Principles and Techniques of Gas and Vapor Detection: Important Methods and Applications

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Learning Objectives

- ***To understand the operating principles, capabilities, limitations and costs of important detection and identification technologies commonly used in direct reading atmospheric monitors***

- ***To be able to select the best field detection and identification tool for a given detection/identification scenario from those available***

- ***Technologies discussed:***
  - ***Electrochemical oxygen and toxic***
  - ***Catalytic pellistor (LEL)***
  - ***Photoionization detectors***
  - ***Infrared NDIR***

Confined Space Entry

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Characteristics of Confined Spaces

- ***Large enough for worker to enter***
- ***Are not designed for continuous worker occupancy***
- ***Limited openings for entry and exit***

Large enough to enter

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Meeting basic CS criteria

- ***Limited means of entry and exit***
- ***Not designed for continuous occupancy***

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Permit Required Confined Spaces

- ***One or more of the following:***
    - ***Hazardous atmosphere (known or potential)***
    - ***Material with the potential for engulfment***
    - ***Inwardly sloping walls or dangerously sloping floors***

      or

    - ***Contains any other serious safety hazard***

Non-Permit Confined Spaces

- *Large enough for worker to enter*
- *Are not designed for continuous worker occupancy*
- *Limited openings for entry and exit*
- *But no other serious safety hazard*

Elevator Pit

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Typical Confined Spaces

- *Storage tanks*
- *Ship compartments*
- *Process vessels*
- *Boilers*
- *Sewers*
- *Tunnels*
- *Underground utility vaults*
- *Pipelines*
- *Storm drains*

Some confined spaces are open topped

- Pits
- Degreasers
- Open-topped water tanks
- Ship holds
- Excavations

5 died trying to save each other

By Mike Martindale
News Staff Writer

MENOMENEE, Mich. –

Bill Hofer was the first to collapse in the dark manure pit.

Inhaling a combination of toxic gases, he quickly lost consciousness and slipped down into the pool of murky liquid in the bottom of the 12-foot hole.

Then one after another, the four men at the top of the pit scrambled in, trying first to save Hofer, and then each other, from the deadly fumes.

Within five minutes all were dead or dying in what is believed to be the worst farm accident in Michigan history.

Killed yesterday along with the 63-year-old Hofer were his uncle, Carl Theuerkauf, Sr., the 65-year old patriarch of the centennial farm; two of Theuerkauf's sons, 37-year old Carl Jr. and 28-year old Tom; and Carl Jr.'s 15-year old son, Daniel.

"I'm sure that when one person slipped or fell, out of love and for help, one after another went in," said Richard Breyer with the county farm extension service in Menominee.

Dorothy Theuerkauf, who lost a husband, two sons, and a grandson in the tragedy said:

"I can't believe something like this could happen. It will probably take me a couple of weeks before it actually sinks in."

On Thursday, investigators said the five men were using a pump to empty a partially covered, 12-foot deep concrete manure pit, and were almost finished when the pump clogged.

Hofer descended into the darkness to clear the block.

"It's unknown which one went in next, but eventually they all went in to save the rest," said Menominee County Sheriffs Deputy Booth Whipp.

County Medical Examiner Dr. Paul Haupt estimates it took about 90 seconds for each of the men to suffocate in the invisible cloud of gas, composed primarily of methane and hydrogen sulfide.

Pittsburgh Post-Gazette - Thursday, May 3, 1990

Methane in well kills three firefighters

HUSTONTOWN, PA (AP) – Residents were mourning yesterday for three volunteer firefighters who died while helping a neighbor to clean out a 38-foot well and were overcome by gas.

The deaths were the first in the 25-year history of the 170-member volunteer company in South Central Fulton County said Assistant Chief Robert Cover.

James F. Chestnut, Jr., 20, and Richard L. Hersey, 40, both of Hustontown, and Thomas L. Lane, 39, of McConnellsburg, died Tuesday, apparently of Methane gas that had built up in the well.

About two dozen other people were treated, including at least six men who inhaled some of the gas.

The firefighters went to the home of Nellie Brown on Monday to pump out her well. She had complained of the odor and suspected that an animal had fallen in and died.

The volunteers used the pump on their truck without success and returned Tuesday afternoon with a portable pump, state police said.

Lane and Larry Traxler of Hustontown entered the well with the pump and took it about halfway down the 3-foot wide shaft. Traxler became dizzy and returned to the surface, but Lane was overcome. Traxler went back for him but lost consciousness. Hersey and Traxler's father, Clair, 41, went in, but Hersey was overcome. Others on the surface then called for additional help.

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What is wrong with this article?

L.I. Landfills are bubbling with dangerous Methane

The gas, which has an odor similar to rotten eggs, reached 100% explosion level at the home, and could have been set off by the slightest spark.

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Most confined space accidents are caused by failure to recognize the hazards!

NIOSH

CRITERIA FOR A RECOMMENDED STANDARD WORKING in CONFINED SPACES

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

65% of fatalities due to atmospheric hazards

Ref. #	Accident Type	Events	Injuries	Deaths
1	Atmospheric condition in CS	80	72	78
2	Explosion or fire in CS	15	49	15
3	Explosion or fire at point of entry	23	20	32
4	Electrical shock or electrocution	11	2	9
5	Caught in / crushed by machinery	10	3	10
6	Engulfment	16	0	16
7	Struck by falling objects	15	15	0
8	Falls inside Confined Space	27	26	1
9	Ingress / egress	33	30	3
10	Insufficient maneuverability	15	15	0
11	Eye injury	10	10	9
12	Other	21	6	15
	Total	276	234	193

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Confined Space Entry Requirements

- ***OSHA 29 CFR 1910.146 "Permit-Required Confined Spaces"***

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National Consensus Standards

- ***Standards developed by NIOSH, ANSI, NFPA, and API referred to as National Consensus Standards***
- ***“National Consensus Standard" means any occupational safety and health standard that has substantial agreement on its adoption***
- ***Unless referenced or incorporated into a governing standard, consensus standards are “Best Practice” advice only***

OSHA 29 CFR 1910.146

- *Permit Required Confined Spaces*
  - *Requirements for practices and procedures to protect employees in general industry from the hazards of entry into permit-required confined spaces*
- *Does not apply to:*
  - *Agriculture*
  - *Construction*
  - *Shipyard employment*



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Vertical vs. Horizontal Standards

- *Vertical standards apply to specific industries or activities*
- *If an employee is working in an industry where a vertical or industry-specific standard applies, then the entry is subject to the vertical standard*
- *If vertical standard not applicable, general industry standard prevails*
- *A list of vertical standards is found in Appendix B of CPL 2.100, p. 8*

List of Vertical Standards

1910.252(a)(4)(i)	1910.261(b)(5)
1910.252(b)(4)(i) to (vii)	1910.268(o)
1910.252(c)(4)	1910.269(e)
1910.252(c)(9)	1910.269(t)
1910.252(c)(10)	1910.272(g)

Construction

- Even though the activity is taking place in a confined space, 1910.146 does not apply to construction
- The activity is regulated by the appropriate vertical standard (e.g. trenching and shoring)
- Construction now has its own proposed CS standard: rule has not been finalized

Construction Exception

- ***29 CFR 1910.146 is not applicable to construction***
- ***However, when construction companies perform work other than construction they are subject to the confined space standard***
- ***For example, maintenance and repair activities, even if performed by a construction company, DO fall under 29 CFR 1910.146***

1910.146 General Requirements

- ***Employers Must:***
  - ***Identify Confined Space hazard areas***
  - ***Inform employees by posting signs where feasible***
  - ***Prevent entry by unauthorized persons***

- ***Employers Must:***
  - ***Establish procedures and practices to allow safe entry (Permit system)***
  - ***Train employees***
  - ***Provide required equipment***
  - ***Control hazards where possible through engineering or work practices***

1910.146 General Requirements

- ***Employers Must:***
  - ***Ensure procedures and equipment necessary for rescue***
  - ***Protect entrants from external hazards***
  - ***Enforce established procedures***

1910.146 General Requirements

- *Employers must provide required equipment:*
  - *Testing and monitoring*
  - *Ventilation*
  - *Communications*
  - *Lighting*
  - *Barriers*
  - *Other personal protective equipment*
  - *Any required rescue and emergency equipment*

1910.146 General Requirements

- ***Options for entry into Permit Required Confined Space (PRCS)***
  - ***Reclassification***
  - ***Alternate entry procedures***
  - ***Permit program***

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Reclassification as non PRCS

- *A PRCS can be reclassified as a non-permit space IF AND ONLY IF the space contains no actual or potential atmospheric hazards, and if all other hazards can be eliminated without entry into the space*
  - *Reclassification requires that no ongoing measures are required to keep the space safe*
  - *The reclassification is valid only as long as the hazard is eliminated*
  - *When hazards are reintroduced into a space, the space becomes a permit space again*

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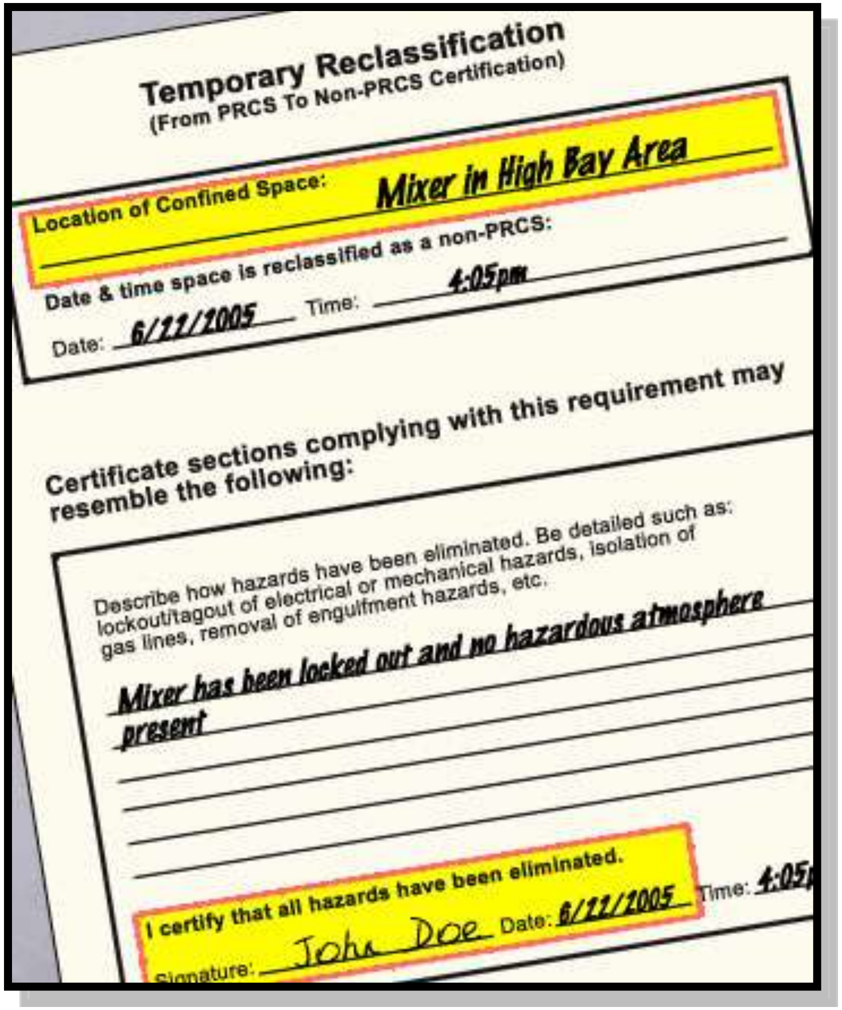
Reclassification as non PRCS

- ***The employer must certify that all hazards from the space have been eliminated and provide that certification to all employees entering that space***

- ***The reclassification is valid only as long as the hazard remains eliminated.***



Elimination of hazardous conditions

- ***In order to reclassify the space, all serious hazards must be eliminated prior to entry***
- ***“Serious” recognized hazard is broadly defined***

Alternate Entry Procedures

- *If a hazard cannot be eliminated, but can be controlled by continuous forced air ventilation, then alternate entry procedures can be used*
- *Paragraph (c)(5)(i) lists the conditions under which alternate entry procedures can be used*
- *Benefits:*
  - *Substantially lower equipment requirements*
  - *No attendants required*
  - *Solo entries permitted*

