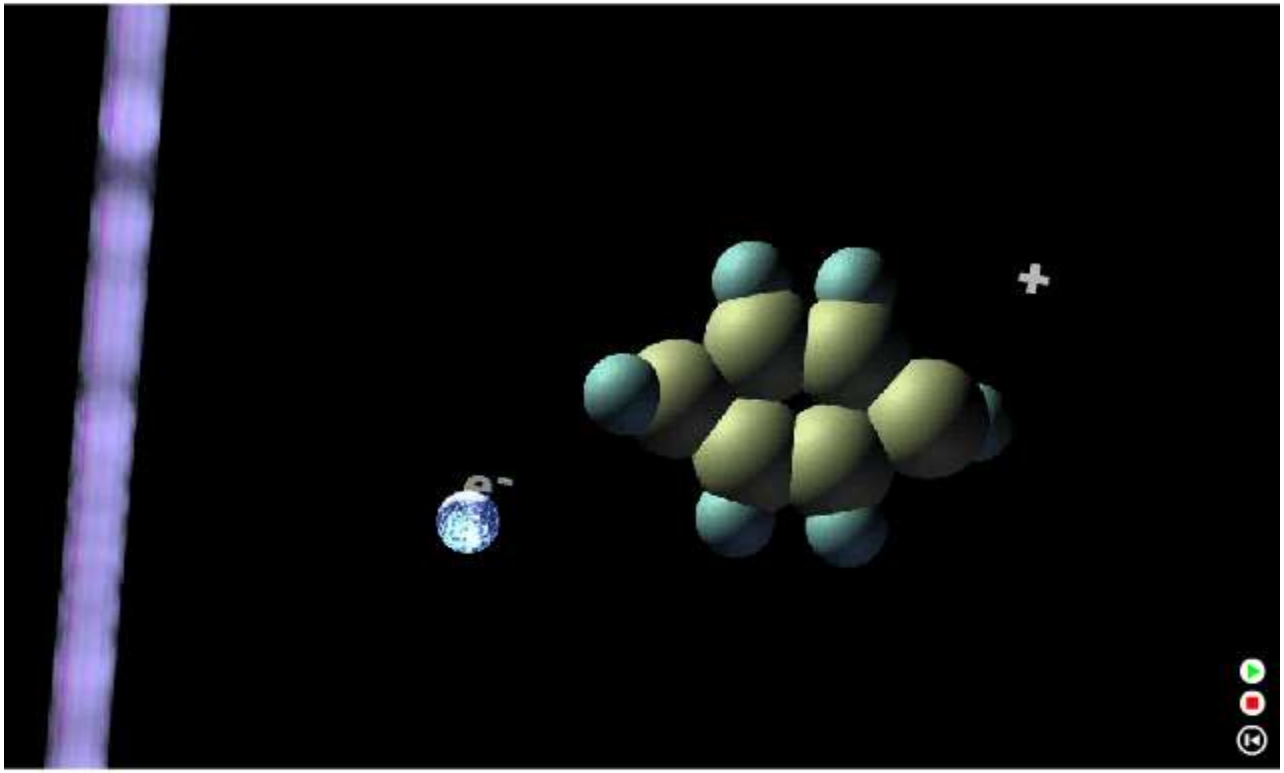
Operation of PID lamp, sensing and counter electrodes

Detection sequence:

4. **Positively charged fragment (ion) is electrostatically accelerated to counter electrode, where it picks up a replacement electron and regains neutral charge**



How does a PID work?



Ionization Potential

- ***IP determines if the PID can detect the gas***
- ***If the IP of the gas is less than the eV output of the lamp the PID can detectthe gas***
- ***Ionization Potential (IP) measures the bond strength of a gas and does not correlate with the Correction Factor***
- ***Ionization Potentials are found in the NIOSH Pocket Guide and many chemical texts***

Ionization Potential Values

Substance	Ionization Energy (eV)
carbon monoxide	14.01
carbon dioxide	13.77
methane	12.98
water	12.59
oxygen	12.08
chlorine	11.48
hydrogen sulfide	10.46
n-hexane	10.18
ammonia	10.16
hexane	10.13
acetone	9.69
benzene	9.25
butadiene	9.07
toluene	8.82

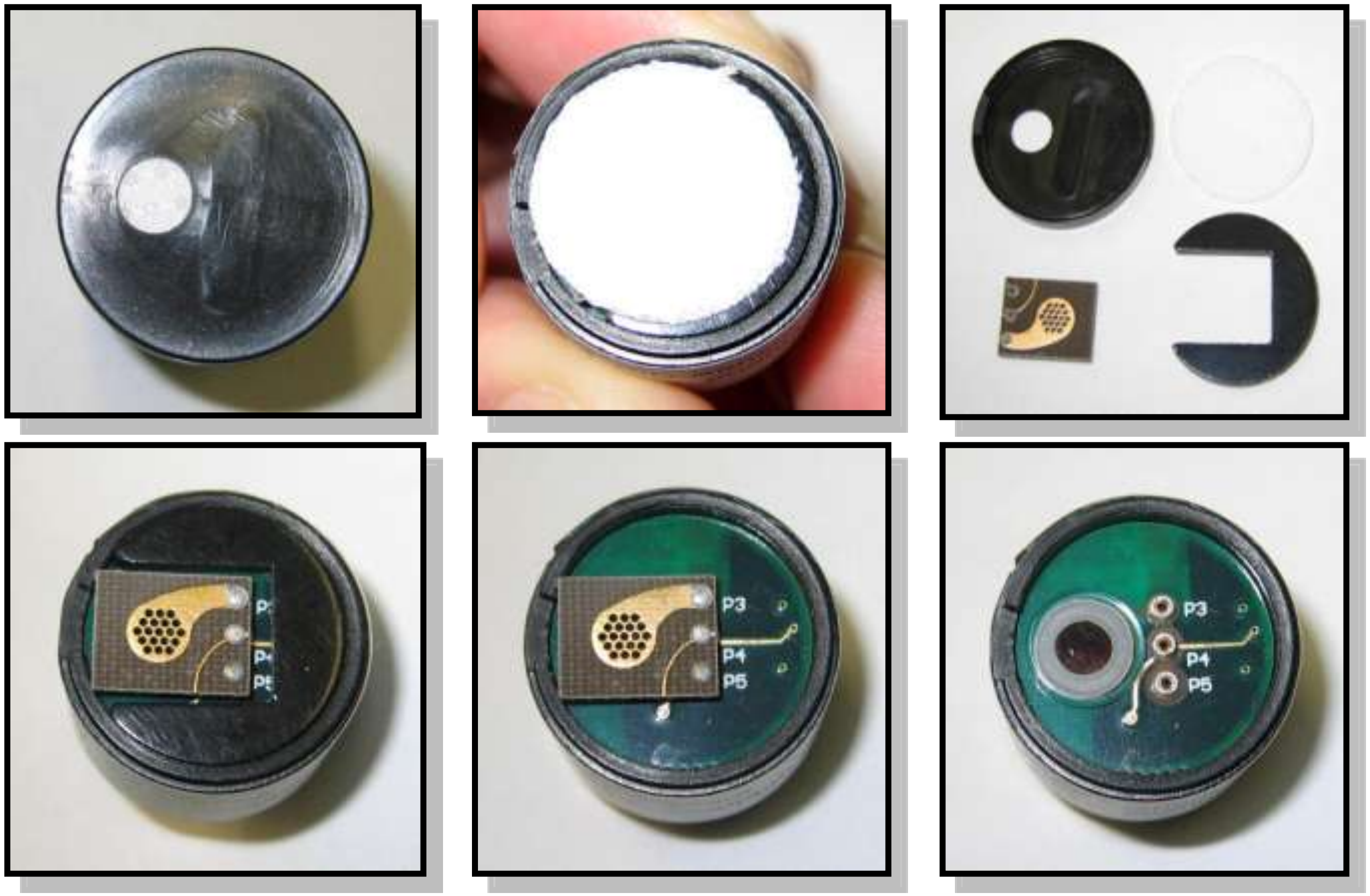
Technical Advances in PIDs

- *Miniaturization*
- *Ruggedness*
- *EMI/RFI resistance*
- *Lower humidity interference*

GfG Instrumentation

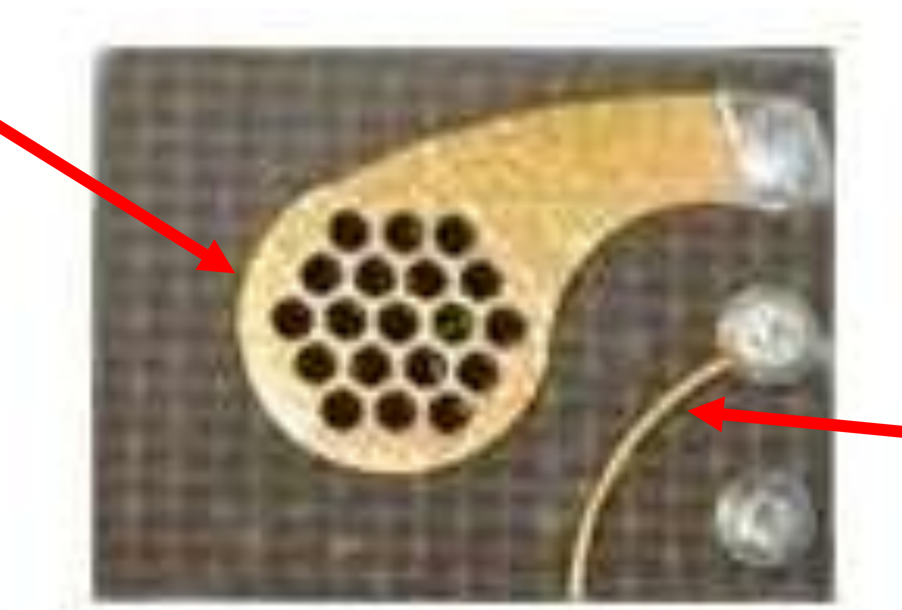
PID Components

- ***Detector assembly***
- ***Electrodes: sensing, counter and (in some designs) fence***
- ***Lamp: most commonly 10.6EV, 11.7eV or 9.8 eV***



PID Sensing and Counter Electrodes

Sensing electrode



Counter electrode

GfG Instrumentation

Characteristics of PID Lamps

- *Sealed borosillicate glass body*
- *Window of specific crystalline material*
- *Filled with specific noble gas or mixture of noble gases*
- *10.6 eV lamp should last 10,000 operating hours or three years or longer*

GfG Instrumentation

Characteristics of PID lamps

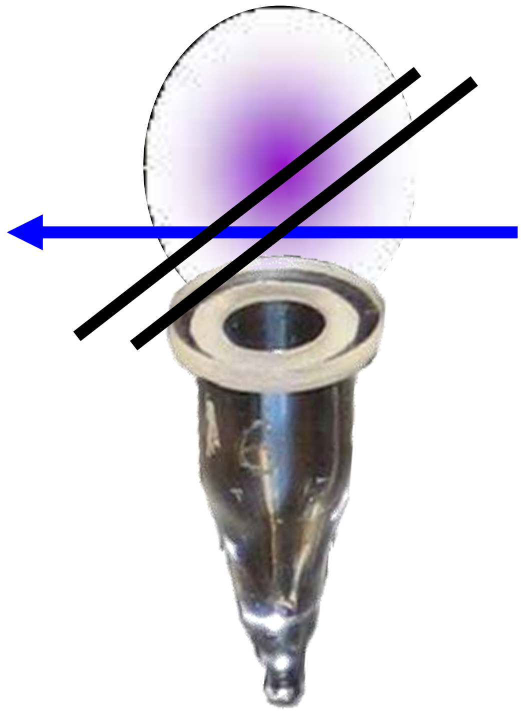
Nominal Lamp Photon Energies	Gas in Lamp	Major Emission Lines		Relative Intensity	Window Crystal	Cystal transmittance λ Range (nm)
		eV	(nm)			
11.7eV	Argon	11.83	104.8	1000	Lithium fluoride (LiF)	105 - 5000
		11.62	106.7	500		
10.6eV	Krypton	10.64	116.5	200	Magnesium fluoride (MgF2)	115 - 7000
		10.03	123.6	650		
9.8eV	Krypton	10.03	123.6	650	Calcium fluoride (CaF2)	125 - 8000

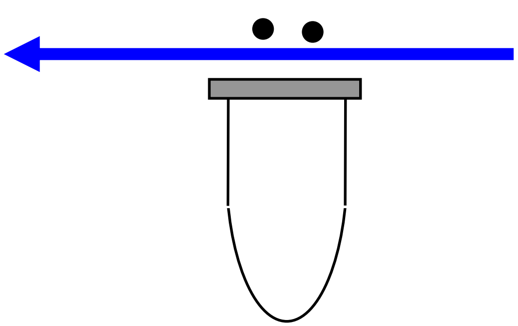
Critical PID Performance Issues: Effects of Humidity and Contamination

- ***Condensation and contamination on lamp window and sensor surfaces can create surface conduction paths between sensing and counter electrodes***
- ***Buildup of contamination provides nucleation points for condensation, leading to surface currents***
- ***If present, surface currents cause false readings and / or add significant noise that masks intended measurement (sometimes called "moisture leakage")***
- ***PID designs <u>MAY</u> require periodic cleaning of the lamp and detector to minimize the effects of contaminants and humidity condensation on PID readings***

GfG Instrumentation

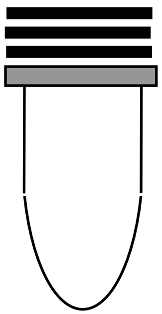
RAE "3D" PID Design





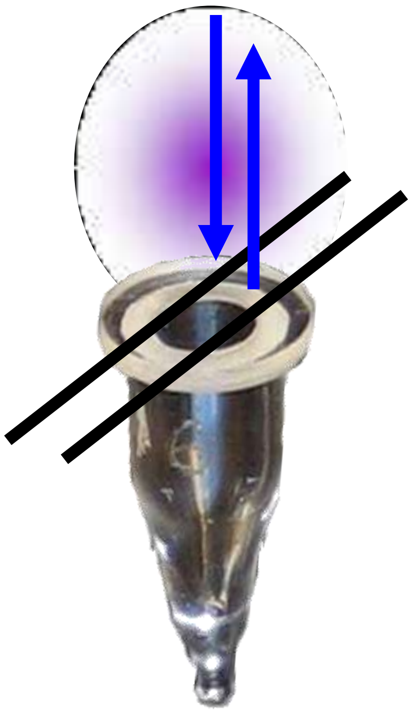
- ***Benefits:***
  - ***Rapid response and clearing times***
- ***Limitations:***
  - ***Gap between window and electrodes increases "quenching" effect of water vapor on signal***
  - ***Potential for drawing particulate contaminants into sensor***
  - ***More ionic fragments left behind to be adsorbed onto electrodes and window***
- ***Results:***
  - ***Increased sensitivity to water vapor and humidity***
  - ***Must clean lamp more frequently***

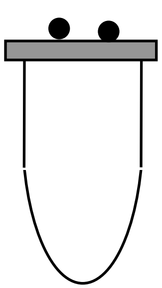
Ion Science (BW) PID Design



- ***Benefits:***
  - ***Design includes "fence electrode" to provide mechanical short circuit between sensing and counter electrodes***
  - ***Electrodes housed in replaceable "stack"***
  - ***Diffusion of molecules into and out of glow zone means less ionic fragments or particulates left behind***
- ***Limitations:***
  - ***Slightly slower response***
  - ***Still vulnerable to H2O signal quenching***
  - ***Operation at higher voltage increases vulnerability to EMI / RFI***
- ***Results:***
  - ***Reduced "moisture leakage" response due to humidity***
  - ***Clean lamp less frequently***

GfG PID Design





- *Benefits:*
  - *No gap at all between electrodes and window*
  - *Diffusion of molecules into and out of glow zone means no ionic fragments or particulates left behind*
- *Limitations:*
  - *Slightly slower response*
- *Results:*
  - *Lower sensitivity to water vapor and humidity*
  - *Clean lamp less frequently*