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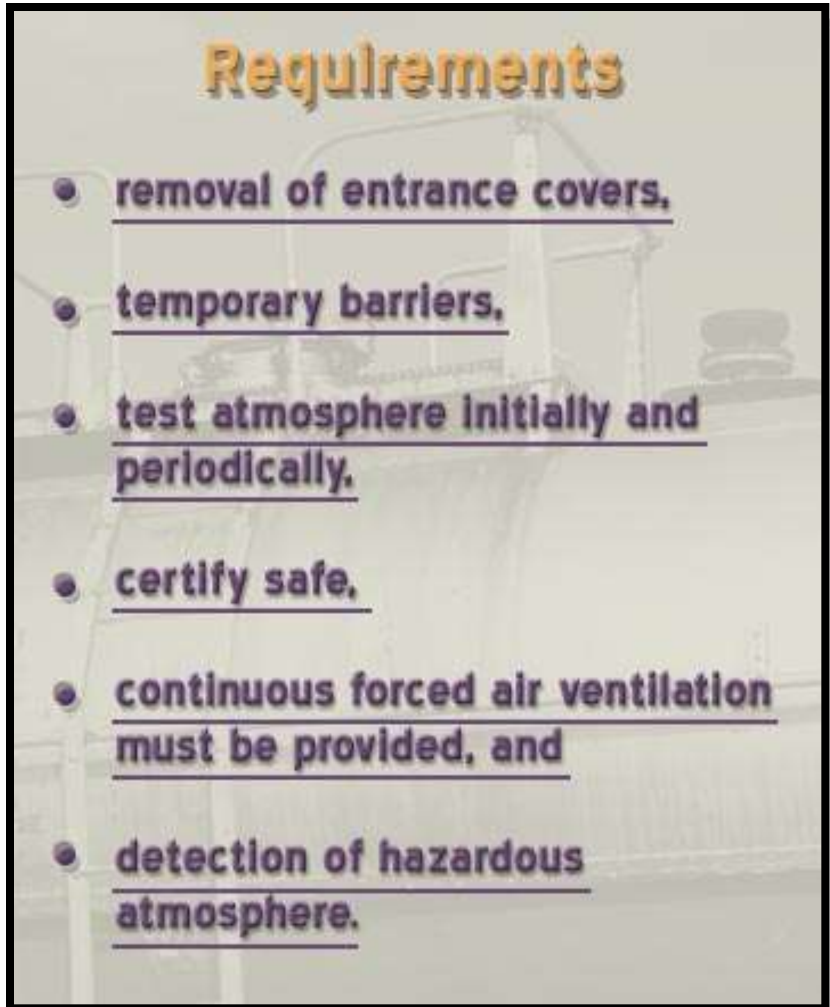
Alternate Entry Procedures

- ***Before employee enters the space, internal atmosphere must be tested with a calibrated, direct-reading instrument for O2, flammable gases and vapors, and for potential toxic air contaminants, in that order***
- ***Once testing is completed, the atmosphere within the space must be periodically tested as necessary to ensure that the continuous forced air ventilation is preventing the accumulation of a hazardous atmosphere***
- ***There may be no hazardous atmosphere within the space whenever any employee is inside the space***



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Alternate Entry Procedures

- ***Continuous forced air ventilation must be used for the entire duration of the entry***
- ***Entry under the alternate entry procedures would not be acceptable if hazards in the space quickly increased if the ventilation were to stop***
- ***Sufficient time must be available for an entrant to safely exit the space if the ventilation stops***

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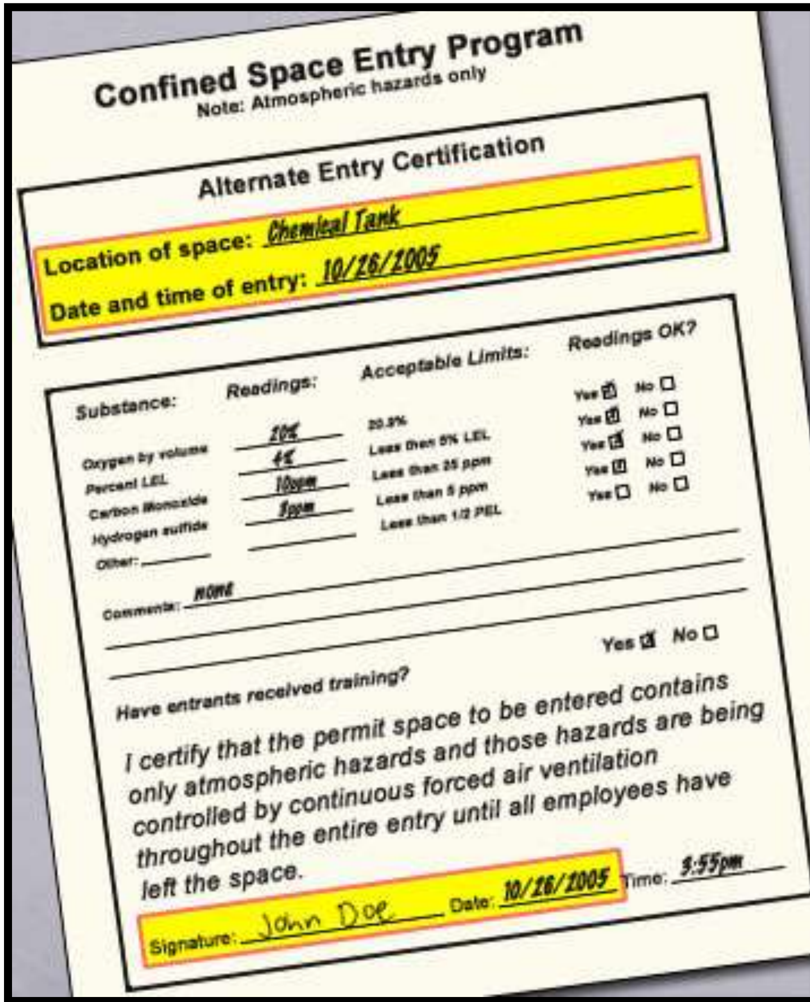
Alternate Entry Procedures in Practice

- ***Some industries, such as telecommunications, have had millions of safe entries into their vaults using ventilation, training and written procedures***
- ***However, many other employers have been cited for using alternate entry procedures inappropriately***

- ***The employer must certify that the space is safe for entry***



Confined Space Entry Program

Note: Atmospheric hazards only

Alternate Entry Certification

Location of space: Chemical Tank

Date and time of entry: 10/26/2005

Substance:	Readings:	Acceptable Limits:	Readings OK?
Oxygen by volume	20%	20.9%	Yes ☑ No ☐
Percent LEL	4%	Less than 5% LEL	Yes ☑ No ☐
Carbon Monoxide	10ppm	Less than 25 ppm	Yes ☑ No ☐
Hydrogen sulfide	5ppm	Less than 5 ppm	Yes ☑ No ☐
Other:		Less than 1/2 PEL	Yes ☐ No ☐

Comments: NONE

Have entrants received training? Yes ☑ No ☐

I certify that the permit space to be entered contains only atmospheric hazards and those hazards are being controlled by continuous forced air ventilation throughout the entire entry until all employees have left the space.

Signature: John Doe Date: 10/26/2005 Time: 3:55pm

Permit Program

- *If hazards cannot be eliminated or controlled, only remaining option is implementation of comprehensive permit space program*
- *Permit specifies means, procedures, and practices for safe entry*
- *Establishes all protective measures have been taken*

CONFINED SPACE ENTRY PERMIT

All copies of permit will remain at job site until project is completed. Permit is good for one shift only.

LOCATION AND DESCRIPTION OF CONFINED SPACE	Process Hall / SPC Mixer		
PURPOSE OF ENTRY	Clean Tank	Date	1-14-98
DEPARTMENT	SWOG	Time	12:15
PERSON IN CHARGE OF WORK	Jim Mayberry		

AUTHORIZED ENTRANTS	TIME IN	TIME OUT
Jim Mayberry	1:45	3:20
Jeff Berry	1:45	3:20
Danny Green	1:45	3:20

If number of entrants exceed available sign-in space, the RWP sign-in form shall be used to track entrants in and out of the space.

SPECIAL REQUIREMENTS	YES	NO	Special Requirements (cont.)	YES	NO
Lockout/Tagout	X		Escape Harness Lifeline		X
Lines Broken-Capped or Blanked		X	Emergency Escape Unit		X
Purge-Flush and Vent		X	Fire Extinguisher	X	
Ventilation	X		Protective Clothing	X	
Secure Area	X		Hot Work		X
Communications Describe: N/A		X	Respirator Type: Dust Mask	X	

ATMOSPHERIC TESTING (Valid for one 8-hour turn only)	P.E.I. (Permissible Exposure Limit)	Yes	No	Test Results			
				12:25			
% of Oxygen	below 19.5% or above 23%			19.0%			
% of L.E.L.	Any % over 10		X				
Carbon Monoxide	Above 35 ppm		X				

Name of Tester Jim Mayberry

Note: Continuous/periodic tests shall be established before beginning job.

INSTRUMENTS USED NAME	TYPE	IDENT. NO.
Mini Gard III	air sampler	

ATTENDENTS	SIGNATURE
Jeff Berry	Jeff Berry
Danny Green	Danny Green

EMERGENCY RESPONSE NOTIFICATION NUMBERS: SAFETY 1385\1382\1384

AMBULANCE: 911 FIRE: 911 RESCUE: 911

ENTRY SUPERVISOR AUTHORIZATION Jim Mayberry DATE 1-14-98

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Emergency Procedures

- ***Must reflect the specific dangers of the confined space***
- ***Attendant should not enter confined space until help arrives***
- ***Two out of three workers killed in confined space accidents are would-be rescuers!***

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Rescue

- ***Self rescue: Entry procedures should aim at getting workers out under their own power BEFORE conditions become life threatening***
- ***Non-entry rescue: Second best approach is to use procedures that allow rescue without having to enter the space***
- ***Rescuer entry: Least desirable, highest risk, most equipment and personnel intensive approach***

Work in confined spaces can produce dangerous atmospheric conditions

- *Welding*
- *Painting*
- *De-greasing*
- *Scraping*
- *Sandblasting*
- *Mucking*
- *Inerting*

Monitor and ventilate continuously

- *Many accidents result from changes in the CS atmosphere which occur after the entry is initiated*
- *Monitoring determines the air is safe, ventilation keeps it that way*
- *The only way to pick up changes before they become life threatening is to monitor continuously!*

Before entry it is mandatory to determine that the CS atmosphere is safe!

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Miner's Canary

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Japanese Waltzing Mouse

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Flame Safety Lamp

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State-of-the-Art CWA detector: “Devil Bird”

- ***Chemical warfare specialist takes care of his pigeon in central Iraq***
- ***The pigeon, called "Devil Bird," is used to detect chemical attacks***

Source: MSNBC “Images of War”

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Capabilities and Limitations of Multi-sensor Instruments

- ***First line screening tool for CS, HAZMAT and WMD response***
- ***Many brands available (BW, MSA, ISC, GfG, RAE, etc.)***
- ***Typically 1 – 6 sensors: O2 / LEL / PID / NDIR and / or 1 to 3 substance-specific toxic gas sensors***
- ***Many new types of sensors available for use in these instruments***

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Choosing the Best Gas Detector

- ***"Best" gas detector doesn't come from any one manufacturer; it's the instrument that best fulfills the requirements for <u>your</u> monitoring program***

- ***Ways in which gas detectors are used can vary widely between different programs***

- ***The instrument that provides the best service and value for one program may not be the best choice for another***

Capabilities and Limitations of Multi-sensor Instruments

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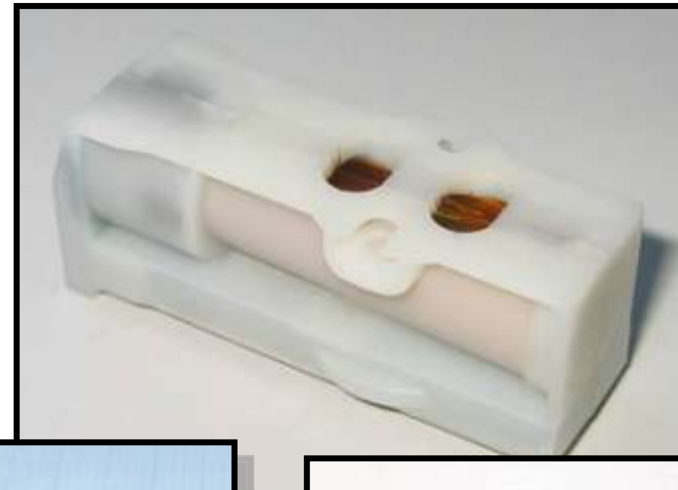
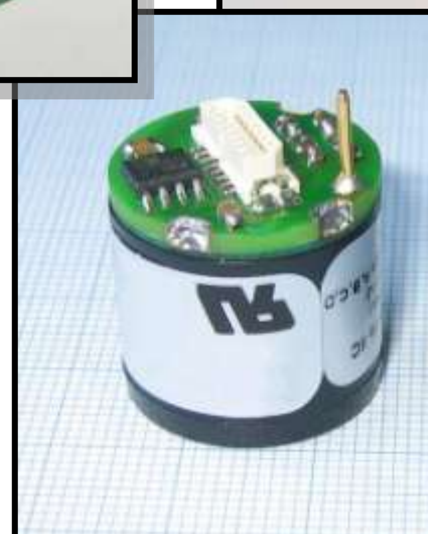
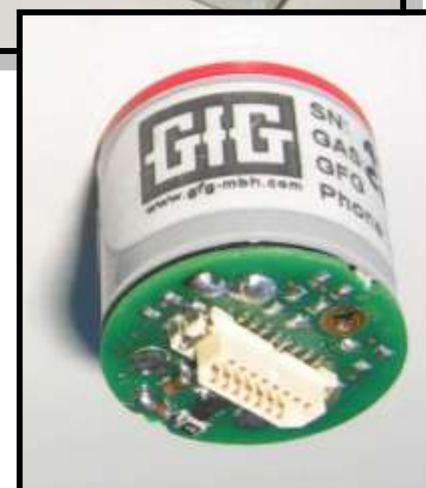
Increasingly wide variety of sensors to choose from

- *Available sensors include:*
  - *O_2*
  - *%LEL*
  - *Infrared %LEL*
  - *Infrared % volume*
  - *CO*
  - *H_2S*
  - *COSH*
  - *PID (VOC)*
  - *Infrared CO_2*
  - *SO_2*
  - *Cl_2*
  - *ClO_2*
  - *O_3*
  - *HF*
  - *NH_3*
  - *H_2*
  - *PH_3*
  - *HCN*
  - *NO*
  - *NO_2*
  - *HCL*
  - *ETO*







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Three basic kinds of atmospheric hazards

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

Measuring Oxygen (Deficiency and Enrichment)

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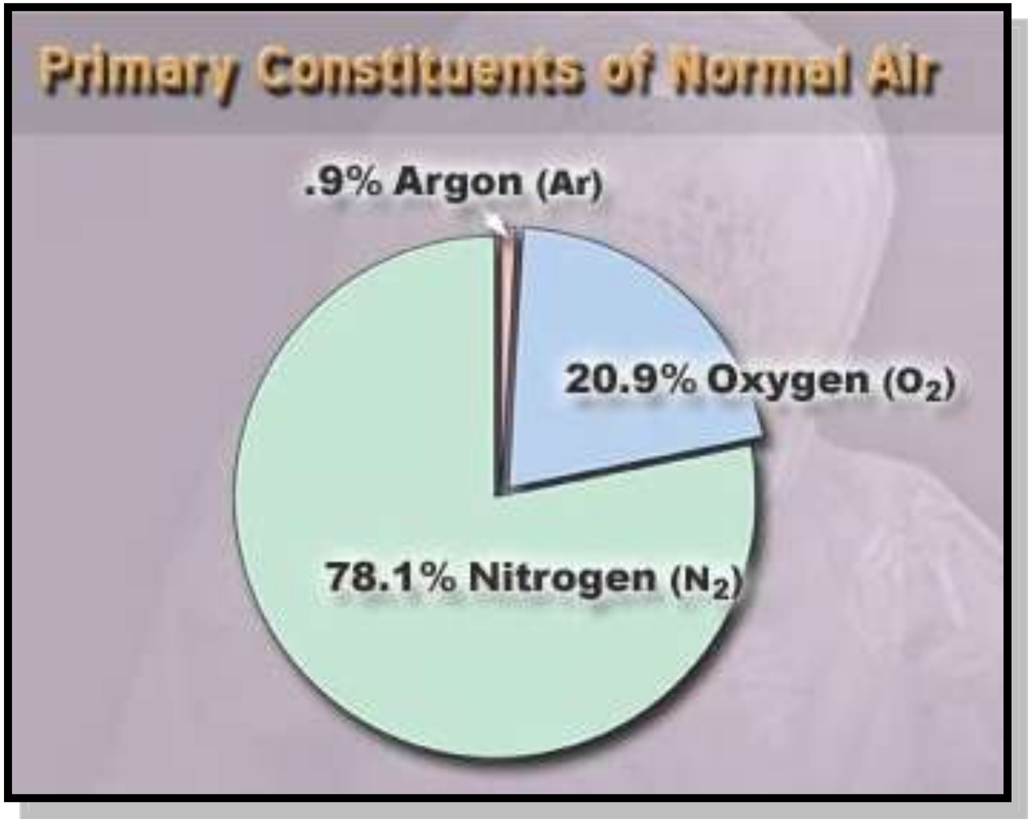
4OX
OXYGEN
CiTicel

Composition of fresh air

- *78.1 % Nitrogen*
- *20.9 % Oxygen*
- *0.9 % Argon*
- *0.1 % All other gases*
    - *Water vapor*
    - *CO_2*
    - *Other trace gases*



Oxygen *Deficiency*

- ***Most widely accepted definition: Air is oxygen deficient whenever concentration is less than 19.5%***

Definitions of Oxygen-Deficient Air

29 CFR 1910.146 (PRCS)	< 19.5%
29 CFR 1910.134 (Respiratory Protection)	< 19.5%[1]
ANSI Z117.1-1995 (Confined Spaces)	< 19.5%
ANSI Z88.2-1992 (Respirator Practices)	16.0%[2]
ACGIH (TLV Booklet)	18.0%

Notes:

[1] Oxygen content below 16% at sea level is considered IDLH -- Oxygen deficient.

[2] Oxygen partial pressure <122 mmHg. Confined space with <20.9% oxygen is IDLH, unless source of oxygen reduction is understood and controlled.

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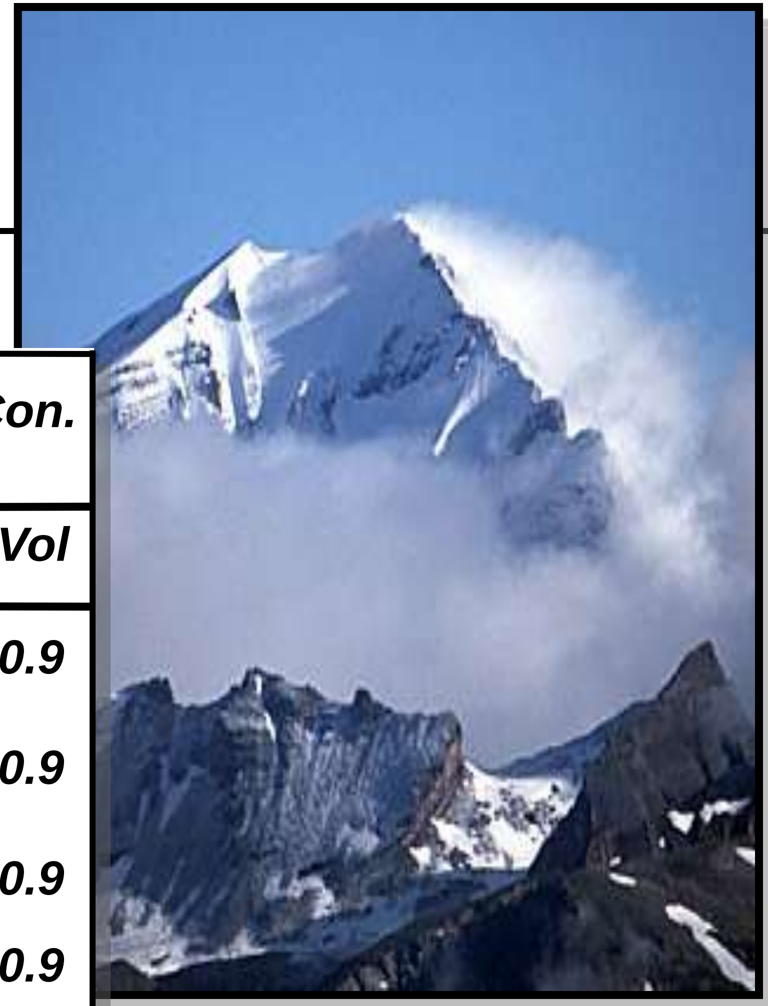
Partial Pressure O_2 vs. % Vol at Varying Altitudes



Height		Atm. Pressure	PO_2		Con.
feet	meters	mmHg	mmHg	kPa	%Vol
16,000	4,810	421.8	88.4	11.8	20.9
10,000	3,050	529.7	111.0	14.8	20.9
5,000	1,525	636.1	133.3	17.8	20.9
3,000	915	683.3	143.3	19.1	20.9
1,000	305	733.6	153.7	20.5	20.9
0	0	760.0	159.2	21.2	20.9

19.5% O_2 at sea level = 18 kPa

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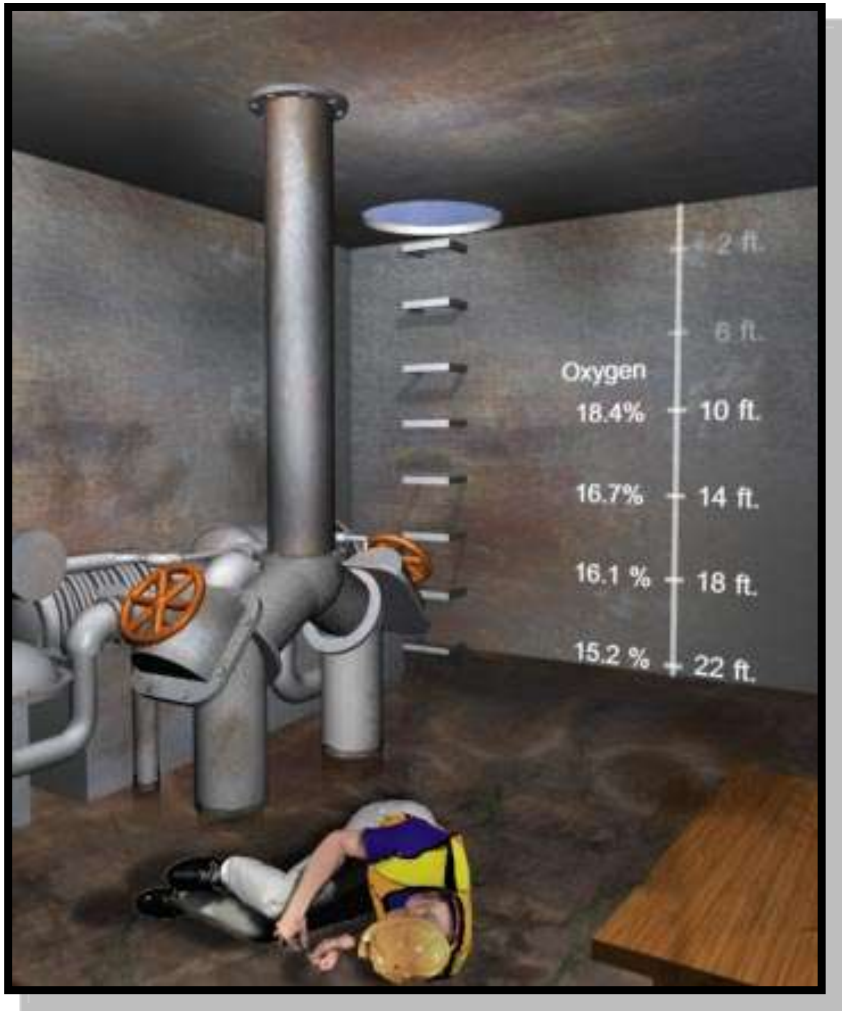
Oxygen Deficiency

- *Occurrence associated with:*
  - *Confined spaces*
  - *Unventilated cellars*
  - *Sewers*
  - *Wells*
  - *Mines*
  - *Ship holds*
  - *Tanks*
  - *Enclosures containing inert atmospheres*

Causes of Oxygen Deficiency

- *Displacement*
- *Microbial action*
- *Oxidation*
- *Combustion*
- *Absorption*