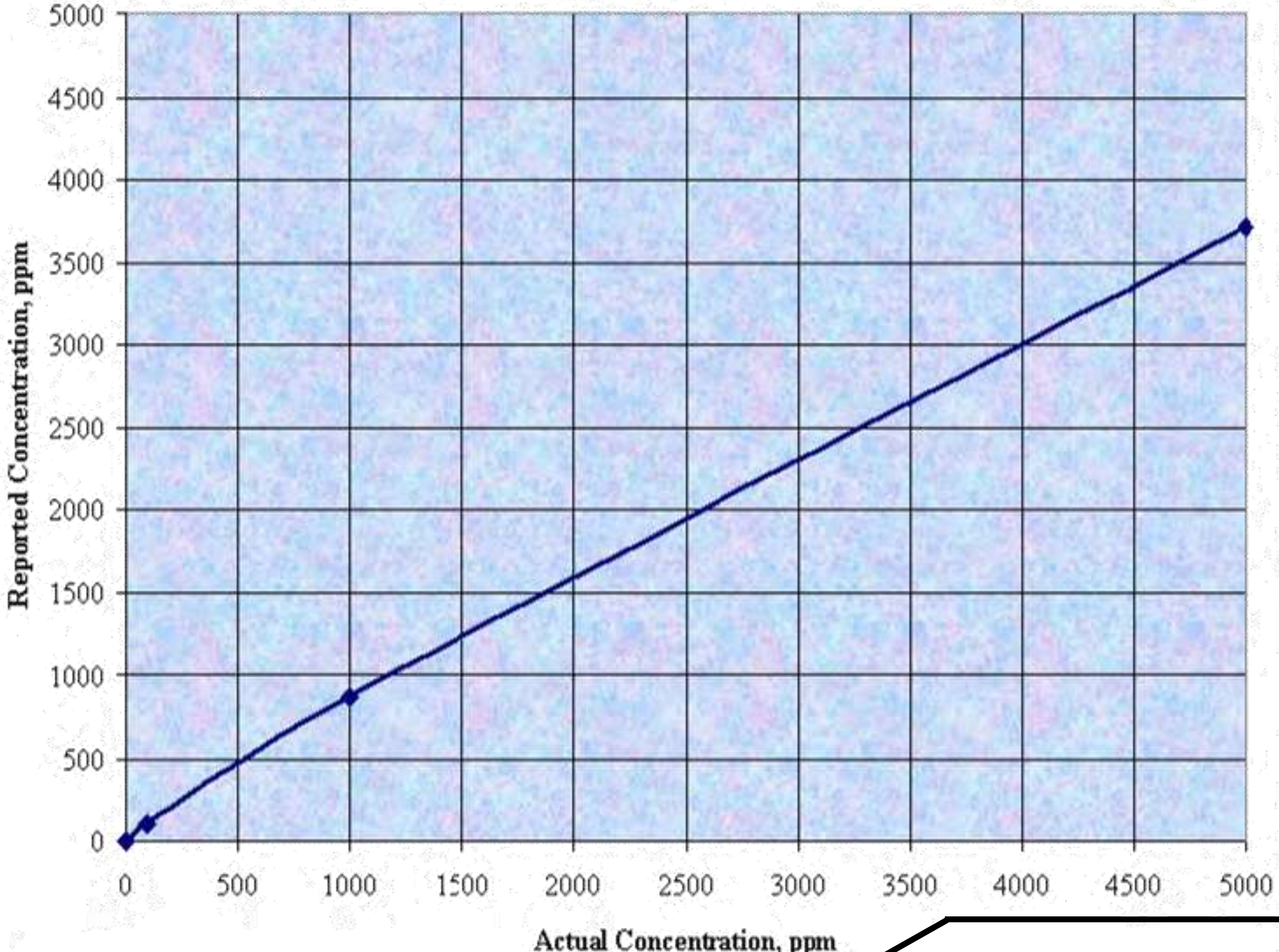
GfG Instrumentation

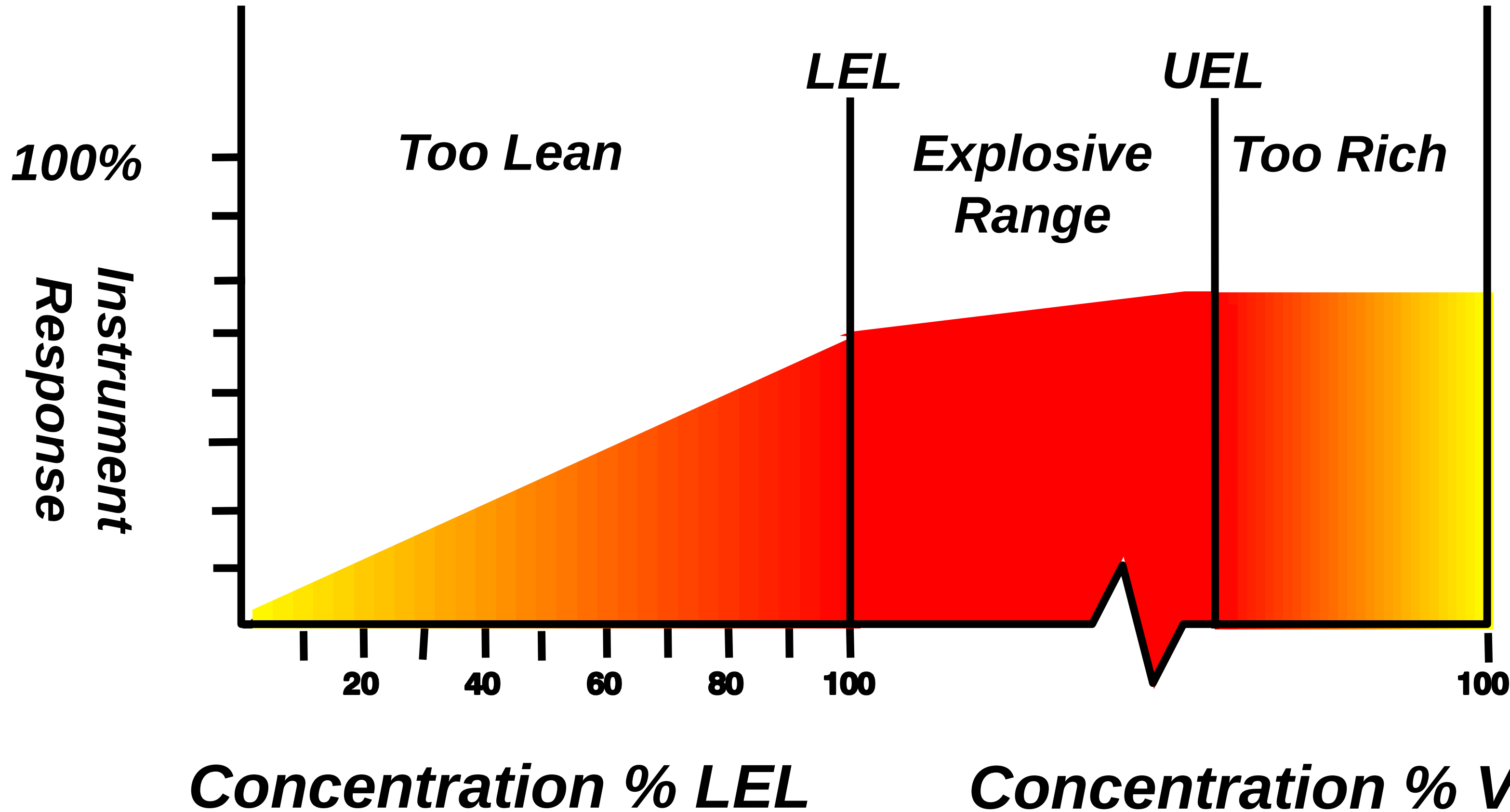
G460 PID Specifications

Target Gases:	VOCs and other gases with IP less than 10.6eV
Lamp Energy:	10.6eV
G460 PID Ranges	0.1 - 500 ppm (isobutylene) 0.5 – 2,000 ppm (isobutylene)
T_{90} Response Time:	< 20 seconds, diffusion mode
Onboard filter:	To remove liquids/particles
Temp Range:	0°C to 40°C
RH Range:	0 to 90% non-condensing
Humidity Response:	< 2ppm @ 90% RH, 25°c
Expected Life:	> 1 year
Package Type:	City Technology^{TM}4P
Position Sensitivity:	None
Certifications:	c-UL-us Class I, Division 1, Groups A,B,C,D ATEX directives EN50014 and EN50020, EEx ia IIC T4 and CE
Warranty Period:	One year

GfG Instrumentation

PID linearity through nominal range




100%
Instrument Response
Too Lean
LEL
Explosive Range
UEL
Too Rich
20
40
60
80
100
100
Concentration % LEL
Concentration % V/V

PID Operating Characteristics

- *Detects Total Volatile Organic Compounds*
- *Accurate, Sensitive to PPM levels*
- *No External Fuel Needed*
- *Minimal Training Needed to Operate*
- *Limitations:*
  - *Non-specific*
  - *Subject to signal loss from:*
    - *High humidity (H2O vapor)*
    - *High CH_4*
    - *High O_2*

GfG Instrumentation

- *High concentrations of methane can "quench" PID signal*

% Methane	Volume % LEL Methane	Reading when exposed to 50 ppm hexane in the presence of Methane
2.5%	50% LEL	26 ppm
1.0%	20% LEL	45 ppm
0.5%	10% LEL	48 ppm
0.25%	4% LEL	49 ppm

PID TVOC Applications

- *Rapid screening technique for initial assessment*
- *Detect wide range of toxic VOCs*
- *Sensitive to PPM levels*
- *Accurate and linear over wide range*
- *Low Cost*
- *Multiple applications:*
  - *PEL/TLV compliance*
  - *Hazardous threshold indication for toxic / combustible*
  - *Hazmat / Emergency response*
  - *IAQ*
  - *WMD / CWA*

PID detectable compounds

- Most VOCs with:
  - Boiling Point <200º C.
  - Vapor Pressures (Pv) > 1.0 mm Hg at 20º C
- Detect some inorganics (e.g. NO, NO_2, NH_3)
- Hydrides (arsine, phosphine)
- Do Not Detect:
  - CO, CO_2, SO_x,
  - Metals
  - Semi-Volatiles - PAH, higher phenols
  - Non-Volatiles - PCBs, pesticides

GfG Instrumentation

Compounds Detectable by PID

Organics: Compounds with carbon

- Aromatic compounds (containing benzene ring): Benzene, Toluene, Xylene
- Ketones and aldehydes (containing C=O bond): Acetone, MEK
- Amines & amides (compounds containing nitrogen): Diethyl amine
- Chlorinated hydrocarbons: Perchlorethylene, Trichloroethylene (TCE)
- Alkanes (saturated hydrocarbons C3 and higher): Pentane, Hexane
- Unsaturated hydrocarbons (double or triple carbon-carbon bonds): Butadiene, Isobutylene
- Alcohols (-OH): Ethanol, Isopropanol

Sulfides and compounds containing sulfur: Mercaptans, Hydrogen sulfide

Inorganics (compounds without carbon): Ammonia, Chlorine

Hydrides: Arsine, Phosphine

Compounds not detectable by PID

Compounds normally present in air: Oxygen, Nitrogen, Carbon dioxide, Argon

Inorganic toxics: Carbon monoxide, Hydrogen cyanide, Ozone (O_3)

Hydrocarbons and VOCs with ionization energies higher than 11.7eV: Methane, Natural gas

Acids: Sulfuric acid (H_2SO_4), Hydrochloric acid (HCl), Nitric acid (HNO_3)

Radiation

Aerosol droplets and particulates

GfG Instrumentation

PID as "Broad-Range" Sensor

- ***VOCs usually detected by means of broad-range sensors***
- ***Broad-range sensors provide overall reading for general class or group of chemically related contaminants***
- ***Cannot distinguish between different contaminants they are able to detect***
- ***Provide single total reading for all detectable substances present***

Response is Relative to Gas Measured

- ***Reading of 10 ppm only indicates ion current equivalent to that produced by 10 ppm concentration calibrant***
- ***Amount of different contaminant needed to produce same current may be larger or smaller than concentration of calibrant***
- ***Since PID readings always relative to calibrant, should be recorded as ppm-calibration gas equivalent units, or PID units, never as true concentrations unless:***
    - ***Contaminant being monitored is same as one used to calibrate instrument, or***
    - ***Reading is corrected to account for difference in relative response***

GfG Instrumentation

PID Correction Factors

- ***Correction Factor (CF) is measure of sensitivity of PID to specific gas***
- ***CFs do not make PID specific to a chemical, only correct the measurement scale to that chemical***
- ***CFs allow calibration on inexpensive, non-toxic "surrogate" gas (like isobutylene)***
- ***Most manufacturers furnish tables, or built-in library of CFs to correct or normalize readings when contaminant is known***
- ***Instrument able to express readings in true parts per million equivalent concentrations for the contaminant measured***

CF measures sensitivity

- *Low CF = high PID sensitivity to a gas*
- *More toxic the gas, more desirable to have low correction factor :*
  - *If Exposure limit is < 10 ppm, CF should be $\leq$ 1*
- *If chemical less toxic, higher CF may be acceptable*
  - *If Exposure limit is > 10 ppm, CF $\leq$ 10*
- *When CF > 10 use PIDs as gross leak detectors only*
  - *High correction factor magnifies effects of interfering gases and vapors*

GfG Instrumentation

PID readings only quantifiable if measuring a known substance

- PID allows quantified readings only when substance measured is known
- If substance is known, readings quantifiable to sub-ppm resolution
- If substance unknown, readings should be expressed as “Isobutylene” or “PID” units
- CF should not be used unless and until contaminant identified

Decision making with a PID

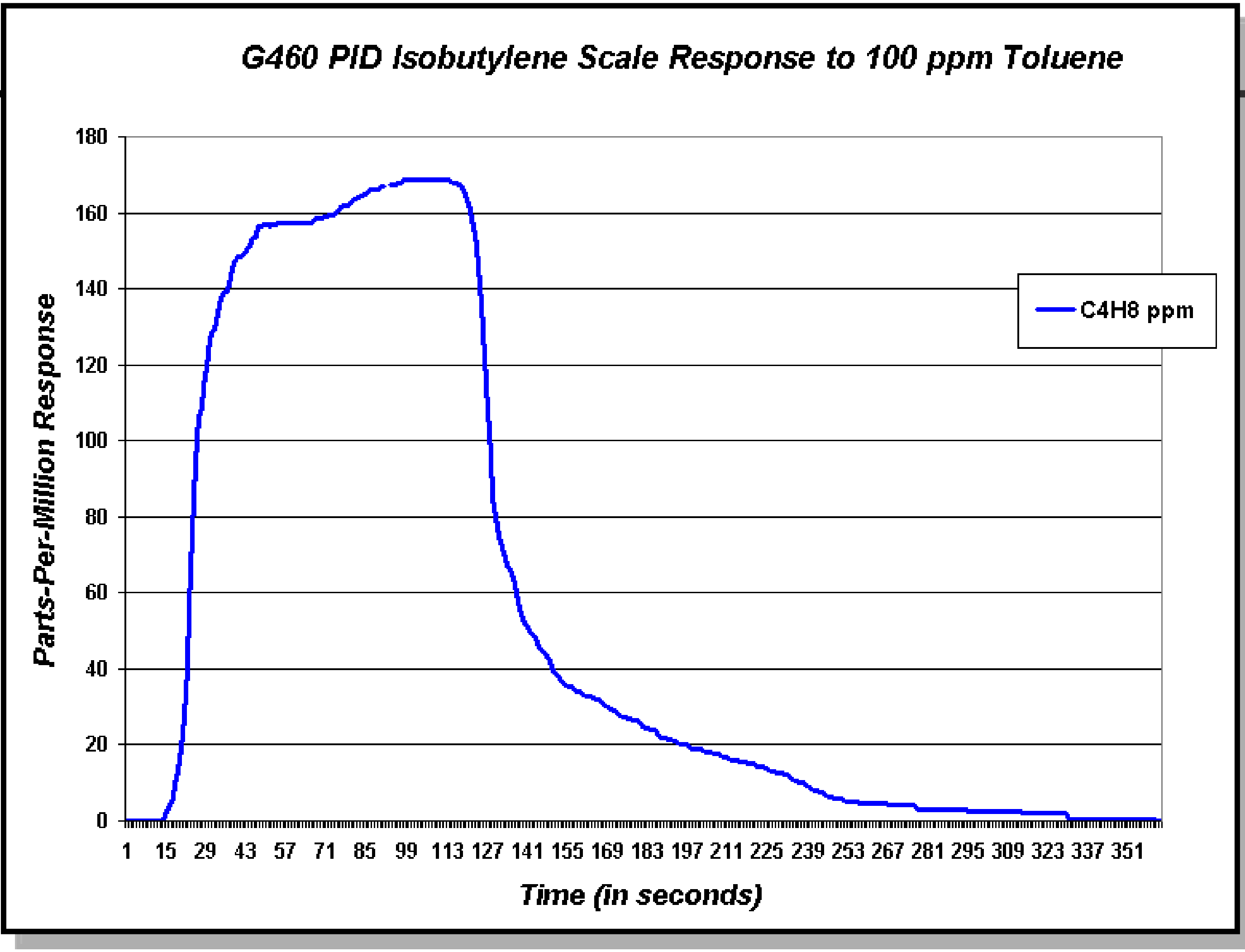
- ***Two sensitivities must be understood to make a decision with a PID***
  - ***Human Sensitivity: as defined by AGCIH, NIOSH, OSHA or corporate exposure limits***
  - ***PID Sensitivity: as defined through testing by the manufacturer of the PID***