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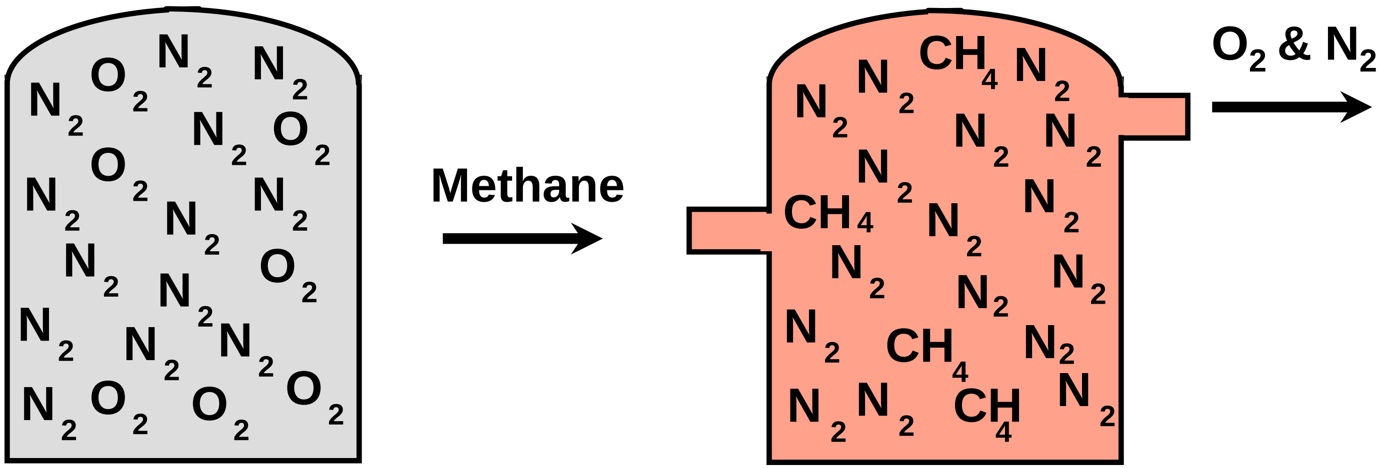
Oxygen displacement in a fully enclosed vessel

- ***For every 5% total volume displaced, O2 concentration drops by about 1%***
- ***If 5% of the fresh air in a closed vessel is displaced by methane, the O2 concentration would be about 19.9%***
- ***The atmosphere would be fully explosive while the O2 concentration would still be above the normal alarm setting!***



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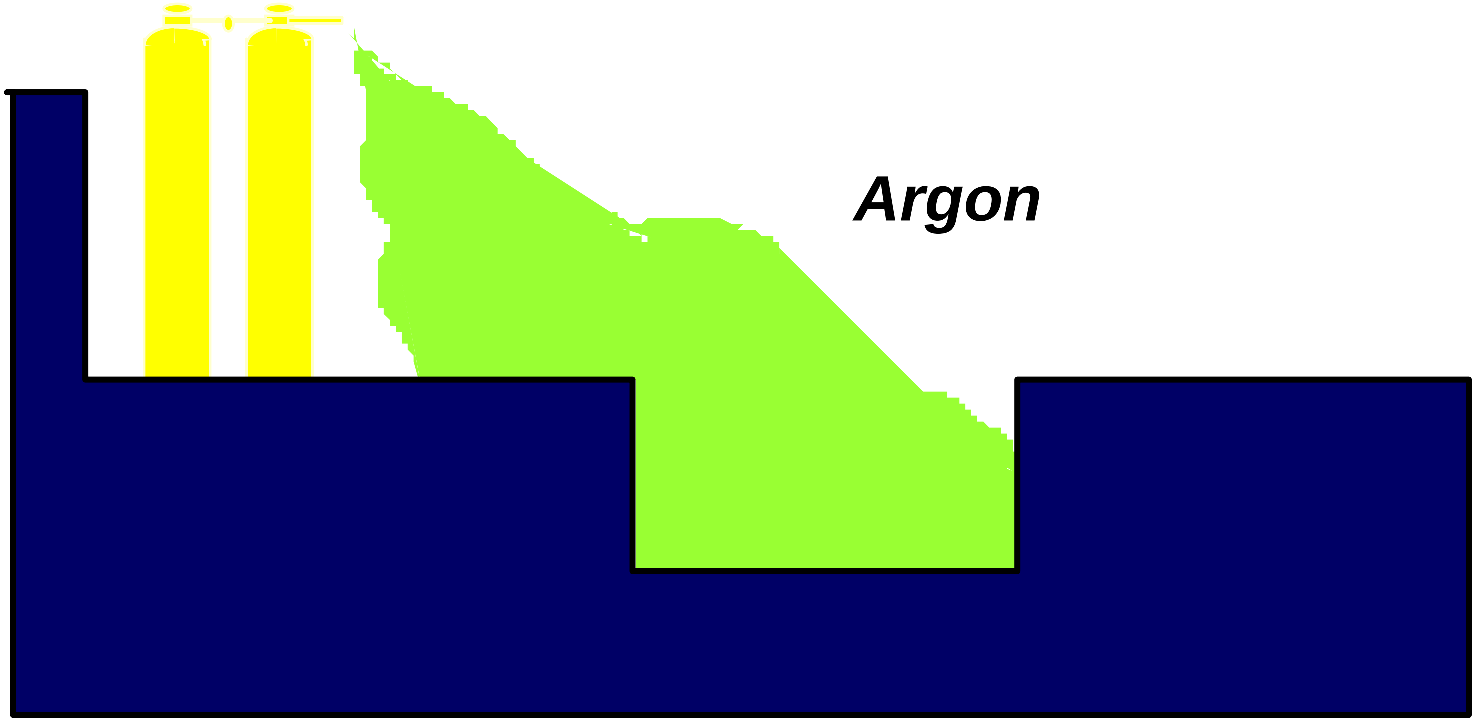
Oxygen displacement in an open topped confined space



Symptoms of Oxygen Deficiency

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

Fuel Cell Oxygen Sensors

- ***Sensor generates electrical current proportional to the O_2 concentration***
- ***Sensor used up over time (usually last one to three years)***
- ***Oxygen reduced to hydroxyl ions at cathode:***

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

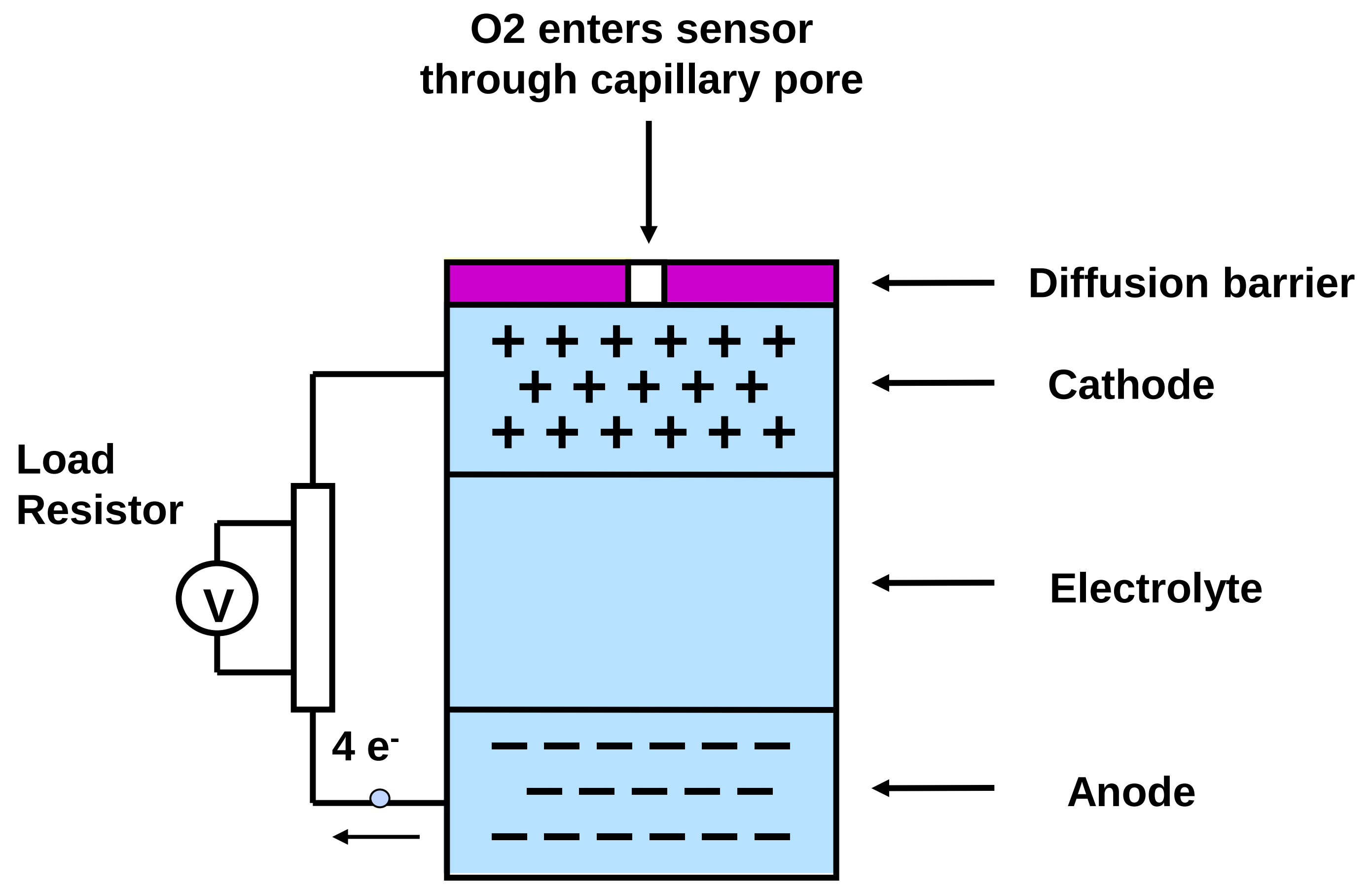
- ***Hydroxyl ions oxidize lead (anode):***

$$2Pb + 4OH^- \longrightarrow 2PbO + 2H_2O + 4e^-$$

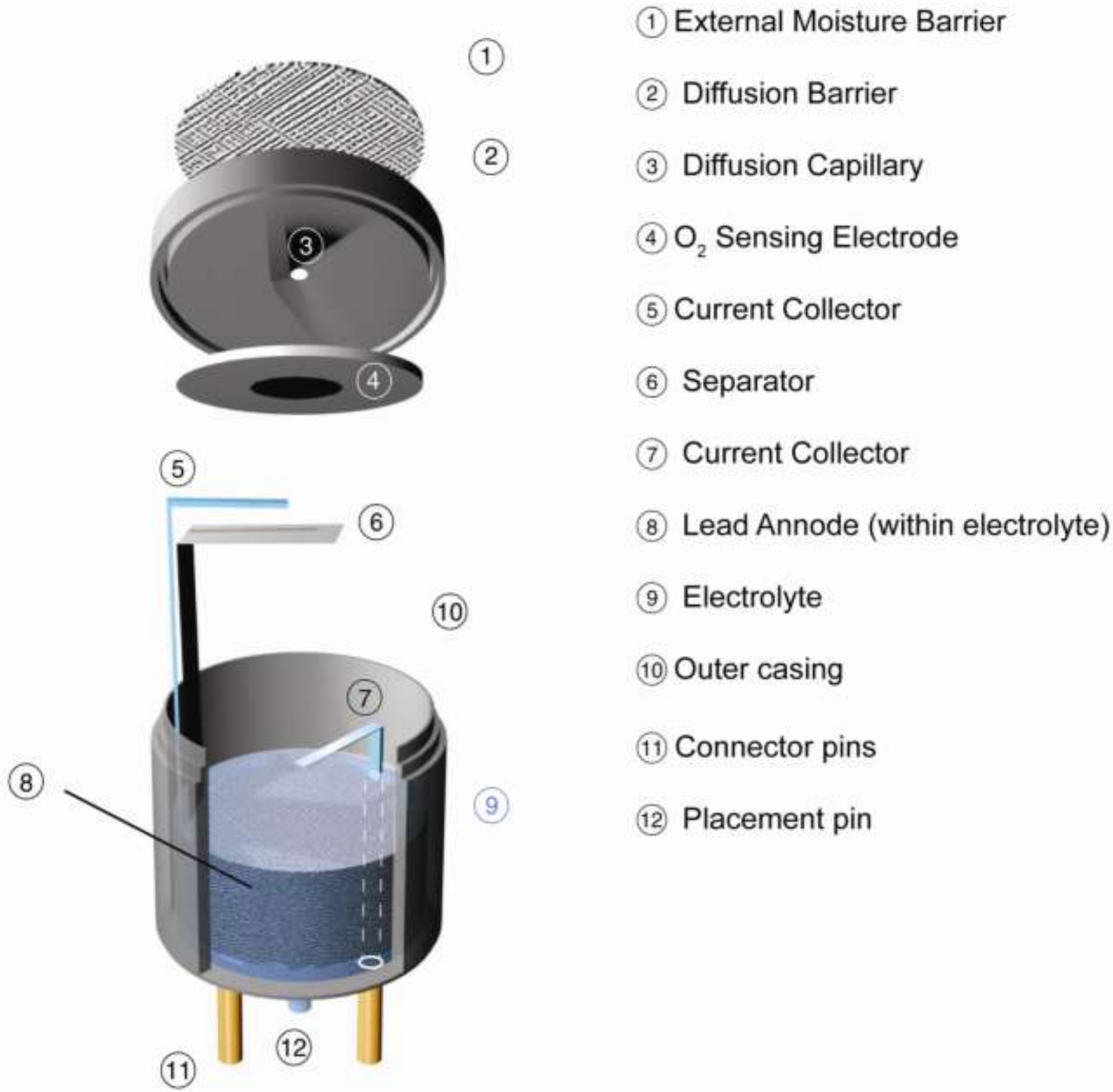
- ***Overall cell reaction:***

$$2Pb + O_2 \longrightarrow 2PbO$$

Oxygen Sensor (Simplified)



Major Components of an Oxygen Sensor



Oxygen Sensor Structure

Capillary Pore Benefits

- *True percent by volume sensor*
- *Not influenced by changes in pressure due to:*
    - *Barometric pressure*
    - *Pressurized buildings*
    - *Altitude*

Capillary pore (located under external moisture barrier filter)

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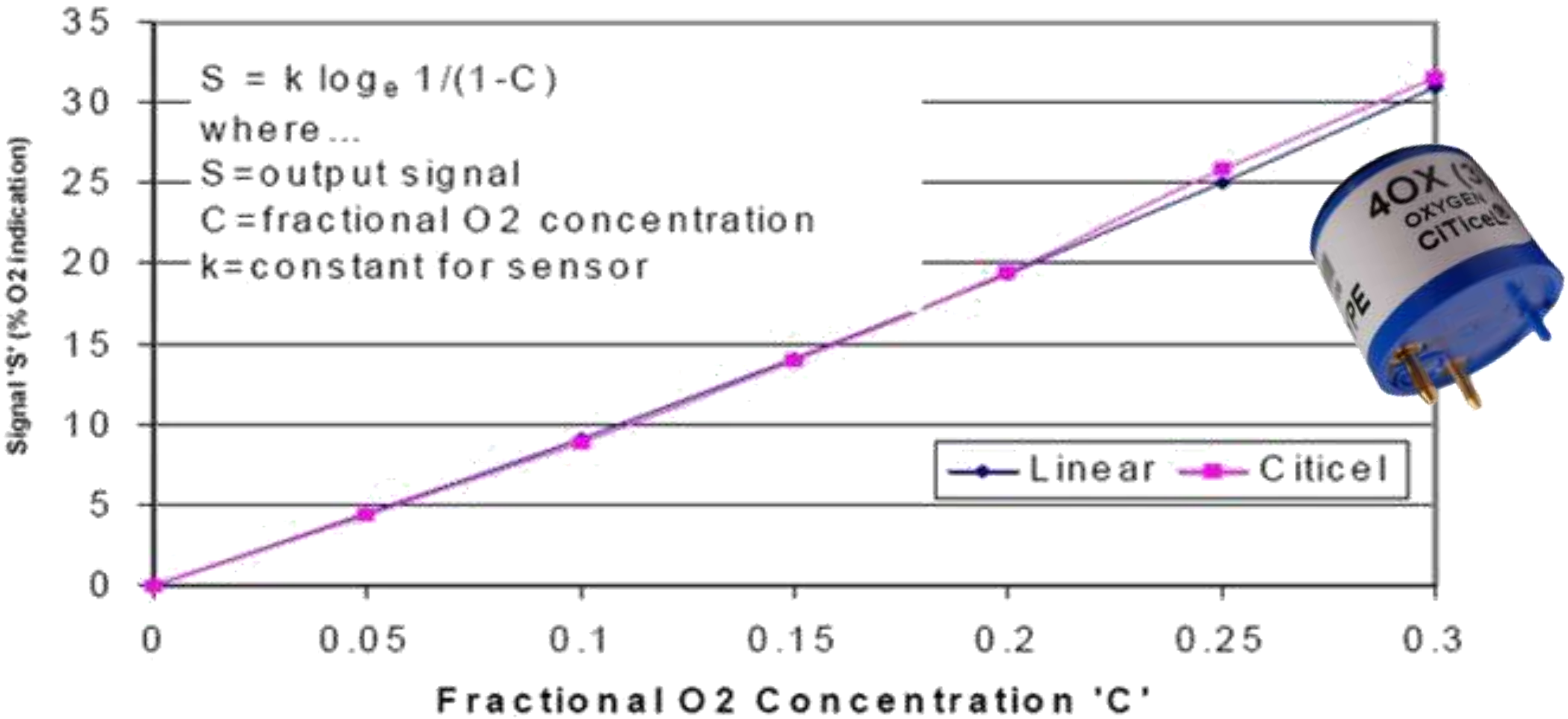
O_2 sensor output as function of concentration



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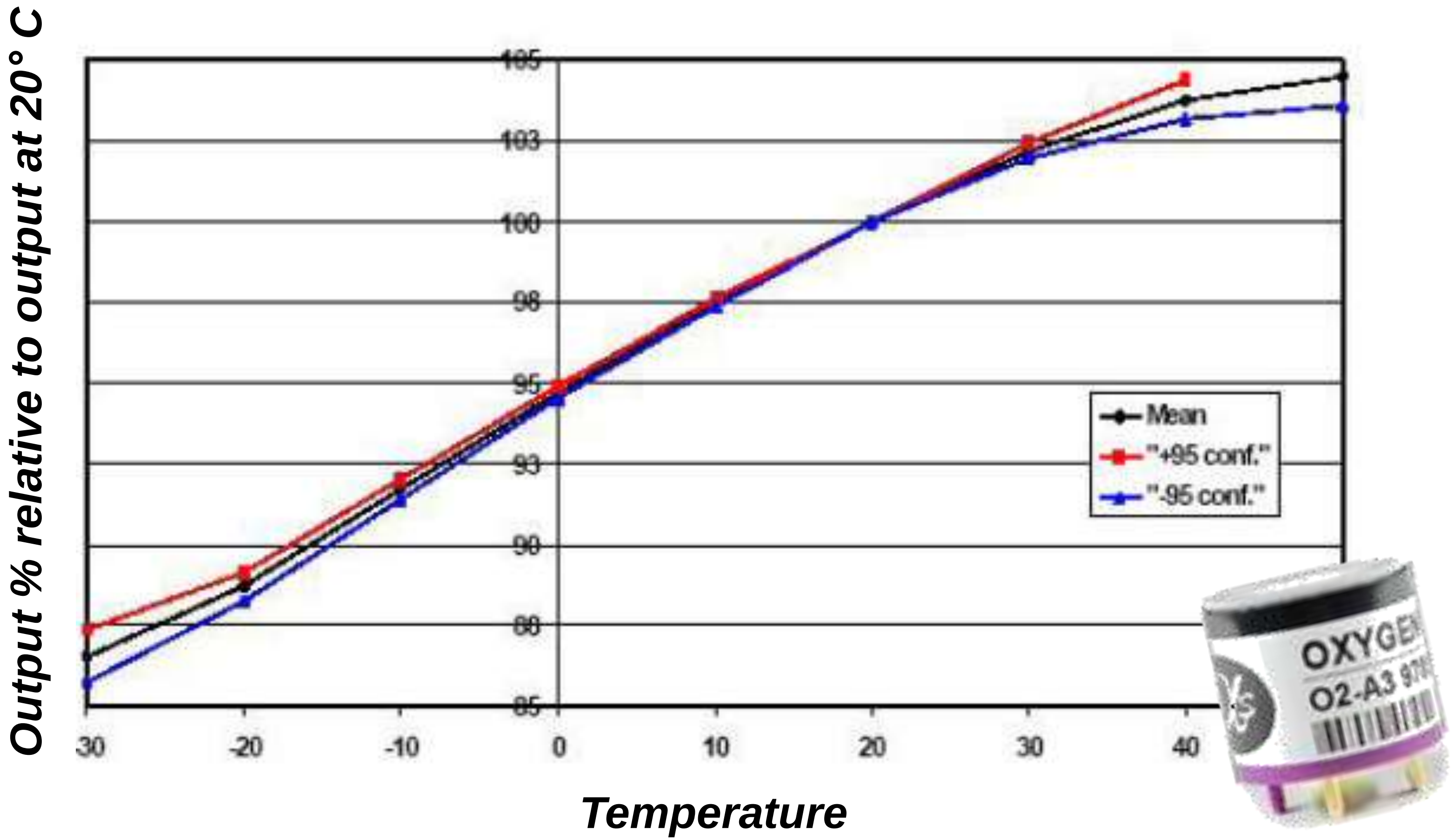
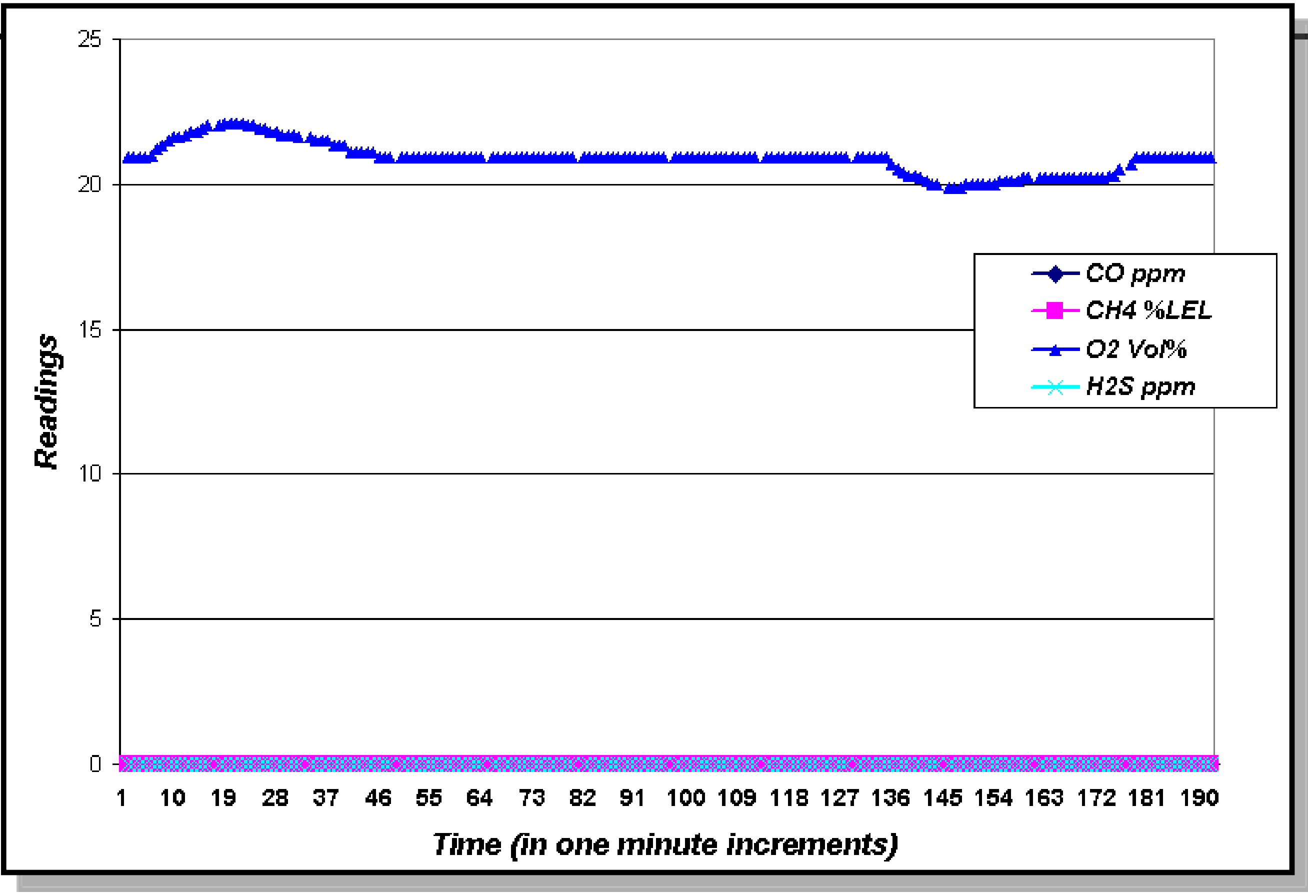
O_2 sensor output as function of the ambient temperature



Actual readings of G450 cycled from +20°C to –20°C then back to +20°C

- ***While temperature dropping O2 readings slightly high***
- ***Once stabilized at –20°, readings return to 20.9%***
- ***As chamber returned to room temperature O2 readings slightly depressed***
- ***Once stabilized at room temperature, O2 readings return to 20.9%***
- ***Other sensor readings (LEL, CO, H2S) unaffected by temperature***