Correction Factors (10.6 eV Lamp)

	RAE	BW	Ion	GfG	IP (eV)
Acetaldehyde	5.5	4.6	4.9	n/a	10.21
Acetone	1.1	0.9	0.7	1.2	9.69
Ammonia	9.7	10.6	8.5	9.4	10.2
Benzene	0.5	0.55	0.5	0.53	9.25
Butadiene	1	0.9	0.85	0.69	9.07
Diesel fuel	0.8	0.93	0.75	0.9	n/a
Ethanol	12	13.2	8.7	10.0	10.48
Ethylene	10	11	8	10.1	10.52
Gasoline	0.9	0.73	1.1	1.1	n/a
n-Hexane	4.3	4	3.3	4.5	10.18
Jet fuel (J.P.8)	0.6	0.51	0.7	0.48	n/a
Kerosine	n/a	1.11	0.8	n/a	n/a
Methylethylketone	0.9	0.78	0.77	0.9	9.53
Naptha (iso-octane)	1.2	1.2	1.1	1.3	9.82
Styrene	0.4	0.45	0.45	0.4	8.47
Toluene	0.5	0.53	0.51	0.53	8.82
Turpentine	0.4	0.45	0.45	0.45	n/a
Vinyl chloride	2	2.19	2.2	1.8	10.0
Xylene	0.4	0.5	0.43	0.5	8.5

Actual response of PID (Isobutylene scale) to 100 ppm Toluene

- ***Official CF = 0.53***
- ***Based on CF expect readings = 189 ppm***
- ***Actual readings = 170 ppm***
- ***Close but not exact!***



GfG Instrumentation

Single Chemical Mixtures

- *Identify the chemical*
- *Set the PID Correction Factor to that chemical*
- *Find the Exposure Limit(s) for the chemical*
- *Set the PID alarms according to the exposure limits*

CF Example: Toluene

- *Toluene CF with 10.6eV lamp is 0.5; so PID is very sensitive to Toluene*
- *If PID reads 100 ppm of isobutylene units in a Toluene atmosphere*
- *Then the actual concentration is 50 ppm Toluene units*

$$0.5_{CF} \times 100\ ppm_{iso} = 50\ ppm_{toluene}$$

GfG Instrumentation

CF Example: Ammonia

- ***Ammonia CF with 10.6eV lamp = 11.2; so PID less sensitive to Ammonia***
- ***If PID reads 10 ppm of isobutylene units in an Ammonia atmosphere***
- ***Then the actual concentration is 112 ppm Ammonia units***

$$11.2_{CF} \times 10\ ppm_{iso} = 112\ ppm_{ammonia}$$

PID Alarms: Varying Mixtures

- *The Controlling Compound*
  - *Every mixture of gases and vapors has a compound that is the most toxic and "controls" the setpoint for the whole mixture*
  - *Determine that chemical and you can determine a conservative mixture setpoint*
  - *If we are safe for the "worst" chemical we will be safe for all chemicals*

PID Alarms: Varying Mixtures

Chemical Name	10.6eV CF	Exposure Limit Chemical
Ethanol	10.0	1000
Turpentine	0.45	100
Acetone	1.2	750

- Ethanol “appears” to be the safest compound
- Turpentine “appears” to be the most toxic
- This table only provides half of the decision making equation

GfG Instrumentation

PID Alarms: Varying Mixtures

- ***Set the PID for the compound with the lowest Exposure Limit (EL) in equivalent units and you are safe for all of the chemicals in the mixture***

- ***Divide the EL in chemical units by CF to get the EL in isobutylene***

$$EL_{Isobutylene} = \frac{EL_{chemical}}{CF_{chemical}}$$

GfG Instrumentation

PID Alarms: Varying Mixtures

Chemical name	CF_{iso} (10.6eV)	OSHA PEL (8 hr. TWA)	$EL_{ISO (PEL)}$	TLV® (8hr. TWA)	$EL_{ISO (TLV)}$
Ethanol	10.0	1000	100.0	1000	100.0
Turpentine	0.45	100	222.3	20	44.5
Acetone	1.2	1000	833.4	500	416.7

- *IF you are following the Federal OSHA PEL ethanol the "controlling compound" when the Exposure Limits are expressed in equivalent "Isobutylene Units"*
- *BE CAREFUL: If you are following the TLV the controlling chemical would be turpentine*

GfG Instrumentation

PID Alarms: Varying Mixtures

- ***Setting the PID to 75 ppm alarm in Isobutylene units protects from all three chemicals no matter what their ratio***

- ***IMPORTANT: Equivalent EL_{iso} is a calculation that involves a manufacturer specific Correction Factor (CF)***

- ***Similar calculations can be done for any PID brand that has a published CF list***

GfG Instrumentation

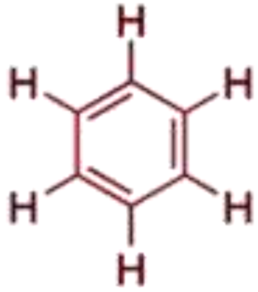
PID Alarms: EL_{iso} & Unknowns

- *Of course, if there are known or suspected chemicals of higher risk a lower alarm might be called for.*
- *In a potential terrorist chemical agent attack, a EL_{iso} of 1.00 ppm might be more appropriate*

GfG Instrumentation

What about benzene?

- ***Benzene is almost never present all by its by itself***
- ***Benzene is usually minor fraction of total VOC present***
- ***Test for total hydrocarbons (TVOC), especially if the combustible liquid has an established PEL or TLV***
    - ***Diesel*** ***15 ppm***
    - ***Kerosene*** ***30 ppm***
    - ***Jet Fuel (JP-8)*** ***30 ppm***
    - ***Gasoline*** ***300 ppm***



GfG Instrumentation

Case Study

- *Fuel barge explosion and cleanup*

- *On February 21, 2003, a fuel barge loaded with gasoline exploded at a fuel loading dock on Staten Island, New York*
- *Two workers were killed and another critically burned*
- *The explosion was the result of an accident, not terrorism or sabotage*
- *The barge had unloaded about half its cargo of 4 million gallons of unleaded gasoline when the explosion occurred*

USCG photo by PA3 Mike Hvozda

GfG Instrumentation

Case Study

- ***As the blaze was at its height, officials used tugs to push a nearby barge loaded with 8 million gallons of gasoline to the other side of the waterway, where they covered it with water and foam to ensure that it did not explode.***

GfG Instrumentation

Case Study

- *Once the fire was extinguished and the barges cooled, Marine Chemist and Coast Guard personnel conducted structural inspections*
- *Exposure to toxic VOCs was a primary concern*
- *Chemicals of concern included the remaining gasoline, benzene, total BTEX (benzene, toluene, ethylbenzene, and xylenes) and total polycyclic aromatic hydrocarbons (such as naphthalene)*

USCG photo by PA3 Mike Hvozda

Actual toxicity testing results from gasoline fuel barge #1

Previous Loadings: Cat Feedstock/Crude Oil/Cat Feedstock				
SPACE	% LEL	PPM TVOC (iso)	PPM Benzene	%TVOC from benzene
No (1) Port Cargo Tank	0	32.8	0.8	2.44 %
No (2) Port Cargo Tank	0	38.2	0.4	1.05%
No (3) Port Cargo Tank	0	45.5	0.4	0.88%
No (4) Port Cargo Tank	0	75.8	0.3	0.4%
No (5) Port Cargo Tank	0	64.3	0.3	0.47%
No (1) Stbd Cargo Tank	0	34.8	0.6	1.72%
No (2) Stbd Cargo Tank	0	44.6	0.3	0.67 %
No (3) Stbd Cargo Tank	0	39.6	0.2	0.51 %
No (4) Stbd Cargo Tank	0	58.4	0.4	0.68 %
No (5) StbdCargoTank	0	64.8	0.5	0.77%

TVOC alarm setting based on fractional concentration benzene for Barge #1

- *Worst case (No 1 Port Cargo Tank)*
  - *TVOC hazardous condition threshold alarm of 172 ppm isobutylene would prevent exceeding the PEL for benzene of 1.0 PPM*

41 x .0244 = 1.0004 ppm

- *TVOC Hazardous Condition Threshold Alarm for compliance with:*

Benzene Exposure Limit	*1.0 PPM*	*0.5 PPM*	*0.1 PPM*
TVOC alarm setting	*41 PPM*	*20.5 PPM*	*4.1 PPM*

GfG Instrumentation

Actual toxicity testing results from gasoline fuel barge #2

Previous Loadings: Natural Gasoline (3X)				
SPACE	% LEL	PPM TVOC (iso)	PPM Benzene	%TVOC from benzene
No (1) Port Cargo Tank	0	37.3	0.0	0 %
No (2) Port Cargo Tank	0	44.1	0.1	0.23%
No (3) Port Cargo Tank	0	53.8	0.2	0.37 %
No (4) Port Cargo Tank	0	48.2	0.1	0.21%
No (5) Port Cargo Tank	0	68.5	0.4	0.58 %
No (1) Stbd Cargo Tank	0	13.2	0.0	0 %
No (2) Stbd Cargo Tank	0	29.0	0.0	0 %
No (3) Stbd Cargo Tank	0	58.1	0.1	0.17%
No (4) Stbd Cargo Tank	0	48.7	0.2	0.41 %
No (5) StbdCargoTank	0	63.3	0.3	0.44%

TVOC alarm setting based on fractional concentration benzene for Barge #2

- *Worst case (No 5 Port Cargo Tank)*
  - *TVOC hazardous condition threshold alarm of 172 ppm isobutylene would prevent exceeding the PEL for benzene of 1.0 PPM*

172 x .0058 = 0.9976 ppm

- *TVOC Hazardous Condition Threshold Alarm for compliance with:*

Benzene Exposure Limit	*1.0 PPM*	*0.5 PPM*	*0.1 PPM*
TVOC alarm setting	*172 PPM*	*86 PPM*	*17.2 PPM*

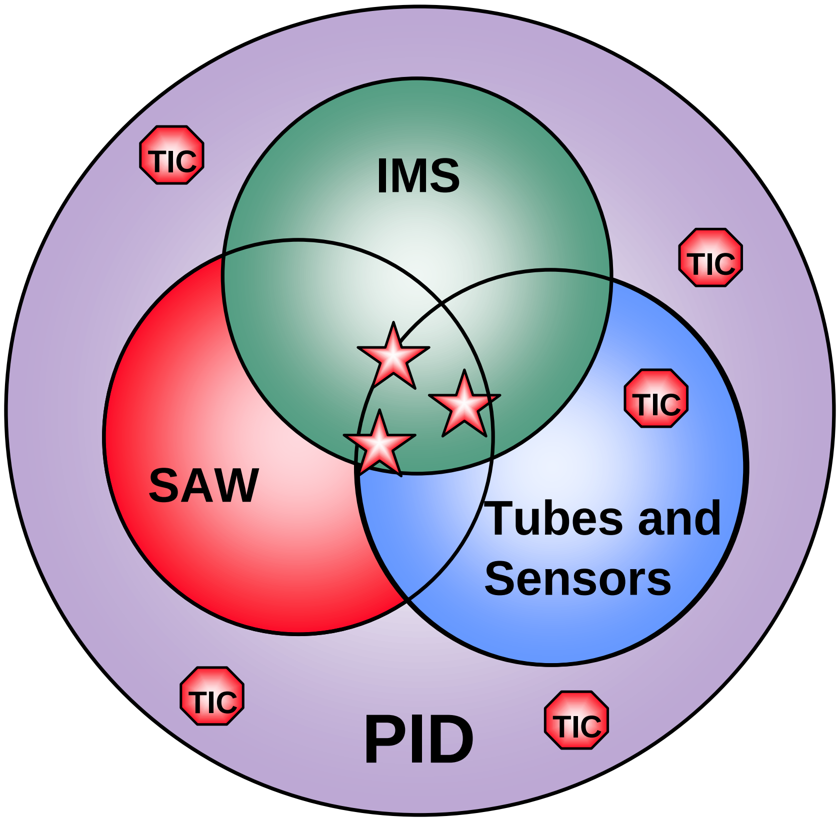
PIDs in WMD and Anti-Terrorist Response

- *Terrorist are not limited to traditional explosives and chemical warfare agents*
- *Weapons of mass destruction (WMD) can be based on:*
  - *Toxic Industrial Chemicals (TICs)*
  - *Chemical Warfare Agents (CWAs)*
  - *Nerve Agents*
  - *Explosives*

Able to detect wide variety recognized military CWAs, nerve agents and vapors associated with explosives:

- ***Lewisite***
- ***Mustard Gas (HD)***
- ***phosgene***
- ***Sarin (GB)***
- ***Soman (GD)***
- ***Tabun***
- ***VX***
- ***GF***
- ***Ammonium nitrate/fuel oil (ANFO)***
- ***Nitroglycerin***
- ***Ammonia***

Integrated gas detection approach to WMD



= Recognized (military) Chemical Warfare Agent

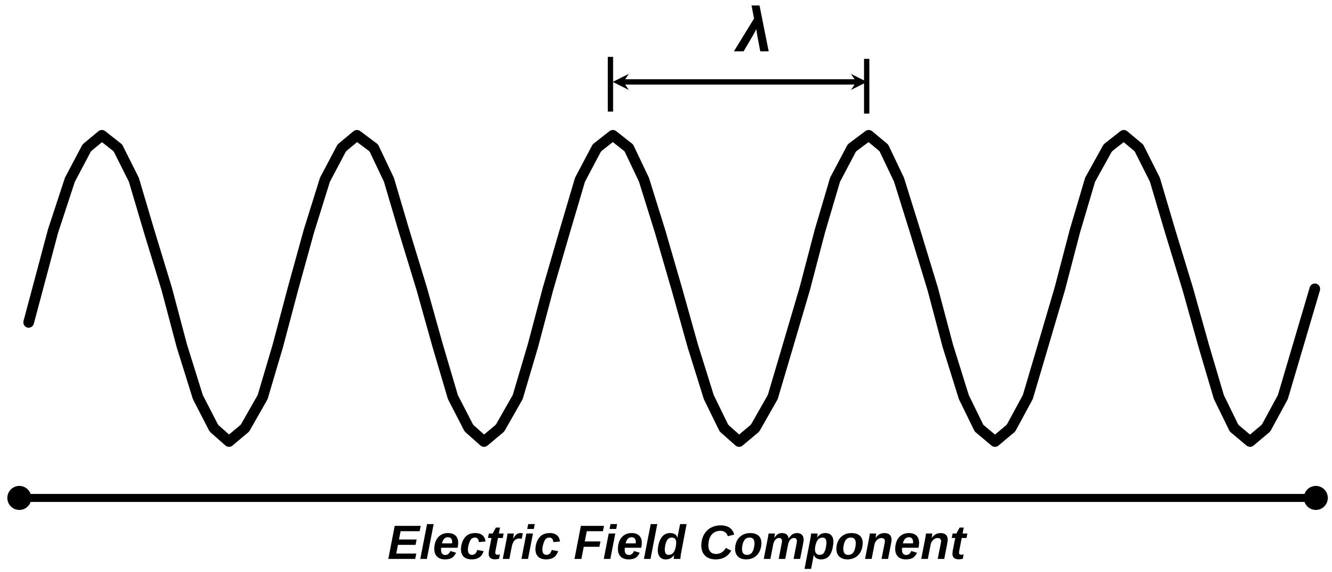
TIC = Toxic Industrial Chemical (TIC)

GfG Instrumentation

Non-dispersive infrared (NDIR) sensors

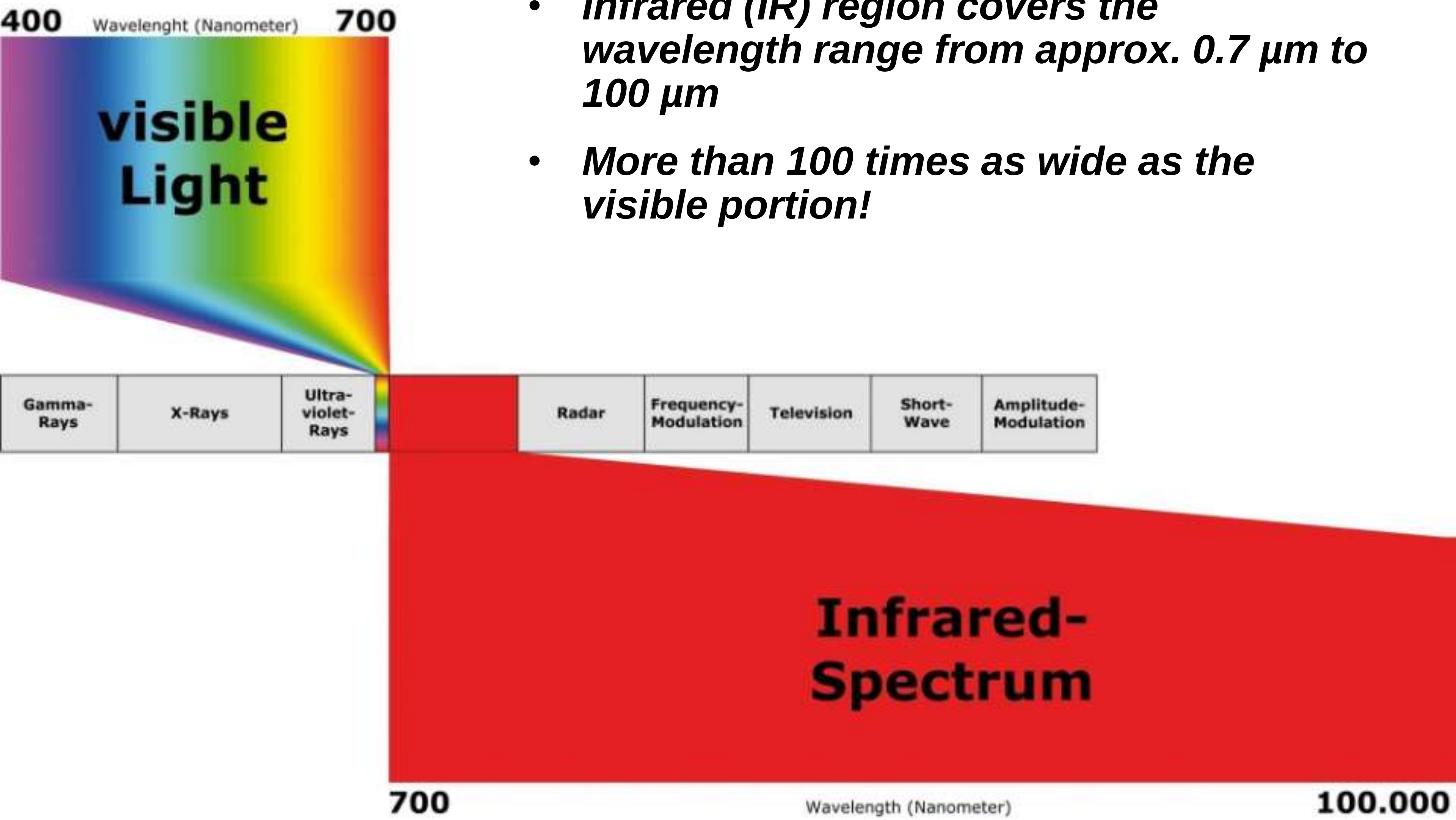
- ***Many gases absorb infrared light at a unique wavelength (color)***
- ***In NDIR sensors the amount of IR light absorbed is proportional to the amount of target gas present***

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



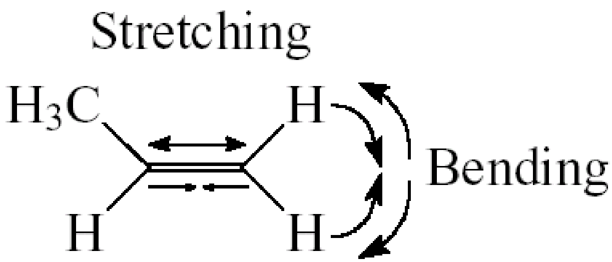
Electromagnetic radiation spectrum

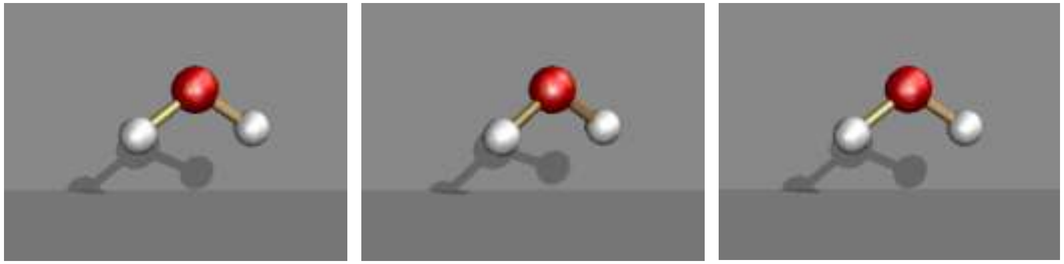
- *Infrared (IR) region covers the wavelength range from approx. 0.7 µm to 100 µm*
- *More than 100 times as wide as the visible portion!*



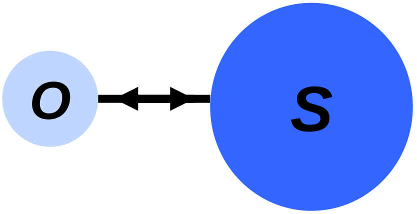
- *Chemical bonds absorb infrared radiation*
- *For infrared energy to be absorbed (that is, for vibrational energy to be transferred to the molecule), the frequency must match the frequency of the mode of vibration*
- *Thus, specific molecules absorb infrared radiation at precise frequencies*

- ***Must have a COVALENT CHEMICAL BOND***





Symmetric Stretch ***Asymmetric Stretch*** ***Bend***



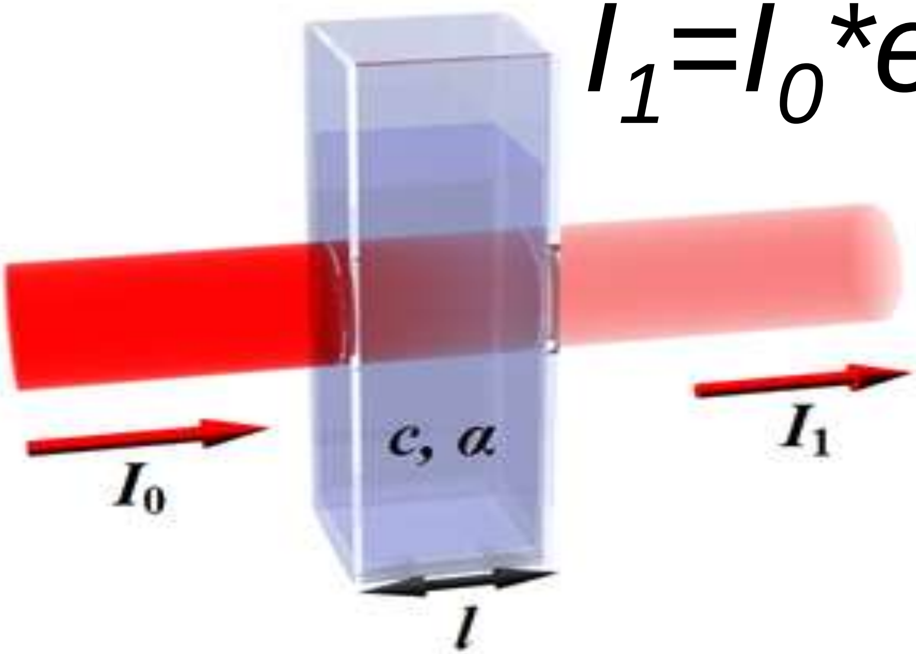
Nonlinear Molecules

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*

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



Size (length) matters...

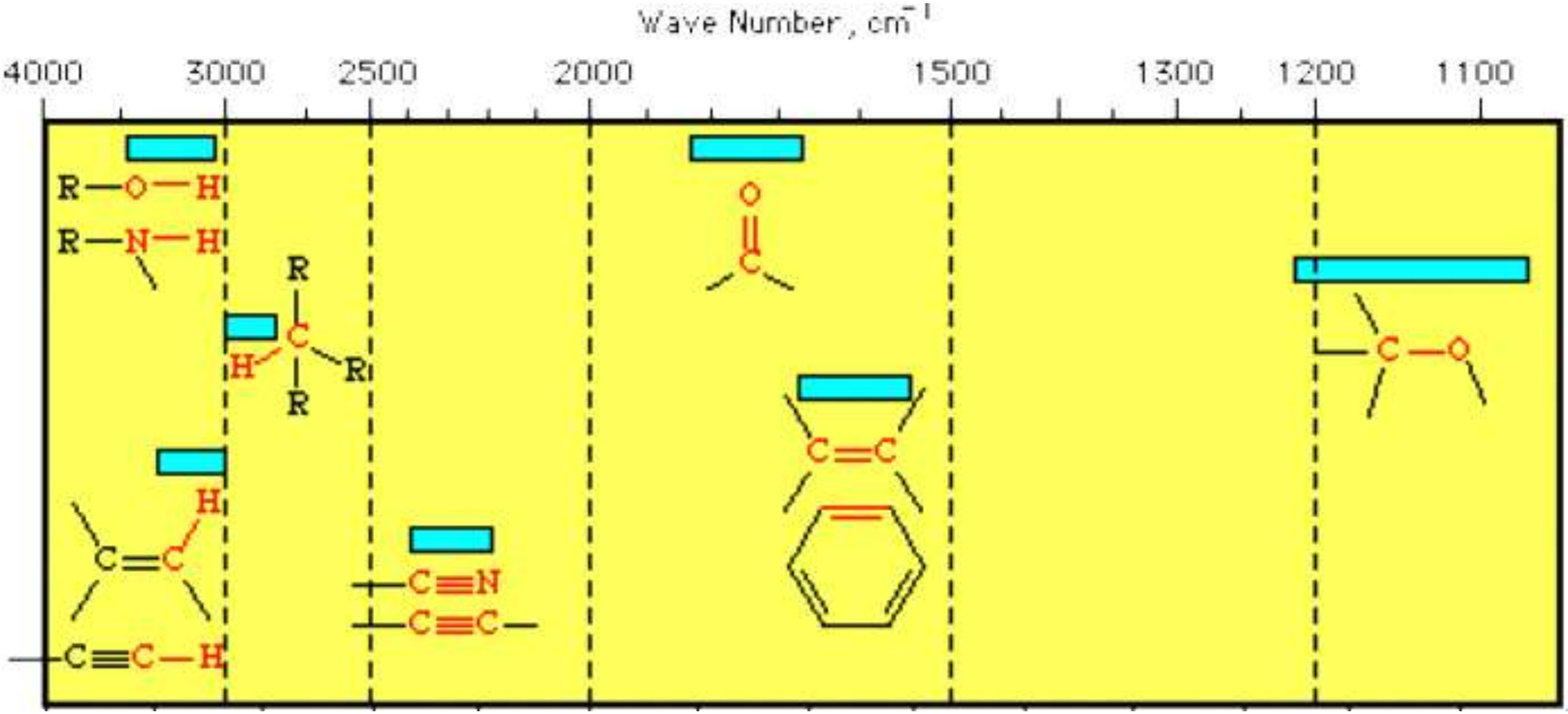
- I_0 *is the intensity of the incident light*
- I_1 *is the intensity after passing through the material*
- L *is the distance that the light travels through the material (the path length)*
- c *is the concentration of absorbing species in the material*
- α *is the absorption coefficient or the molar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

GfG Instrumentation

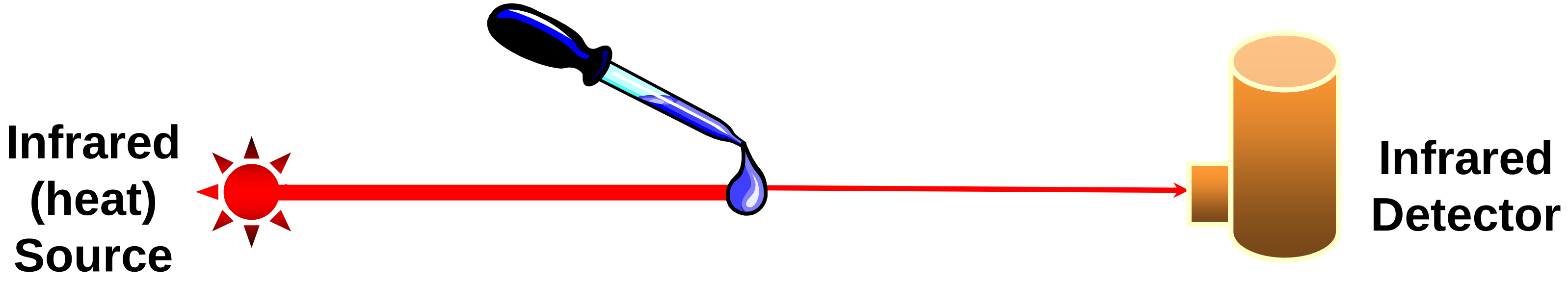
Requirements for IR Absorption

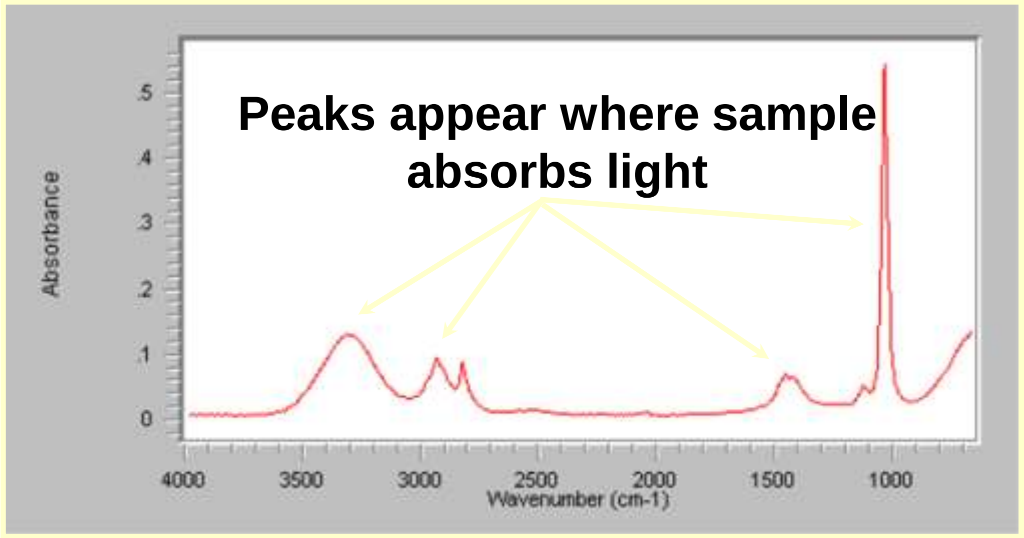
- *Lower quantum levels must be "populated"*
- *Dipole moment (degree of charge imbalance) must change with the vibrational "motion"*
  - *CO_2 and CH_4 absorb IR*
  - *Homonuclear diatomics such as H_2 DO NOT absorb IR*
  - *Also IR-transparent:*
    - *N_2*
    - *O_2*
    - *F_2*
    - *Cl_2*
   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