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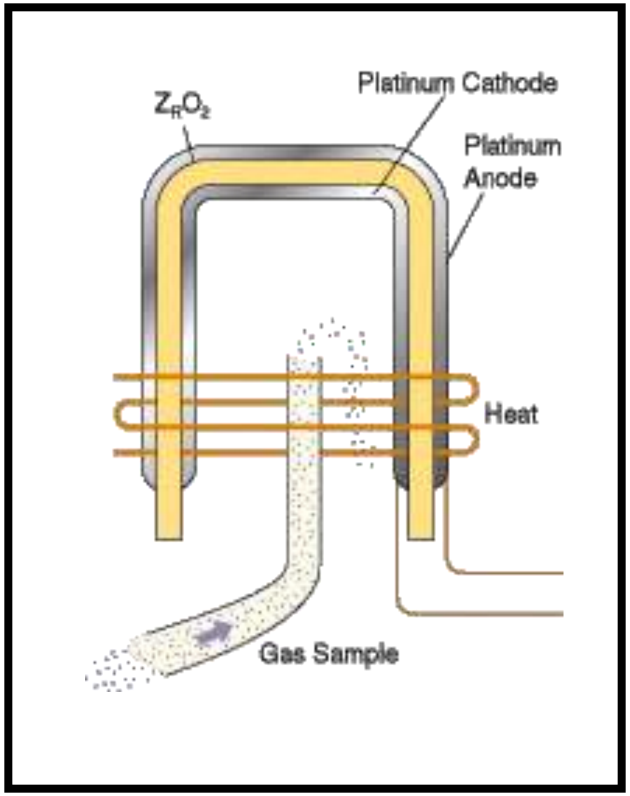
O_2 Sensor Failure Mechanisms

- *Lower current output:*
  - *All available surface of Pb anode converted to PbO_2*
  - *Electrolyte poisoned by exposure to contaminants*
  - *Electrolyte leakage*
  - *Desiccation*
  - *Blockage of capillary pore*
- *Higher current output:*
  - *Short-term upward “ramping” readings due to cracks, tears or leaks allowing O2 direct access to anode*
  - *Contraction of “bubbles” in electrolyte due to rapid temp change*
- *Readings do not change:*
  - *Loss (reduction) in platinum content in current collector and / or sensing electrode*
  - *Partial occlusion of capillary pore*
- *Test sensor before each day’s use!*

Zirconium Oxide "High Temperature" O_2 Sensors

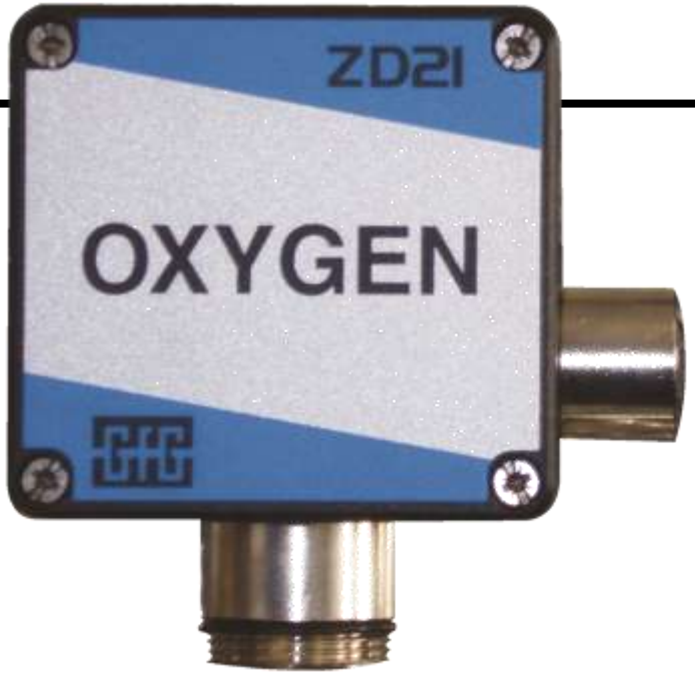
- *Sensing element is porous ceramic zirconium oxide lattice stabilized with yttrium*
- *Coated on inside and outside with porous platinum that serves as electrodes*
- *At high temperatures (above 650 degrees C) openings in lattice permit passage of O2 ions*
- *Passage of O2 ions through lattice produces voltage across the Pt electrodes proportional to the O2 concentration*
- *Voltage increases as O2 concentration decreases*
- *Sensor produces no voltage when O2 concentration same on both sides of the lattice*



GfG Instrumentation

Zirconium Oxide O_2 Sensors

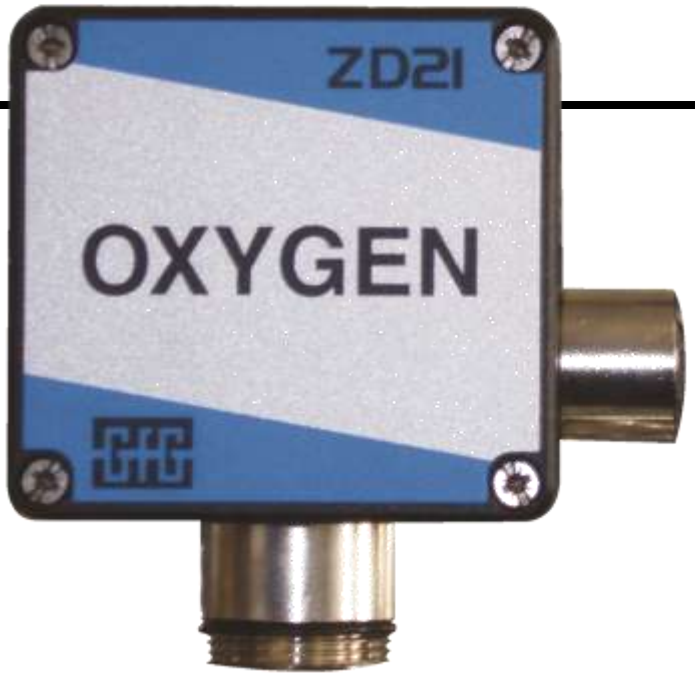
- *Long sensor life (5 years or longer)*
- *Wide temperature range*
- *Multiple ranges: (0 to 2%, 5%, 96% volume and 0 to 1,000 ppm)*
- *Fast response time*
- *Not affected by temperature, humidity, or pressure changes*
- *Not damaged by CO_2 exposure*
- *Low cost of ownership*
- *1 year calibration*



GfG Instrumentation

Zirconium Oxide Failure Mechanisms

- ***Zirconium oxide sensors are very resistant to damage***
  - ***As long as sensing element is under power it is very difficult to harm***
  - ***While under power sensing element is heated to 650°***
  - ***At this temperature contaminants are pyrolized (cooked off) before they can cause damage***
  - ***If it is necessary to cut power to the sensors, the protective cap (supplied with the transmitter) should be placed over the sensor to prevent exposure to contaminants***



GfG Instrumentation

Oxygen Pump (Lead Free) O2 Sensors

- *European Union (EU) "Reduction of Hazardous Substances" (ROHS) directive restricts use of certain substances in new electronic equipment*
  - *Pb, Cd, Hg, hexavalent chromium, polybrominated biphenyls (PBB's), and polybrominated diphenyl ethers (PBDE's)*
- *Lead containing "fuel cell" sensors specifically excluded (for the time being)*
- *"Oxygen pump" sensors are lead-free alternative to fuel cell sensors*
- *Oxygen passively diffuses into polymer (catalyst) substrate*
- *Power from instrument battery used to "pump" the oxygen back out*

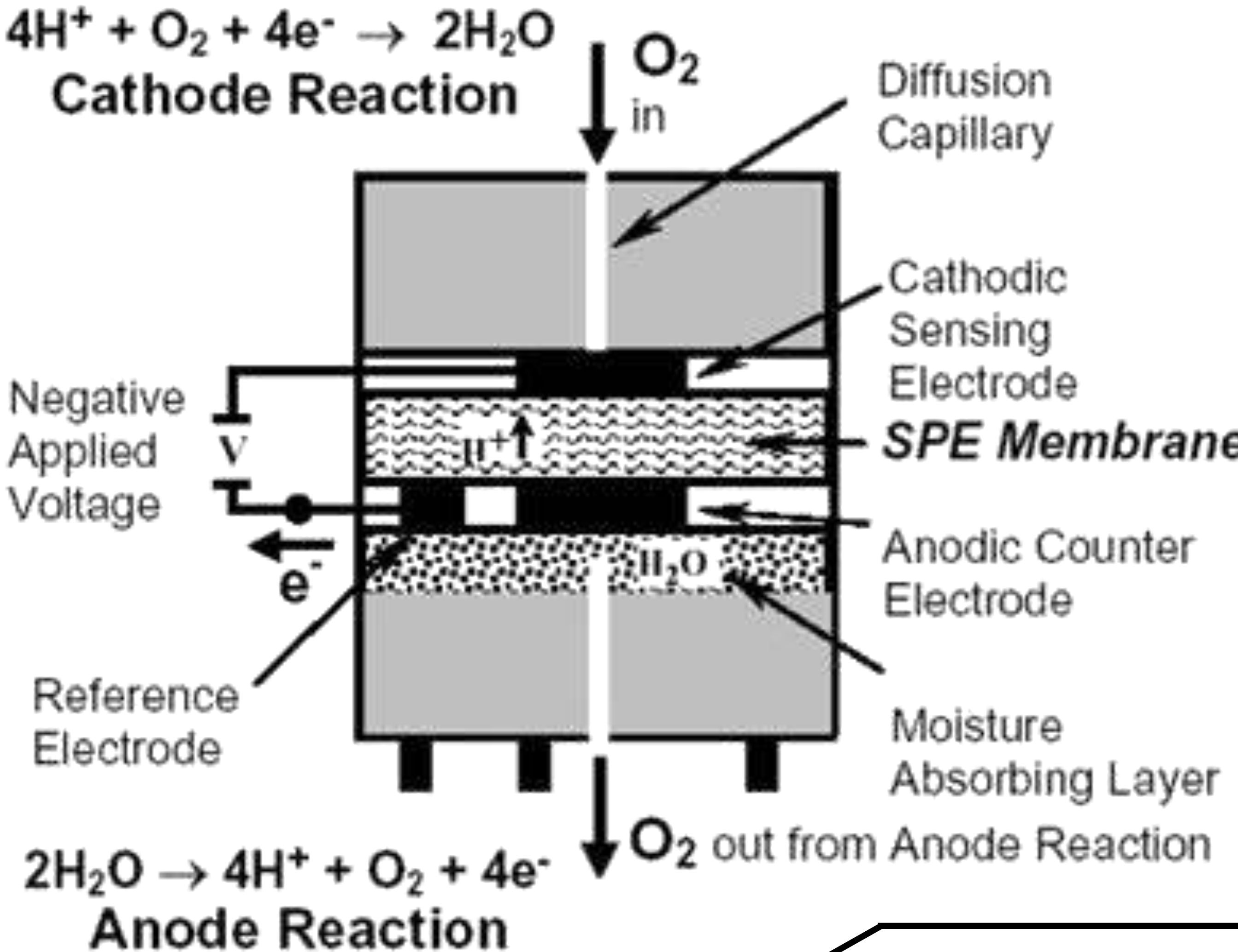
Oxygen Pump Detection Principle

- *Oxygen passively diffuses into polymer (catalyst) substrate*
- *Power from instrument battery used to "pump" the oxygen back out*
- *Reactions: Oxidation / Reduction of target gas by catalyst*

  Sensing: $O_2 + 4H^+ + 4e^- \rightarrow 2\ H_2O$

  Counter: $2\ H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- *Oxygen generated on counter electrode*
- *Amount electricity required to remove reaction product and return sensor to ground state (by generating O_2 at counter electrode) proportional to concentration of oxygen present*
- *Only thing consumed is electricity from instrument power supply*
- *Advantages:*
  - *Non-consuming detection technique (sensor does not lose sensitivity or consume itself over time)*
- *Disadvantages / concerns:*
  - *Detection reaction may be influenced by shifts in humidity*
  - *Sensor is net consumer of electricity (drain on power supply)*
  - *Important to ensure that reaction product (H2O) is removed from sensor*