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

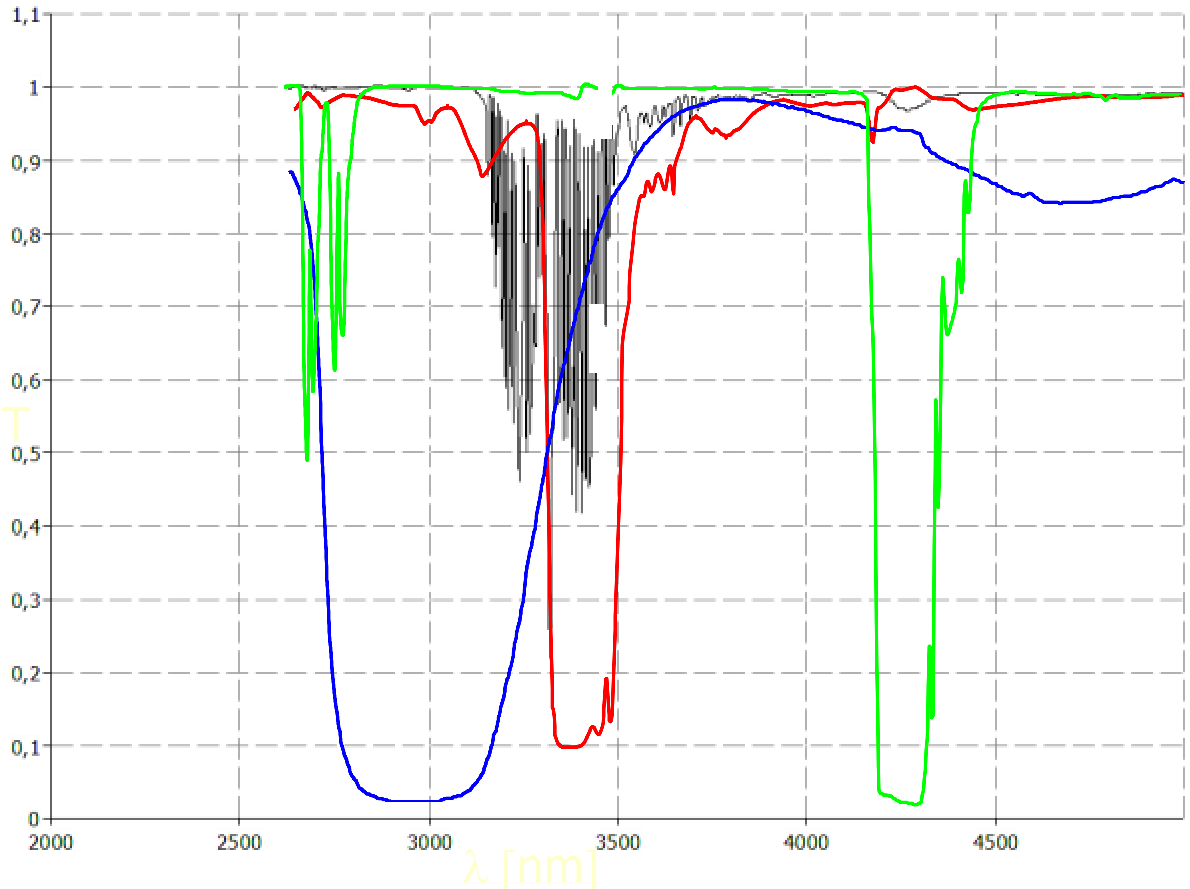


- ***A spectrum is a graph of how much infrared light is absorbed by molecules at each wavenumber of infrared light***





Infrared absorption spectra for several gases



Gas absorption spectra

Methane CH_4

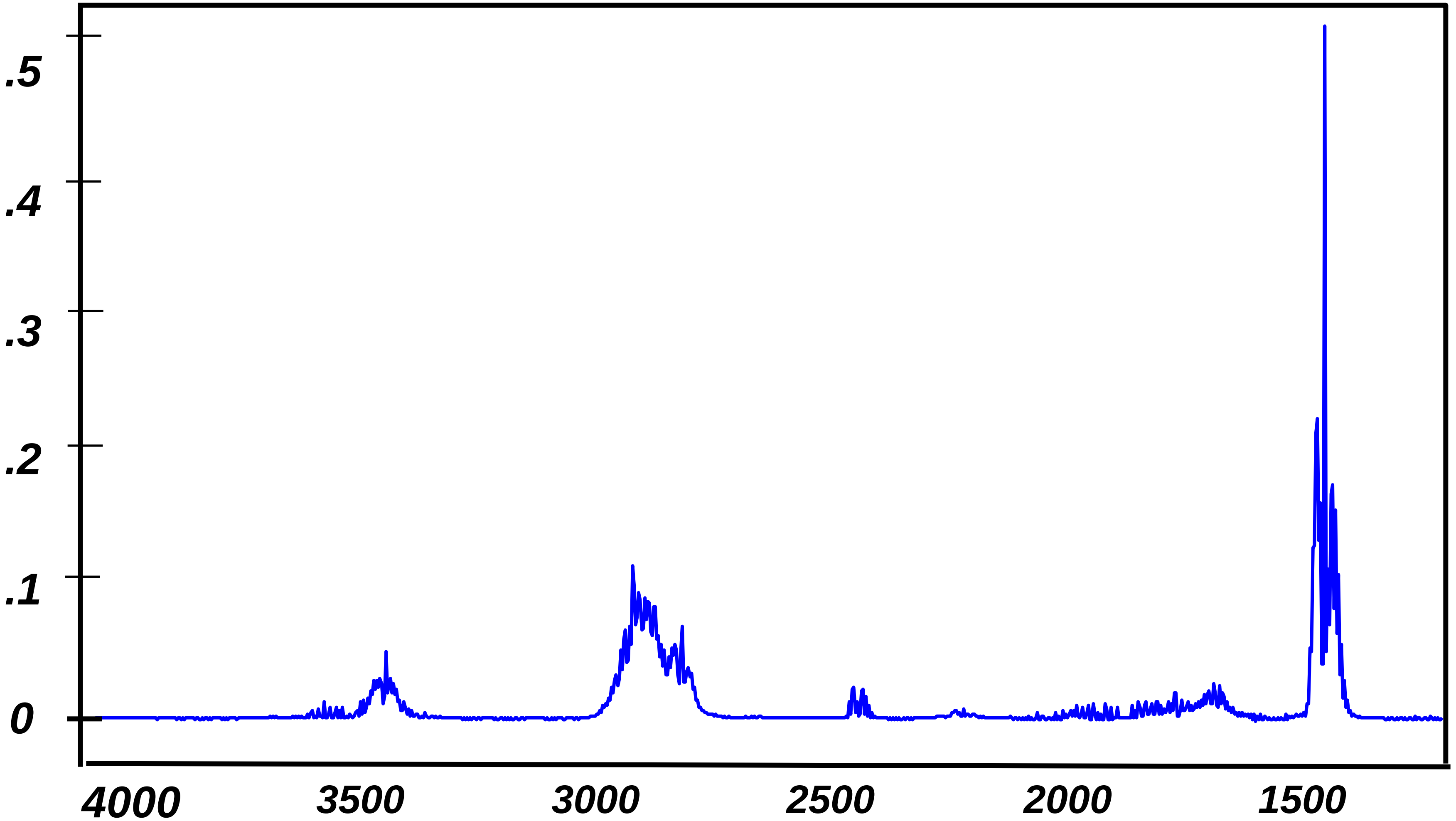
Propane C_3H_8

Water H_2O

Carbon dioxide CO_2

GfG Instrumentation

Methanol (CH_3OH) Absorbance Spectrum



GfG Instrumentation

- *NDIR sensors measure absorbance at specific wavelength to determine concentration of target gas*
- *NDIR sensor consists of:*
  - *Infrared emitter*
  - *Optical filters that limit IR source to specific infrared wavelength range*
  - *Optical chamber*
  - *Pyroelectric detectors (active and reference)*

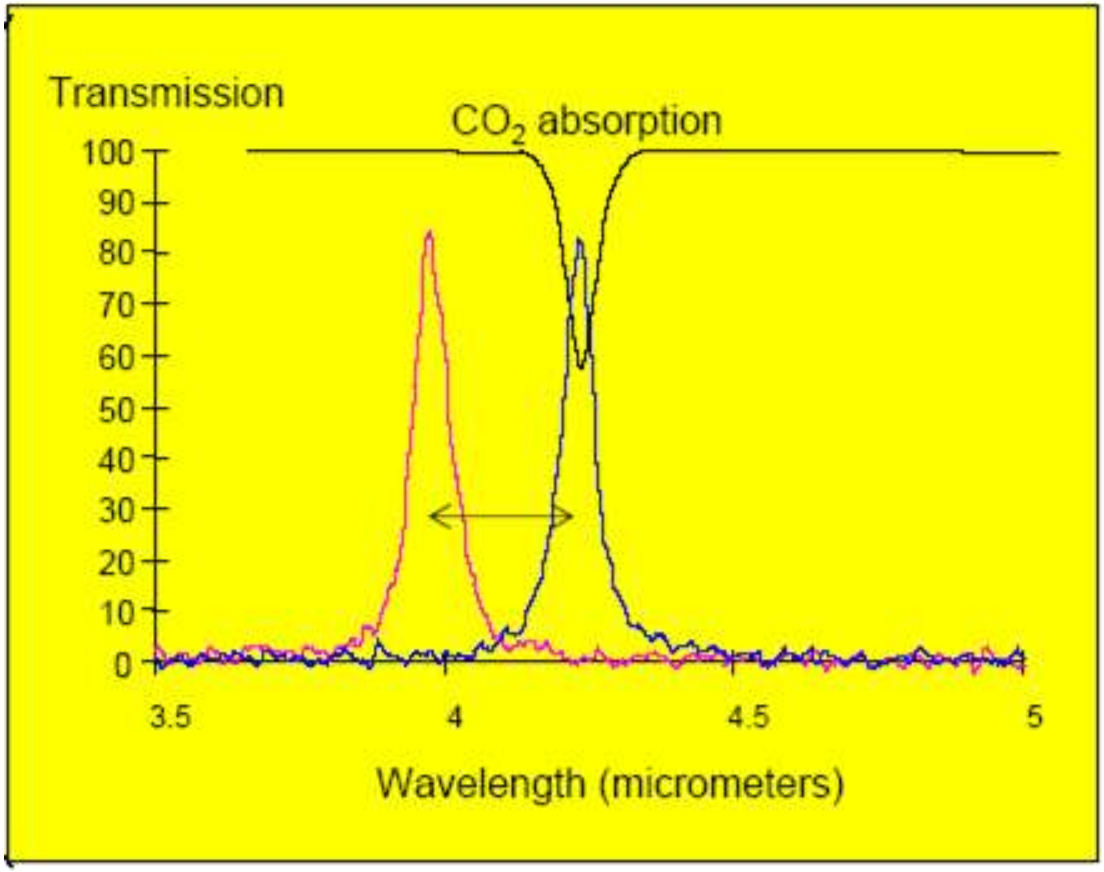
- *Example: NDIR CO2 sensor*
  - *Infrared absorption of CO_2 molecules at a specific wavelength of 4.26 μm*
  - *Sensor consists of IR source, light path, active detector and reference detector*
  - *Concentration of CO_2 determines intensity of light striking active detector*
  - *Reference detector provides a real-time signal to compensate the variation of light intensity due to ambient or sensor itself/*

Double wavelength NDIR sensors

- *Commonly used in many portable instruments*

GfG IR sensor (Note longer pathlength)

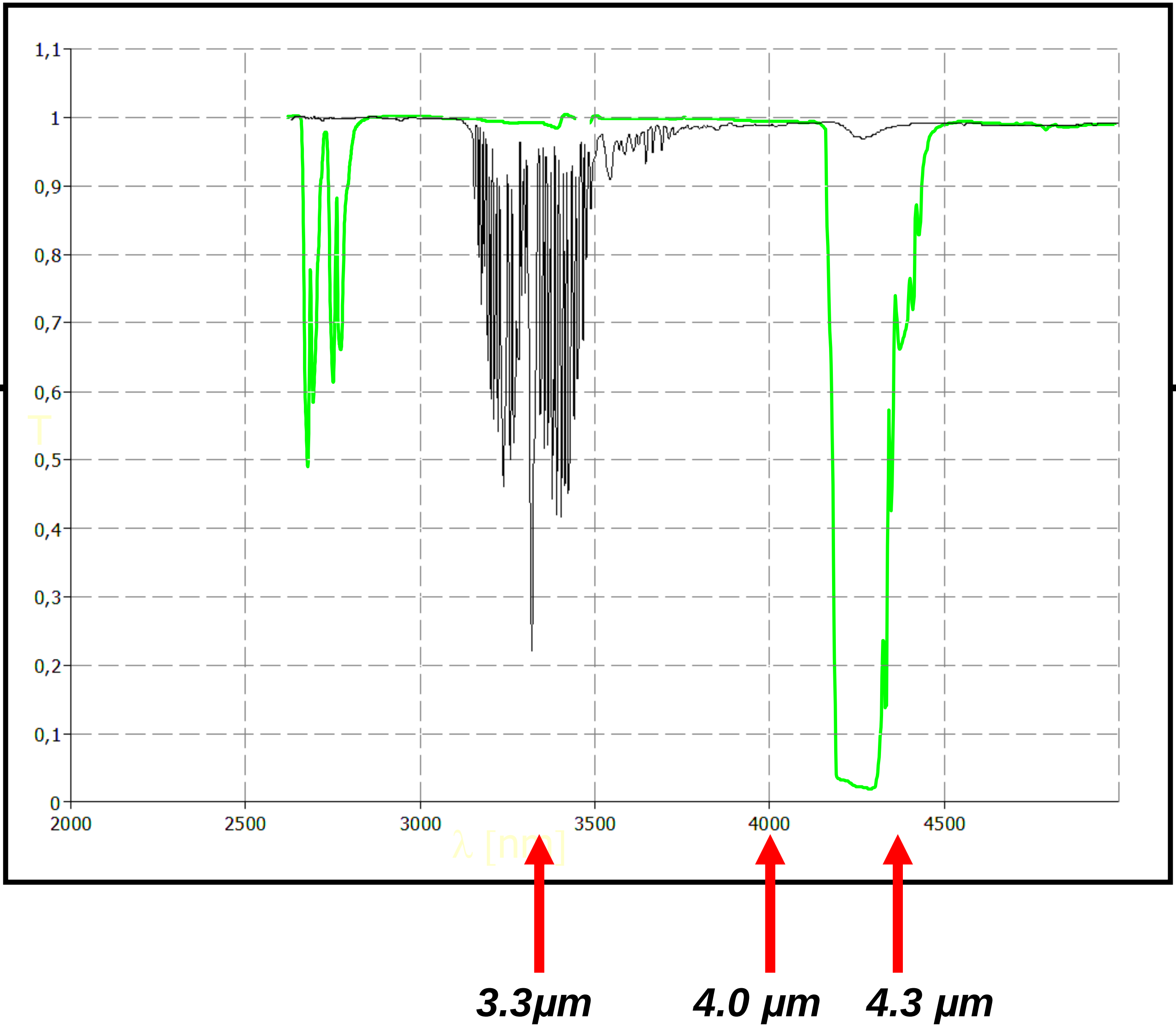
"4 Series" sized format used by City Tech, Dynament and E2V infrared sensors (Note shorter pathlength)



Measurement at CO_2 absorption wavelength and at a reference wavelength

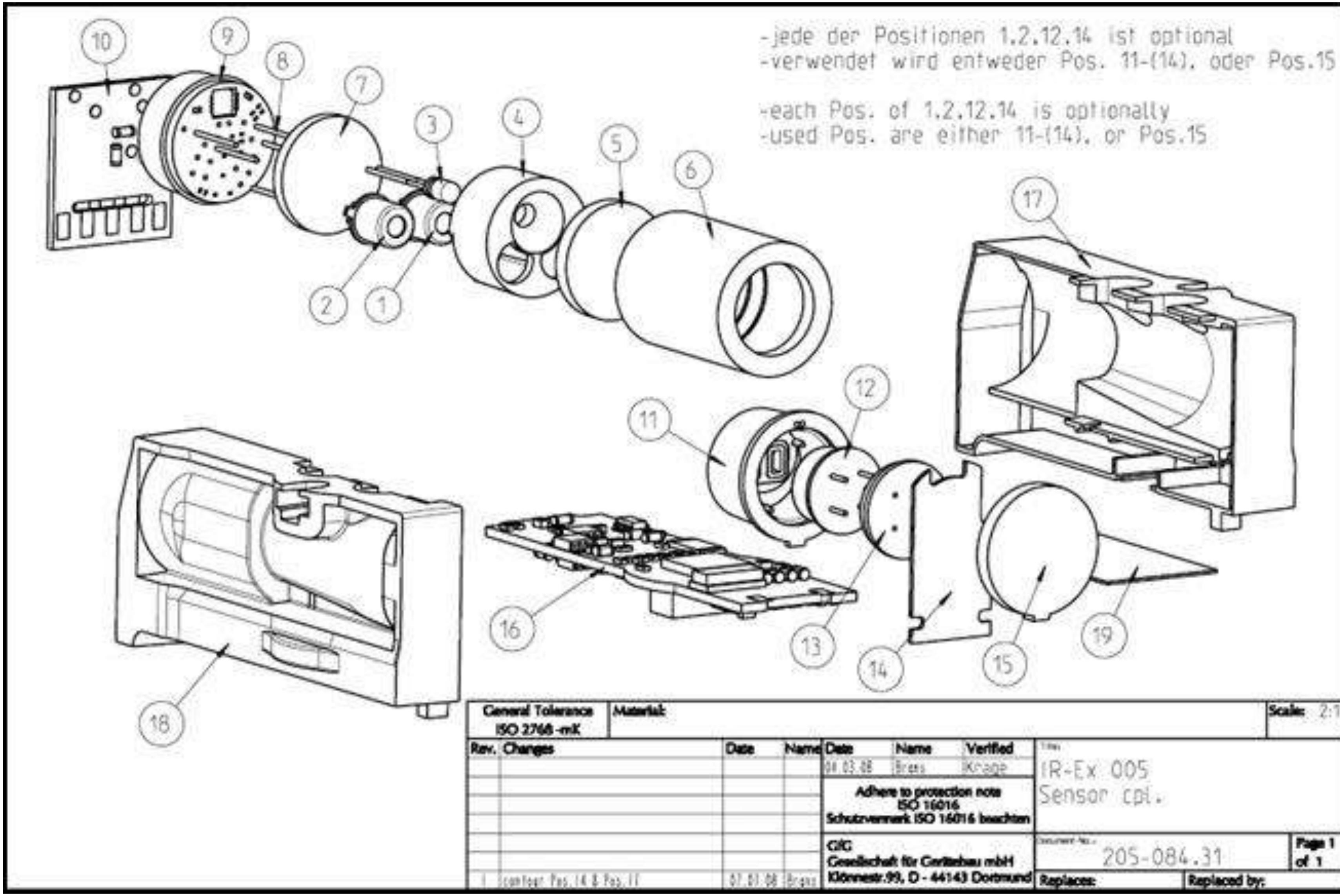
Three wavelength NDIR sensors

- Simultaneous measurement CO_2 and combustible gas
  - LEL: 3.3 µm
  - CO_2: 4.3µm
  - Ref: 4.0µm

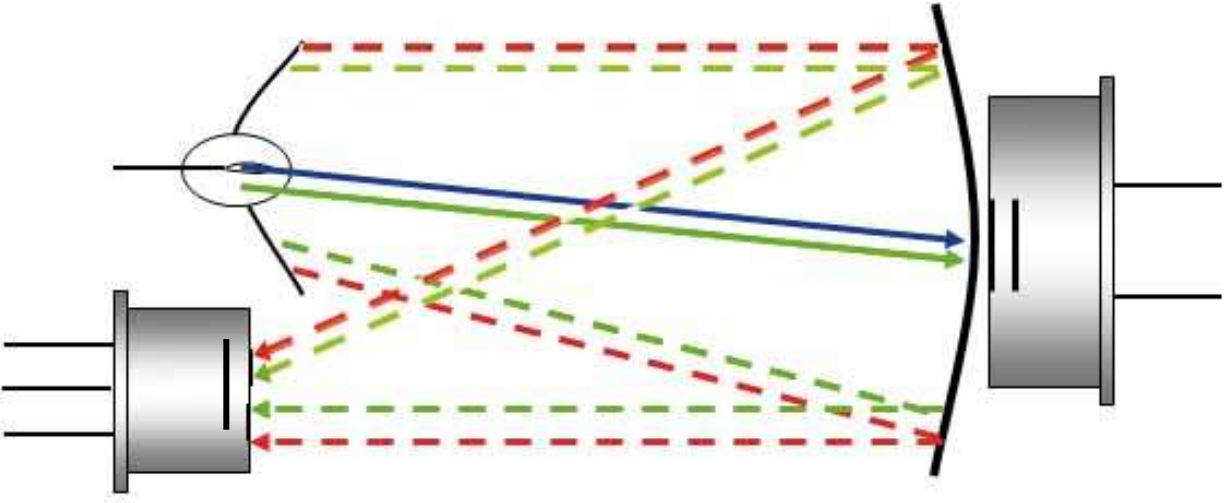


GfG Instrumentation

Three wavelength NDIR sensors



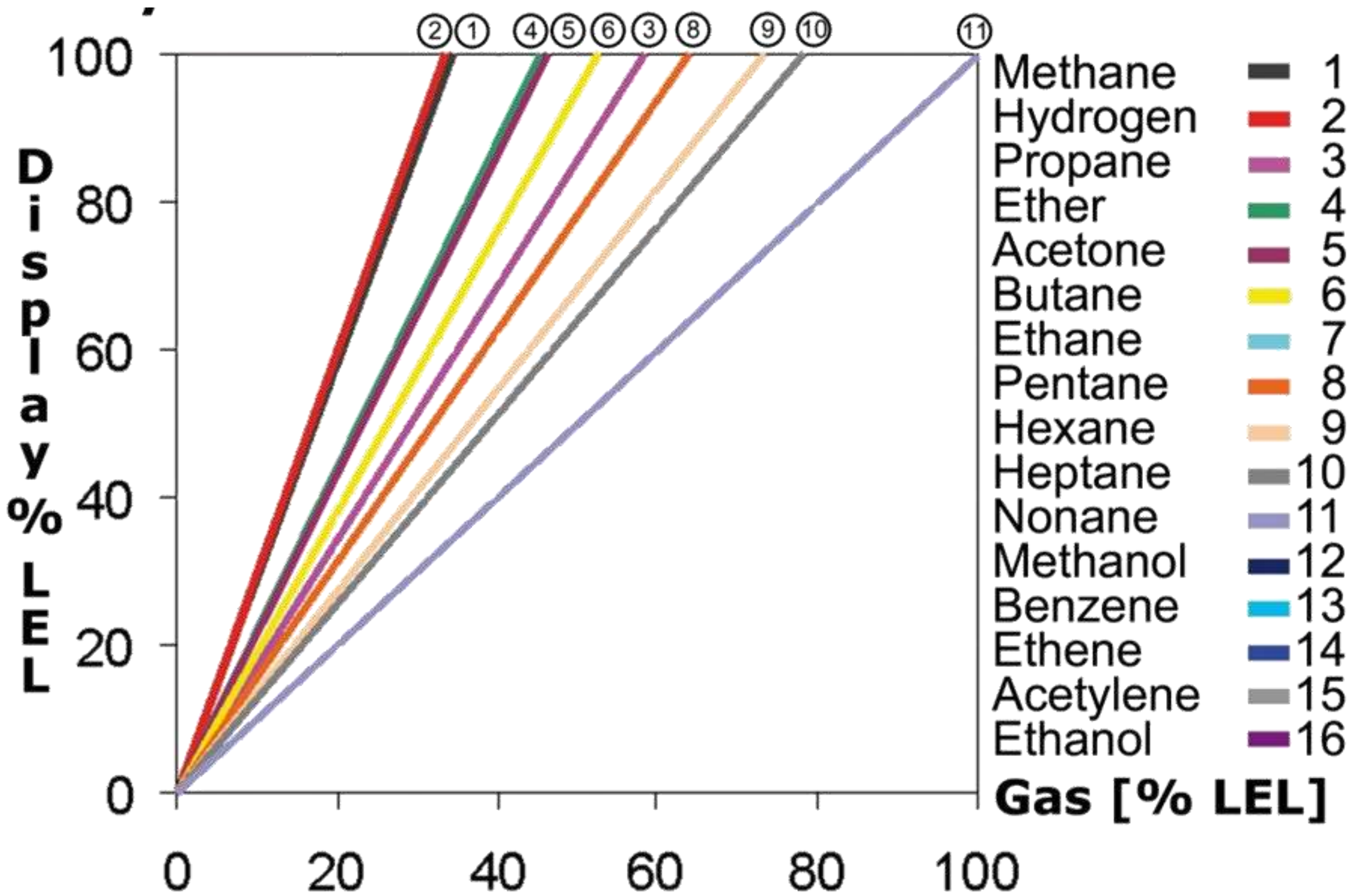
Light path through three wavelength NDIR sensor



- *Affected by:*
  - *Humidity*
  - *Temperature*
  - *Pressure*
  - *Ageing of detector*
- *Not affected by:*
  - *Dust*
  - *Ageing of IR-emitter*

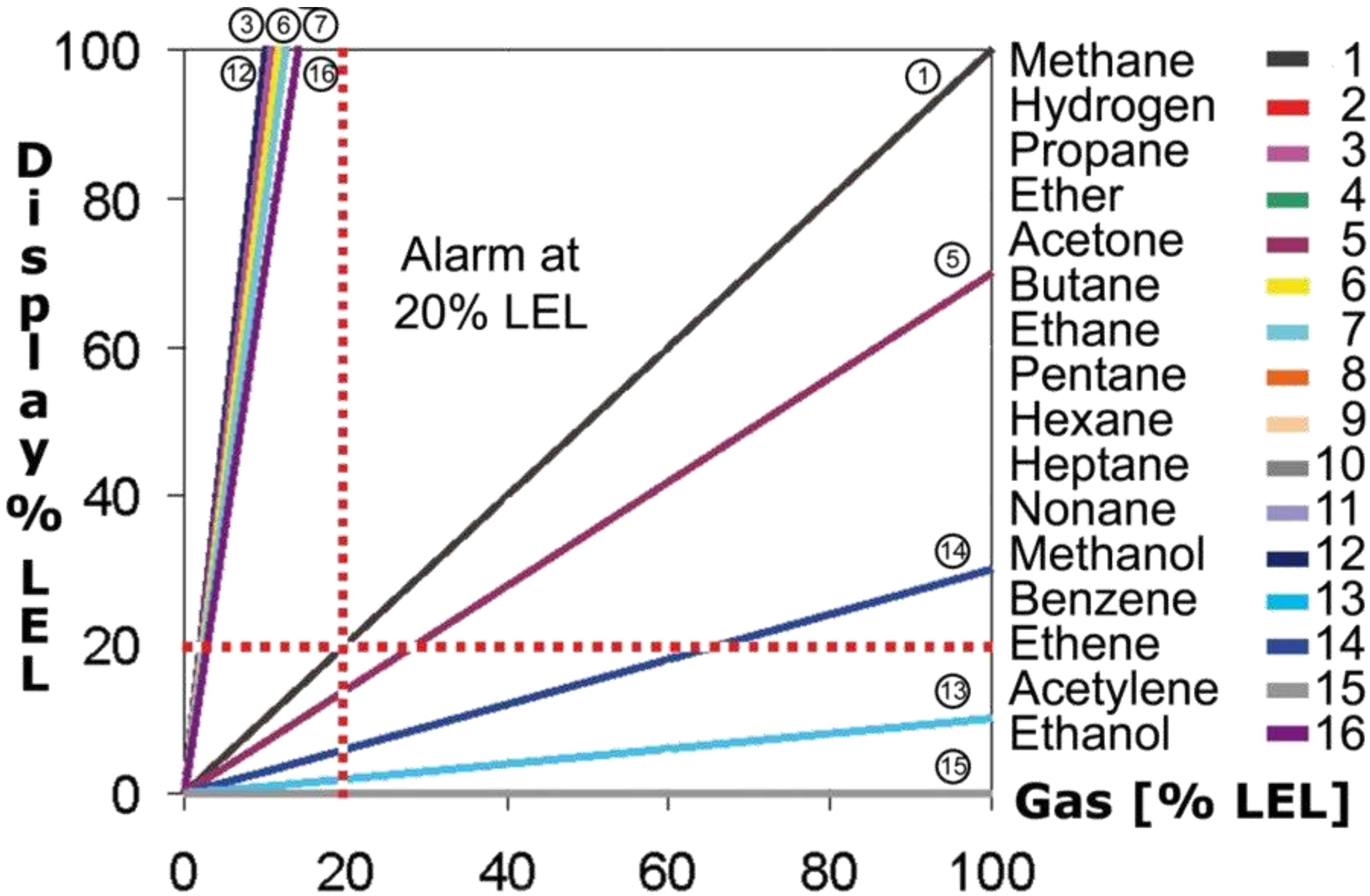
GfG Instrumentation

Catalytic pellistor combustible gas response curves



GfG Instrumentation

Two wavelength NDIR combustible gas response curves

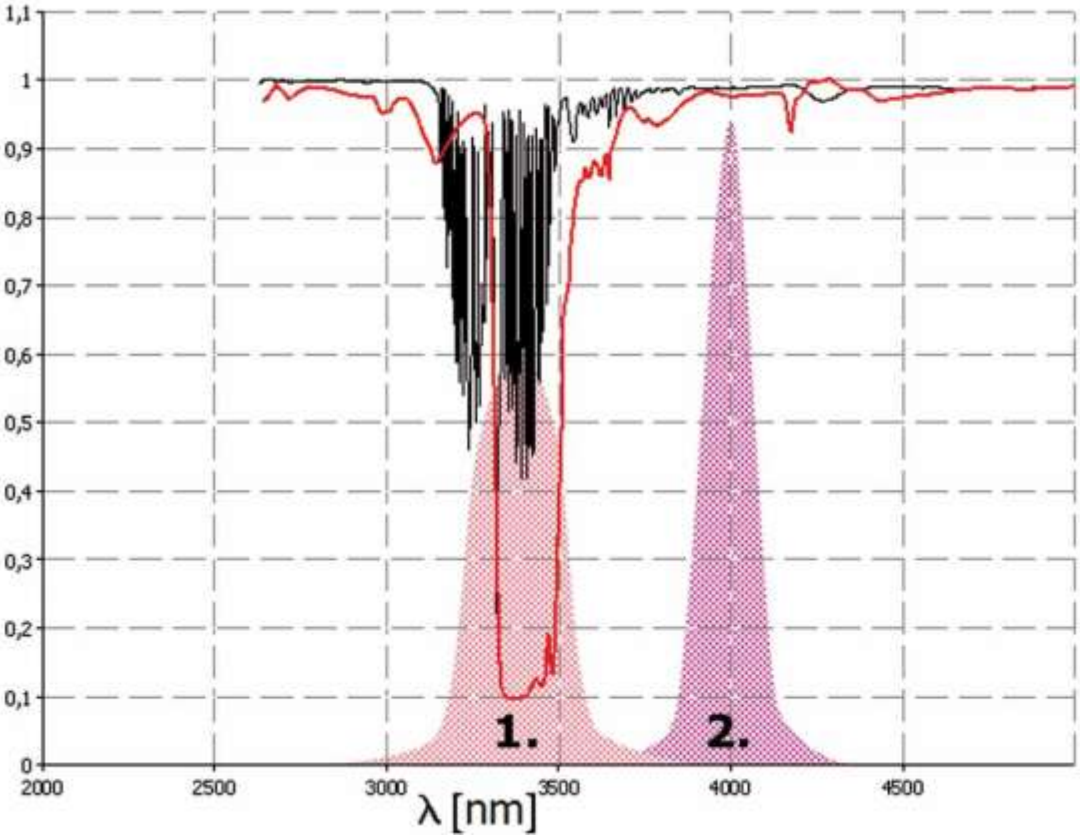


GfG Instrumentation

Next on the horizon: Four wavelength NDIR combustible gas sensors

- ***Measure at two wavelengths for combustible gas***
- ***Measure at one reference wavelength***
- ***Measure water vapor at another wavelength and deduct interfering effect from combustible gas reading***