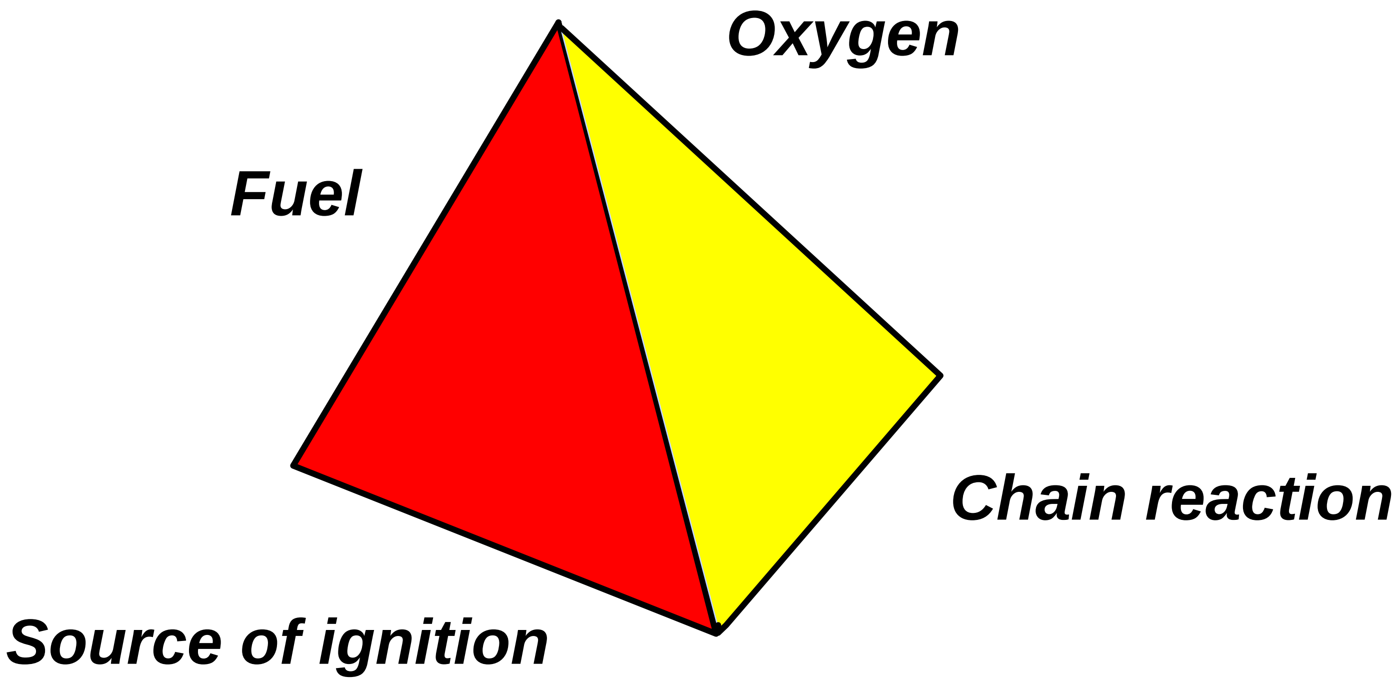
SPE Oxygen Pump Sensor



GfG Instrumentation

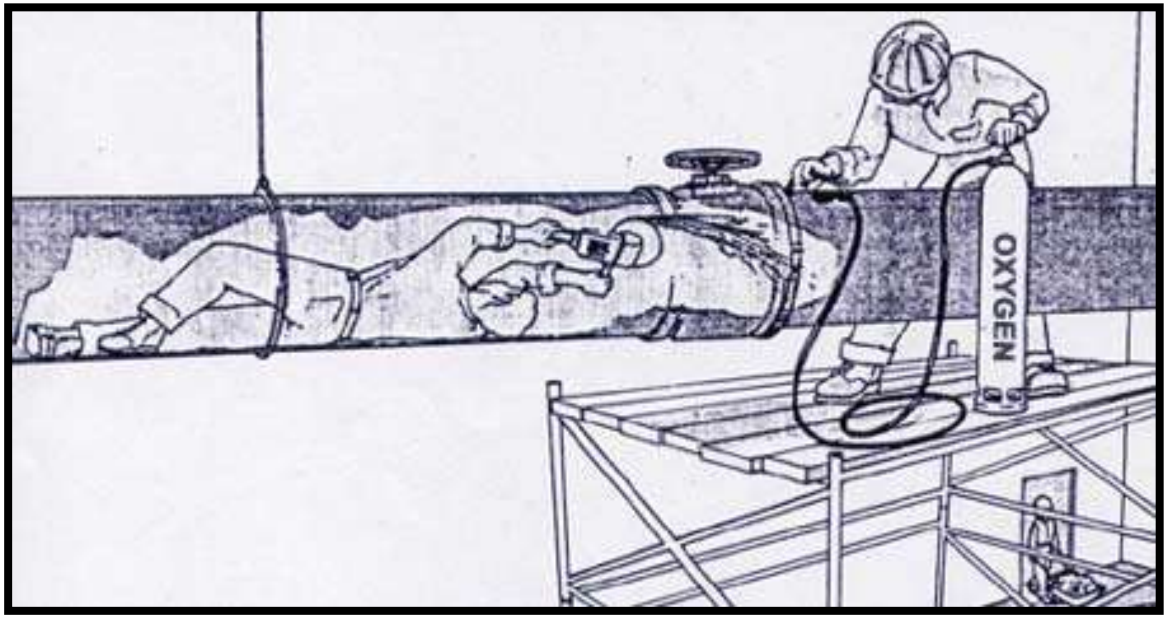
Explosive or Flammable Atmospheres

GfG Instrumentation


Oxygen
Fuel
Chain reaction
Source of ignition

Oxygen Enrichment

- ***Proportionally increases the rate of many chemical reactions***
- ***Can cause ordinary combustible materials to become flammable or explosive***



GfG Instrumentation

Oxygen Enrichment

- ***Many standards (including USA 29 CFR 1910.146) Specify 23.5 % as oxygen enriched***
  - ***Other codes (such as USA 29 CFR 1915 and NFPA guidelines) are more stringent***
  - ***More conservative approach is to use 22.5 % as hazardous condition threshold***

Lower Explosive Limit (L.E.L.)

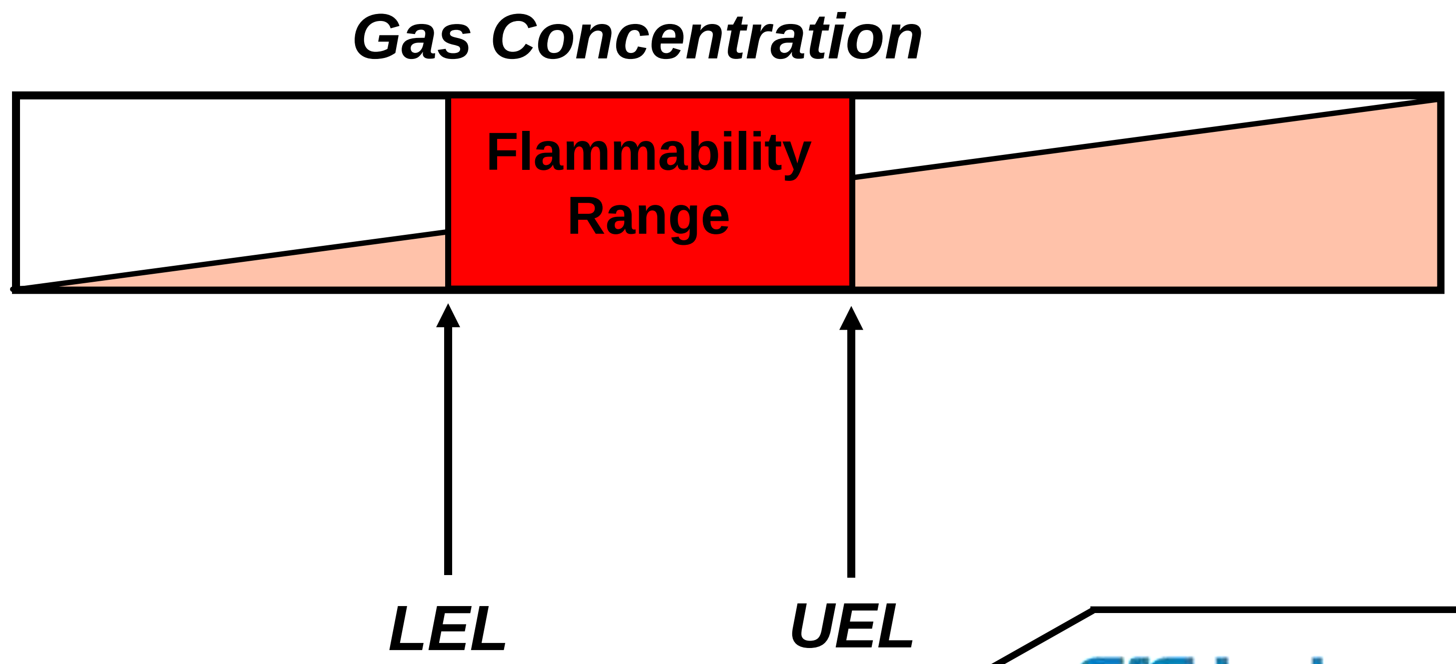
- ***Minimum concentration of a combustible gas or vapor in air which will ignite if a source of ignition is present***