GfG Instrumentation

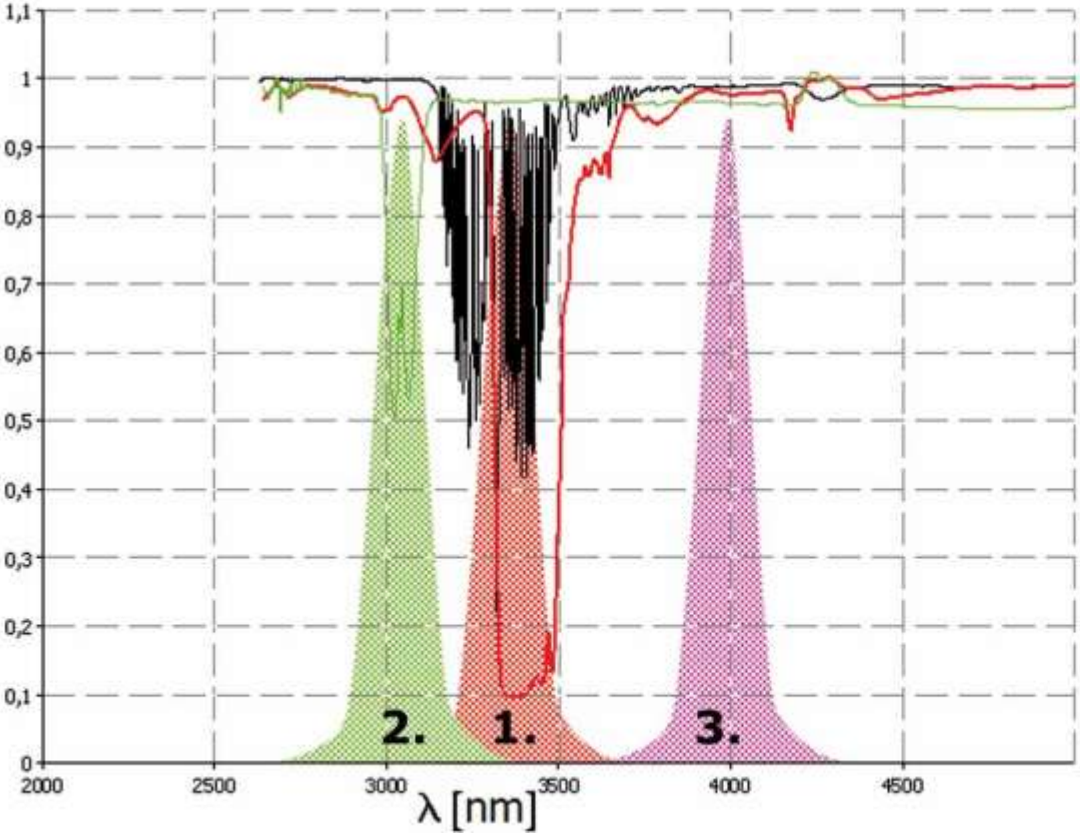


2-wavelength Hydrocarbon-Detection

1. Methane CH_4 } 3,3 µm
   Propane C_3H_8 } 3,3 µm

2. Reference 4,0 µm

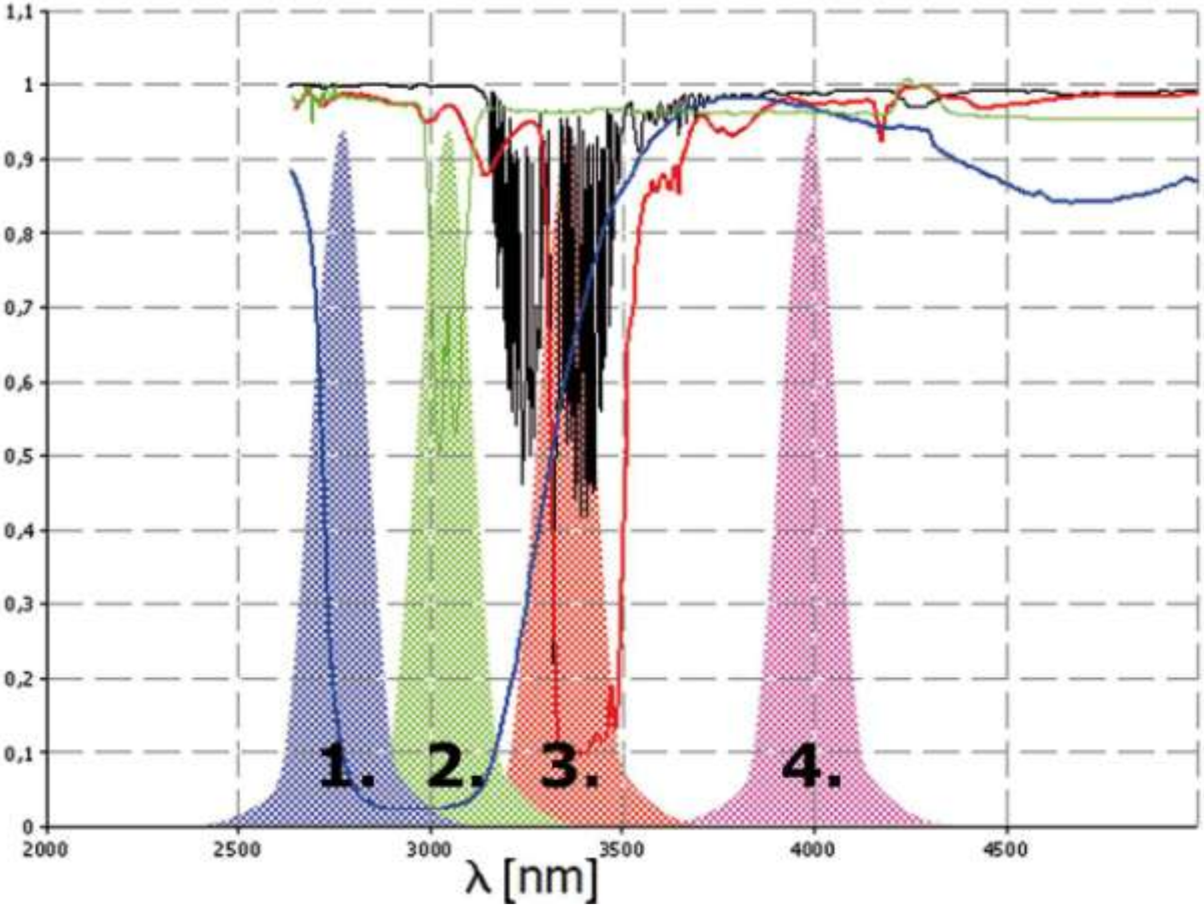
GfG Instrumentation



3-wavelength Hydrocarbon-Detection

1. Methane CH_4 } 3,3 µm
   Propane C_3H_8 }
2. Acetylene C_2H_2 3,1 µm
3. Reference 4,0 µm

GfG Instrumentation



4-wavelength Hydrocarbon-Detection

1. Water H_2O 2,7 µm

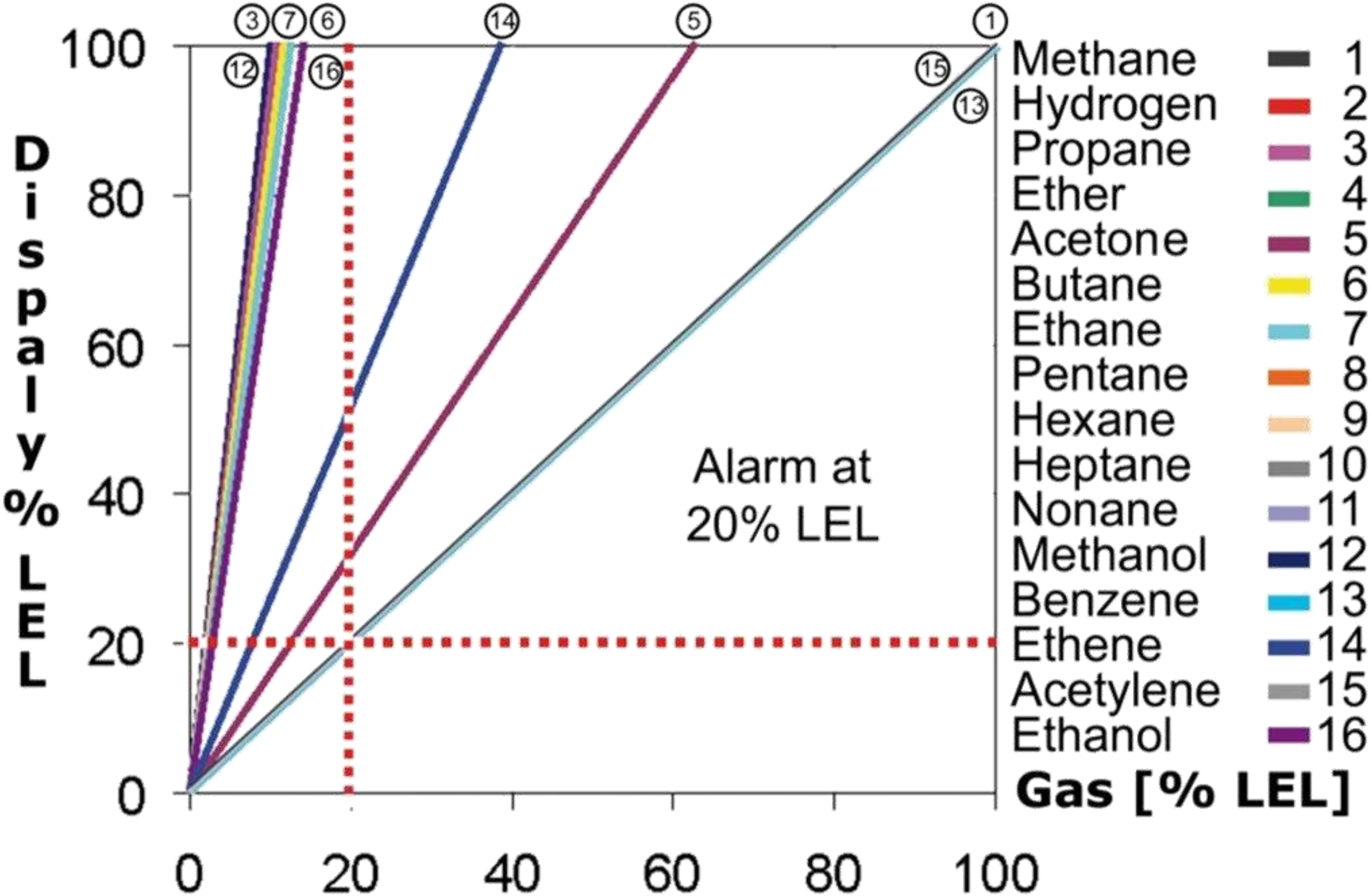
2. Acetylene C_2H_2 3,1 µm

3. Methane CH_4 } 3,3 µm
   Propane C_3H_8

4. Reference 4,0 µm

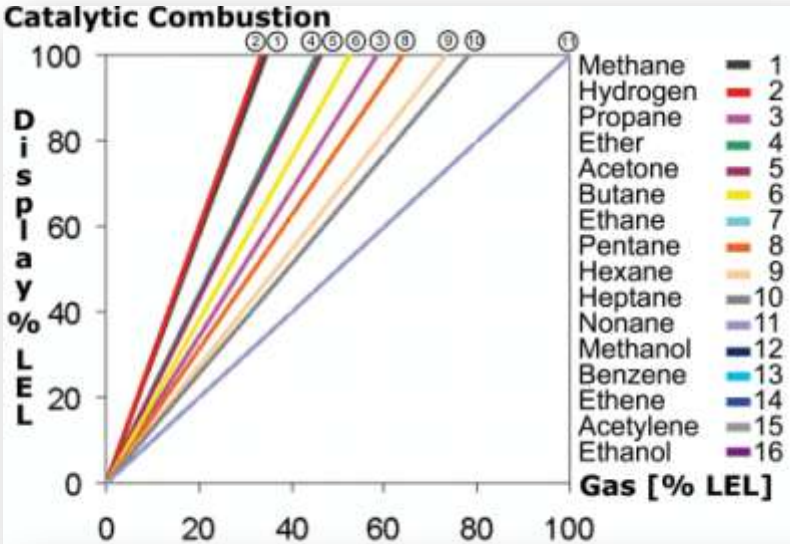
GfG Instrumentation

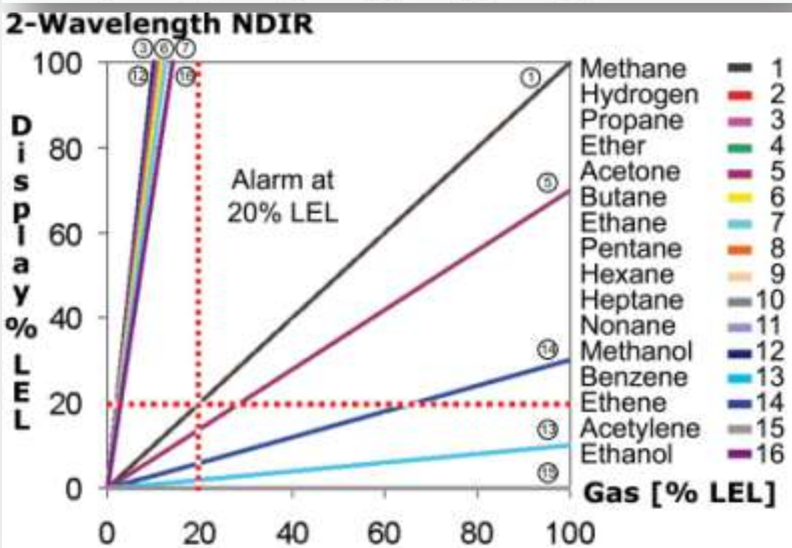
Four wavelength NDIR combustible gas response curves



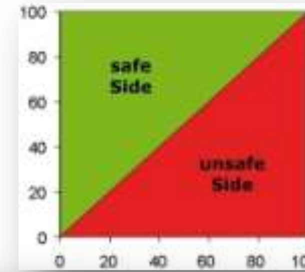
GfG Instrumentation

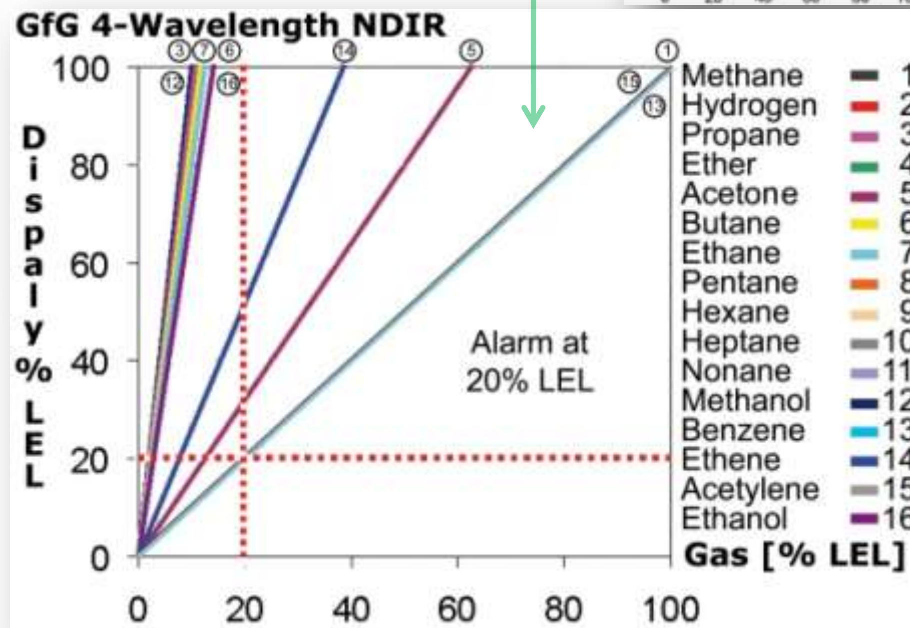
Side by side comparison





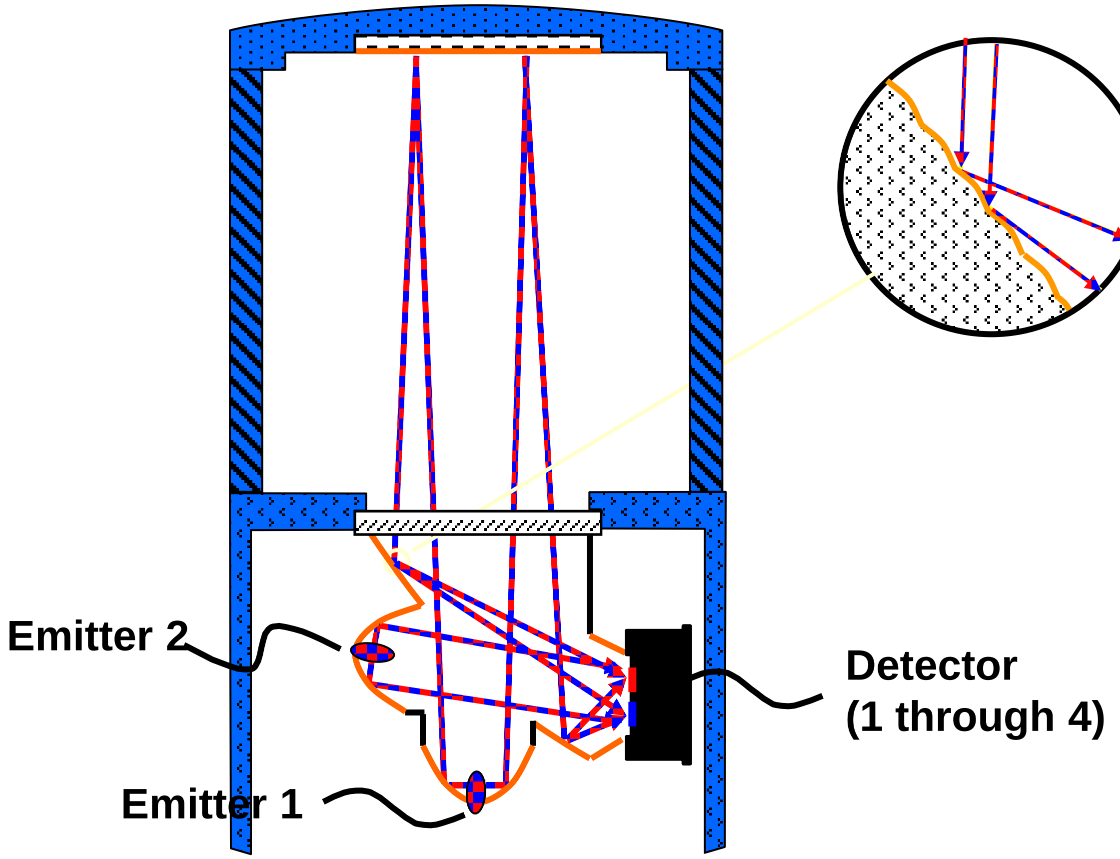
All gases on the safe side



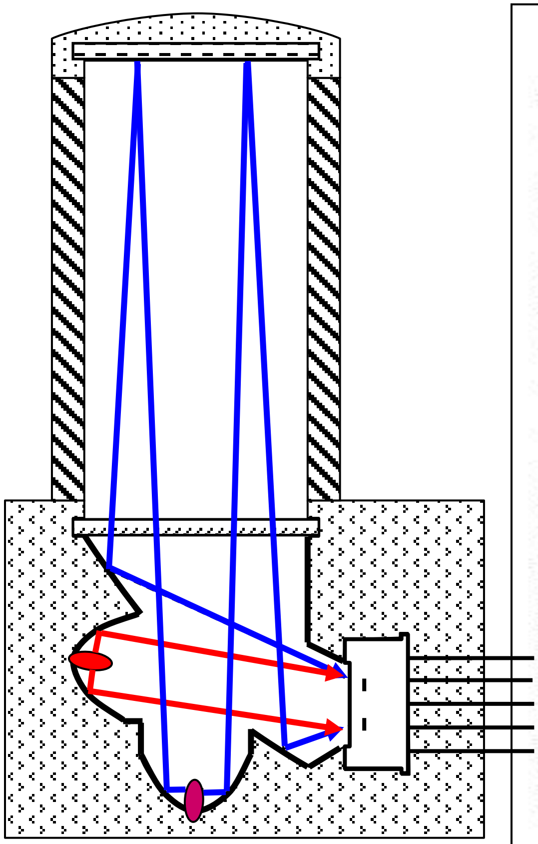


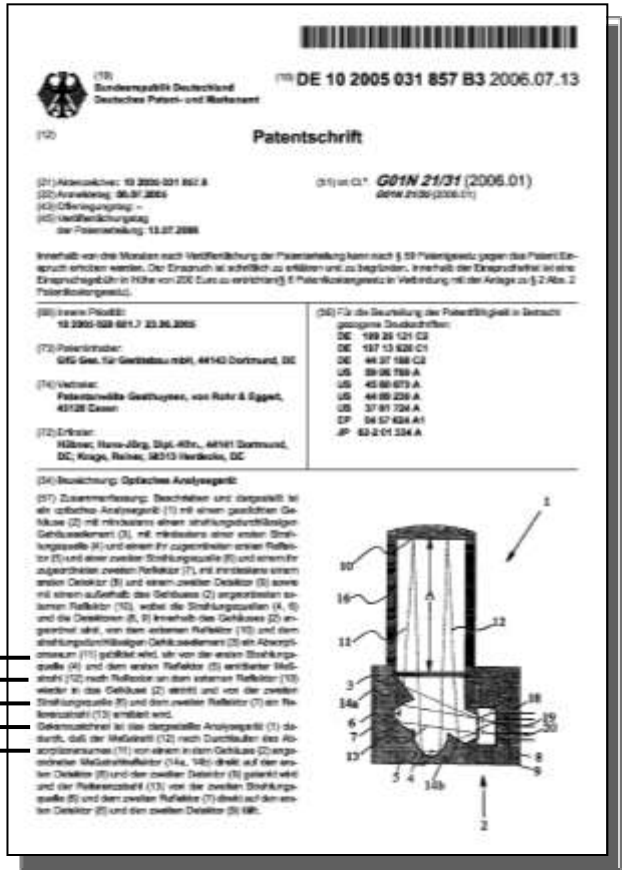
GfG Instrumentation

- *Multi wavelength, dual path for long-term stability and accuracy*
- *External gas measuring path for fast and accurate response*
- *Possibility of long measuring path for low measurement range (target: 0.1% LEL CH4)*
- *Optional "multigas calibration" for improved broad range characteristics*



- ***Multi wavelength***
- ***Dual path***
- ***Variable path length***
- ***No dichroic beamsplitter***





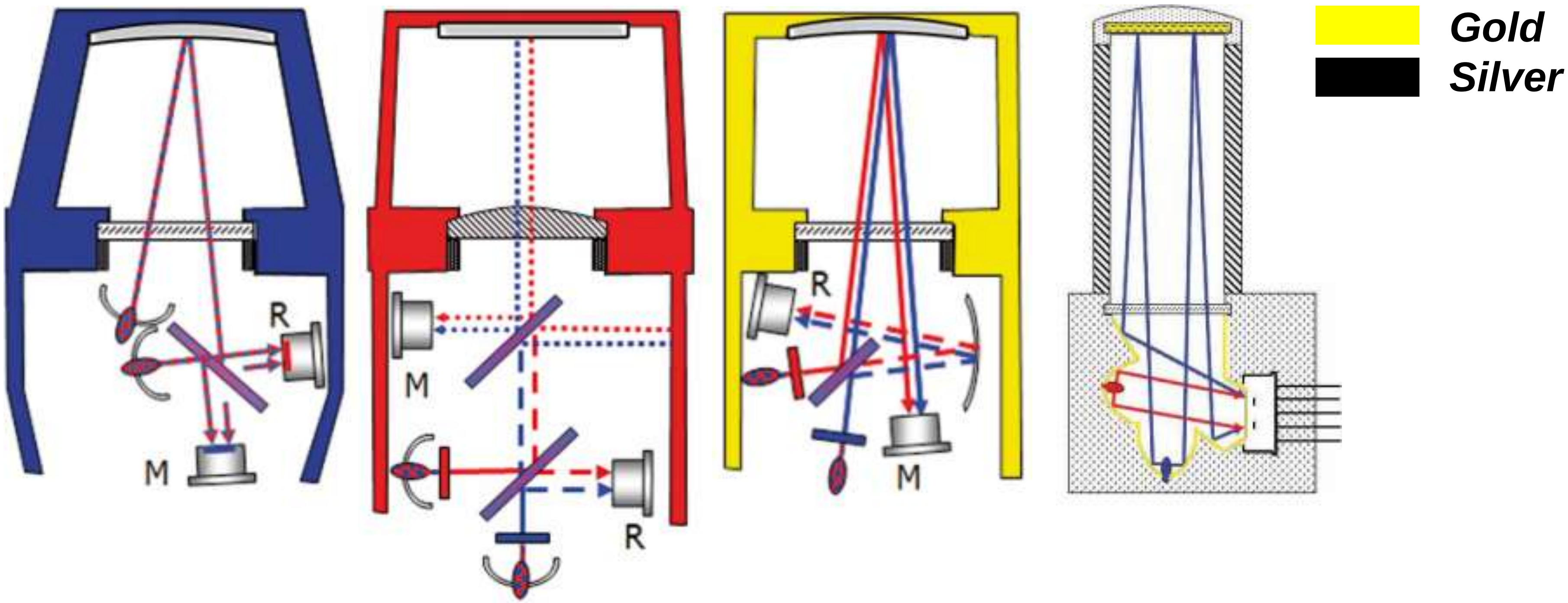
(19) DE 10 2005 031 857 B3 2006.07.13

(12) Patentschrift

(51) Int Cl.: G01N 21/31 (2006.01)

- **Not affected by:**
  - ***Humidity***
  - ***Temperature***
  - ***Pressure***
  - ***Aging of detector***
  - ***Dust***
  - ***Aging of IR-emitter***

IR-29 Pathfinder
Closed Path IR Transmitters



Greater than 55% | Greater than 85% | Greater than 55% | Less than 10%

- *Signal losses by mirror, beamsplitter and optical surfaces*
- *Realisation of IR-principles cause different hights of measuring signals*

GfG Instrumentation

IR-29 Closed Path Infrared Transmitters

- *Pressure sensor*
- *Housing material: stainless steel V4A*
- *Accessories: sample flow housing*
  weather protection
- *Display, RC2, IR-remote control, memory card*
- *Optical and acoustic alarm*

GfG Instrumentation

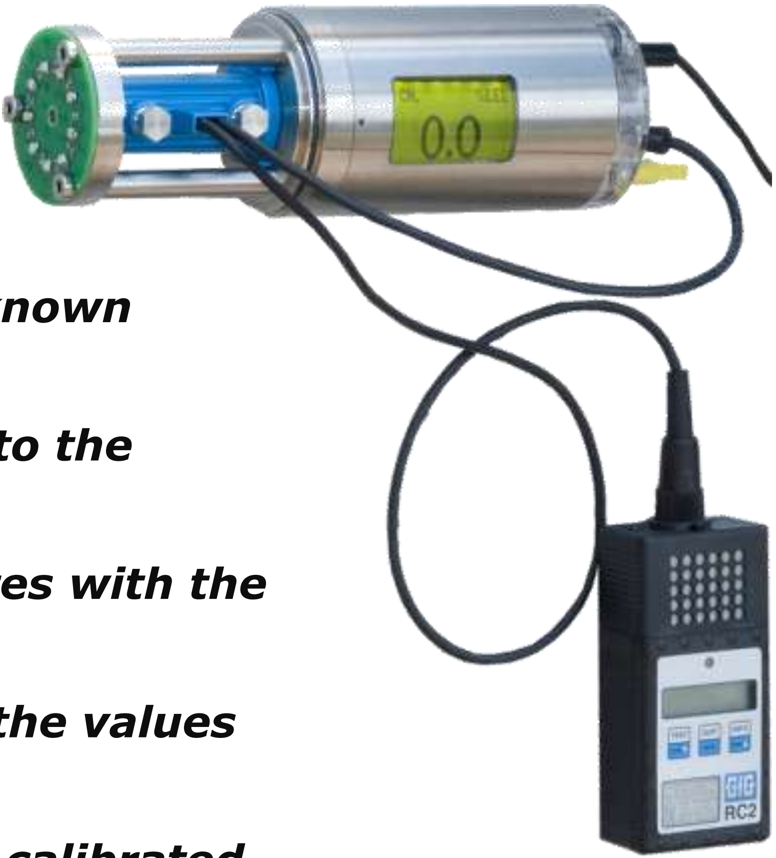
IR-29 Closed Path Infrared Transmitters

- ***Interface:*** ***ModBus, 4 -20 mA, relay***
- ***250V AC:*** ***2 relays: 1-normally closed (NC), 1-normally open (NO)***
  8 terminals relays <u>or</u> ModBus
- ***45V DC:*** ***3 relays: 1-normally closed (NC), 2-normally open (NO)***
  14 terminals

GfG Instrumentation

Accessory "gasfree calibration"

Cuvette with an integrated EPROM for a gasfree calibration.



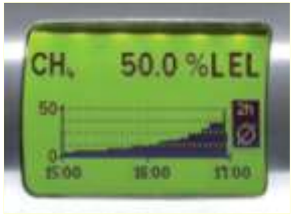
- ***Gas cell is sealed after filling with a known concentration of gas.***
- ***A cable connects the gas cell EPROM to the transmitter via the RC2 interface.***
- ***The gas cell EPROM then communicates with the transmitter.***
- ***Measurement values are matched to the values stored on the EPROM.***
- ***The transmitter will be automatically calibrated. No need for gas cylinders!***

IR-29 Closed Path Infrared Transmitters

- *"One-man-calibration" at transmitter*
- *With hard-wired remote control RC2*
- *With wireless IR-remote control RC3*

GfG Instrumentation

- *Integrated data logger / micro SD card for data storage of 30 years measurement values*
- *Histogram for recorded measurement data over most recent 24 hours*
- *Min, max, and average*



IR-29 Closed Path Infrared Transmitters

- ***Available in intrinsically safe, increased safe and explosion proof versions***

GfG Instrumentation

Questions?