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*

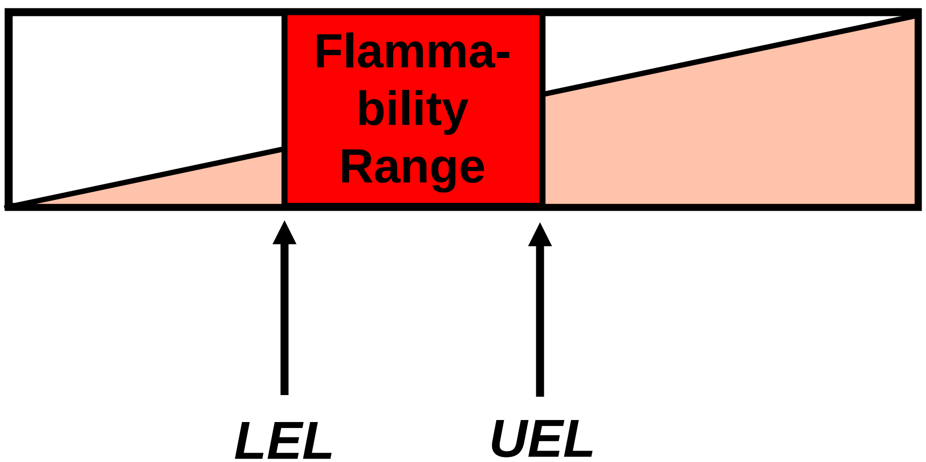
GfG Instrumentation

- *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*



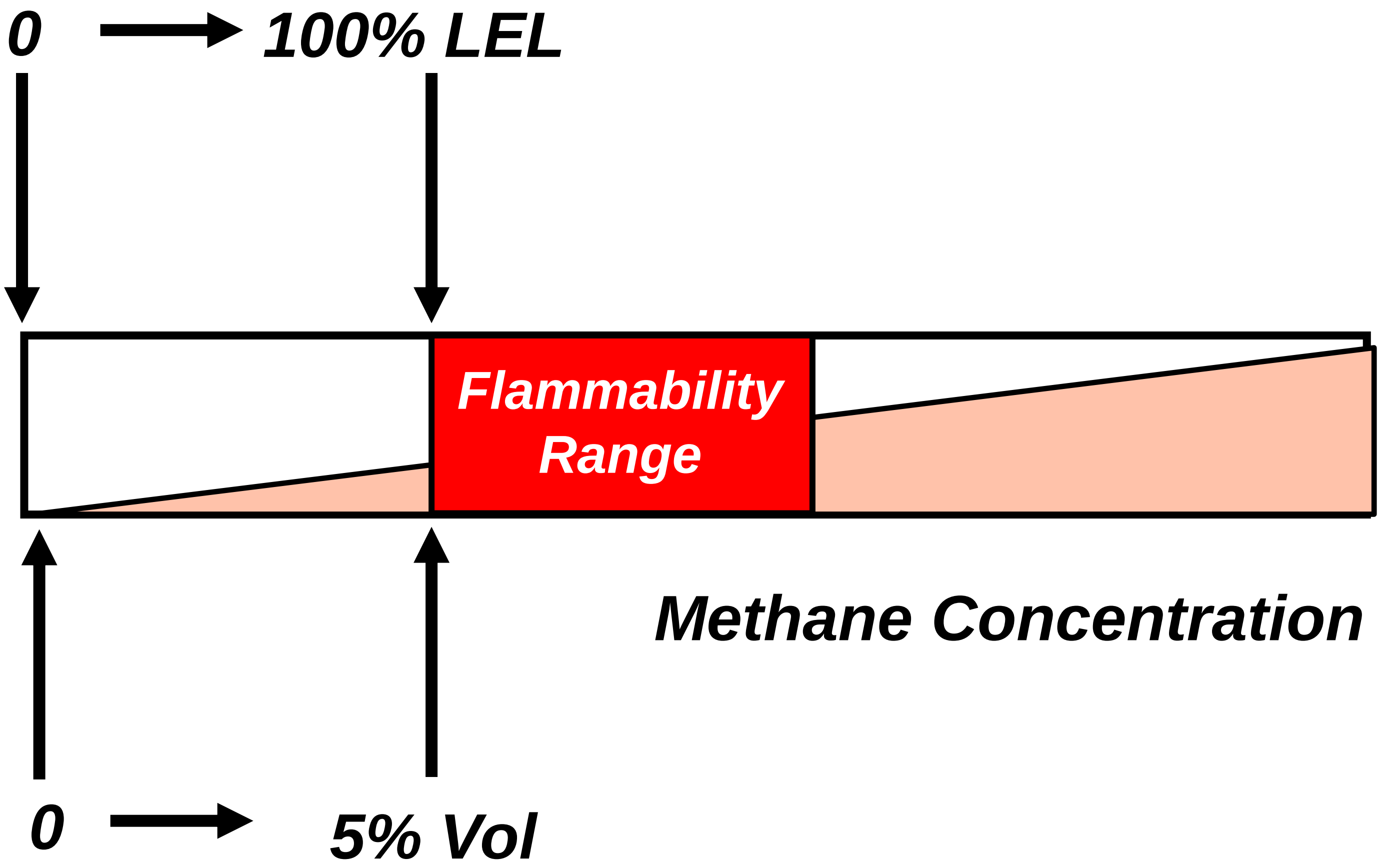
Common Flammability Ranges

Gas Concentration



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

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



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

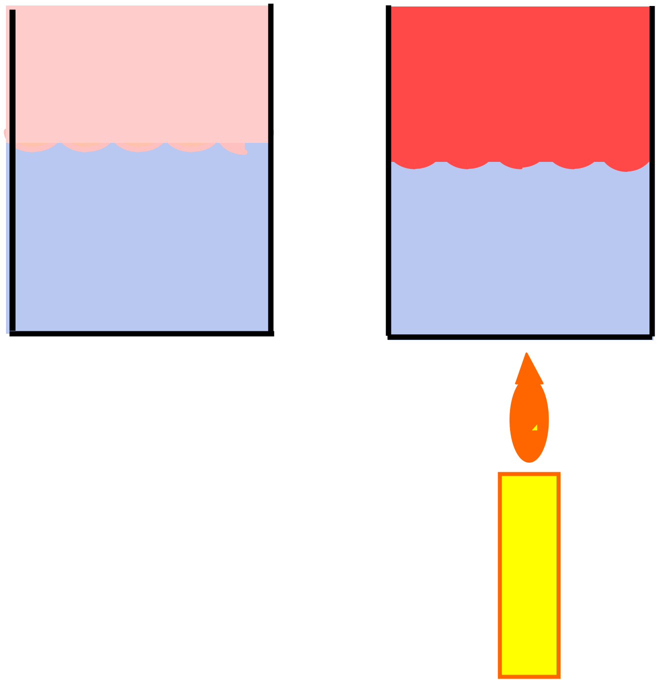
- *A combustible hazard exists whenever the combustible gas concentration exceeds 10% LEL*
- *This is the general hazardous condition threshold, NOT the concentration that should always be used for the LEL alarm set-point*
- *According to the original preamble to 1910.146, if Alternate Entry Procedures 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*

Vapors

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

Vaporization is a function of temperature

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



GfG Instrumentation

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

GfG Instrumentation

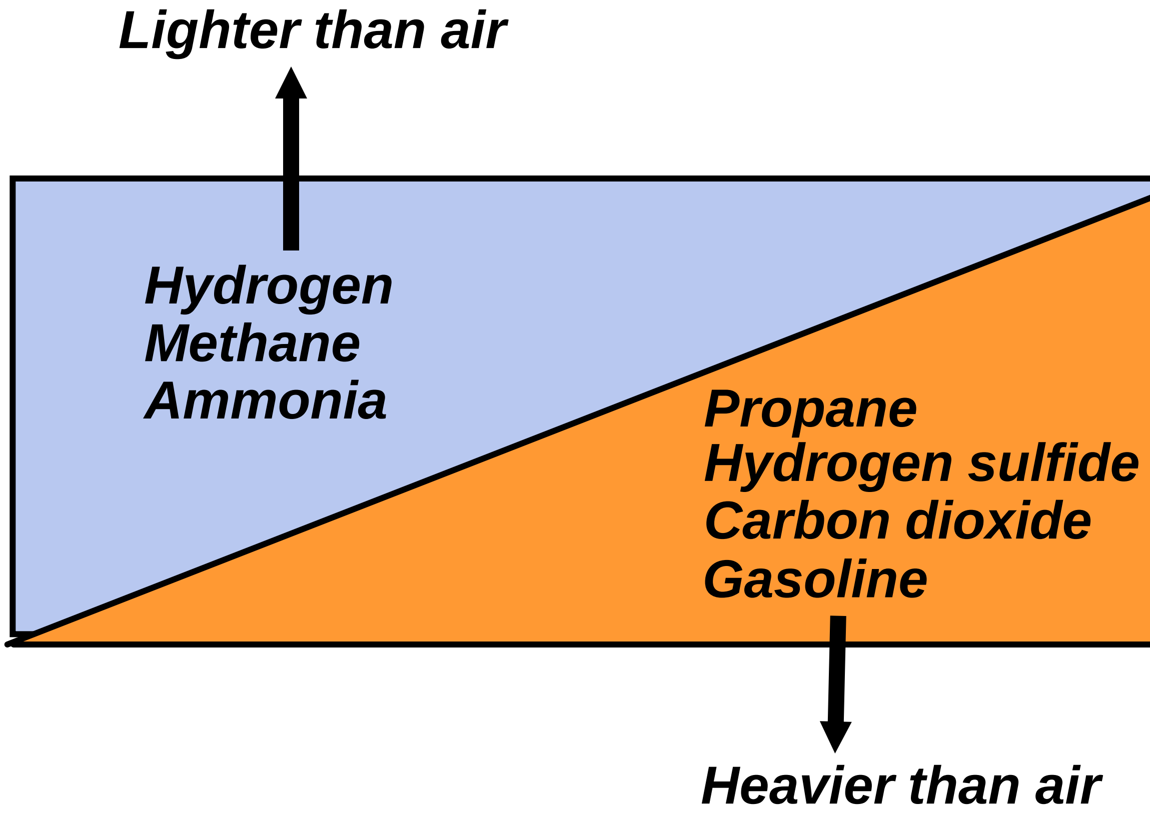
Flammable and combustible liquid classifications (OSHA 29 CFR 1910.106)

	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		

Vapor Density

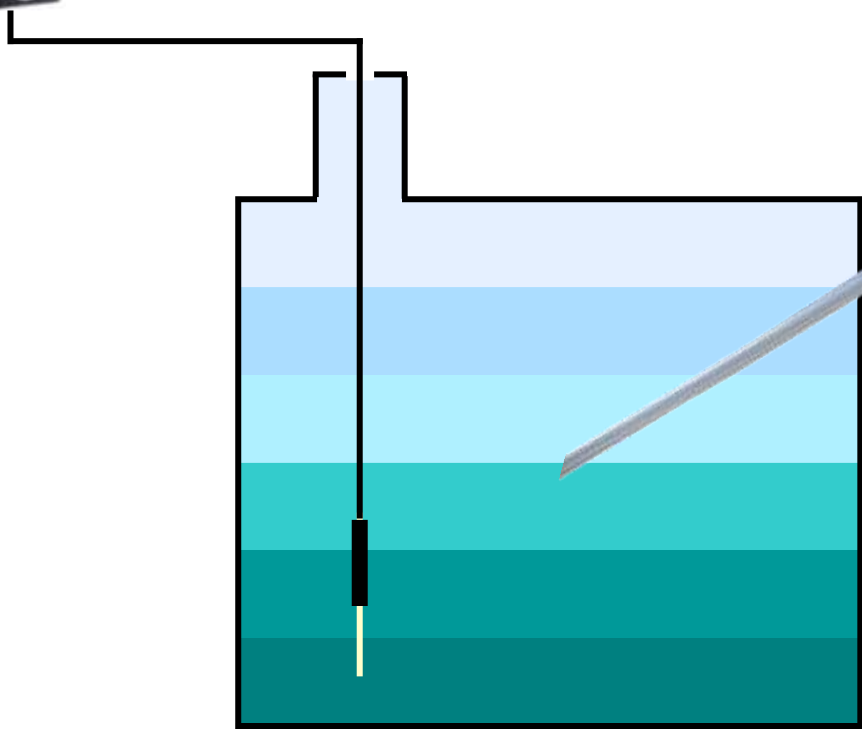
- ***Measure of a vapor's weight compared to air***
- ***Gases lighter than air tend to rise; gases heavier than air tend to sink***

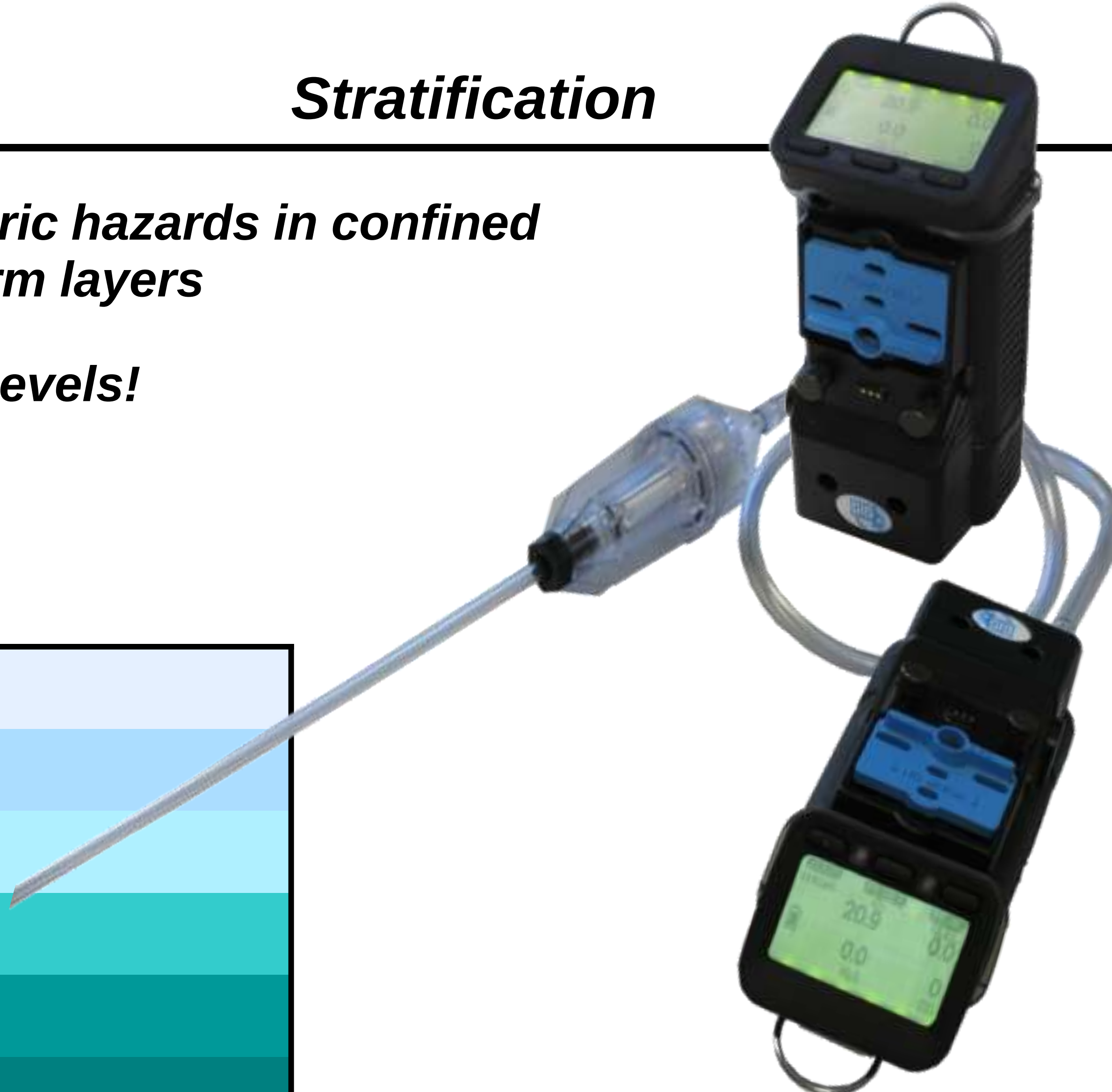
Vapor Density



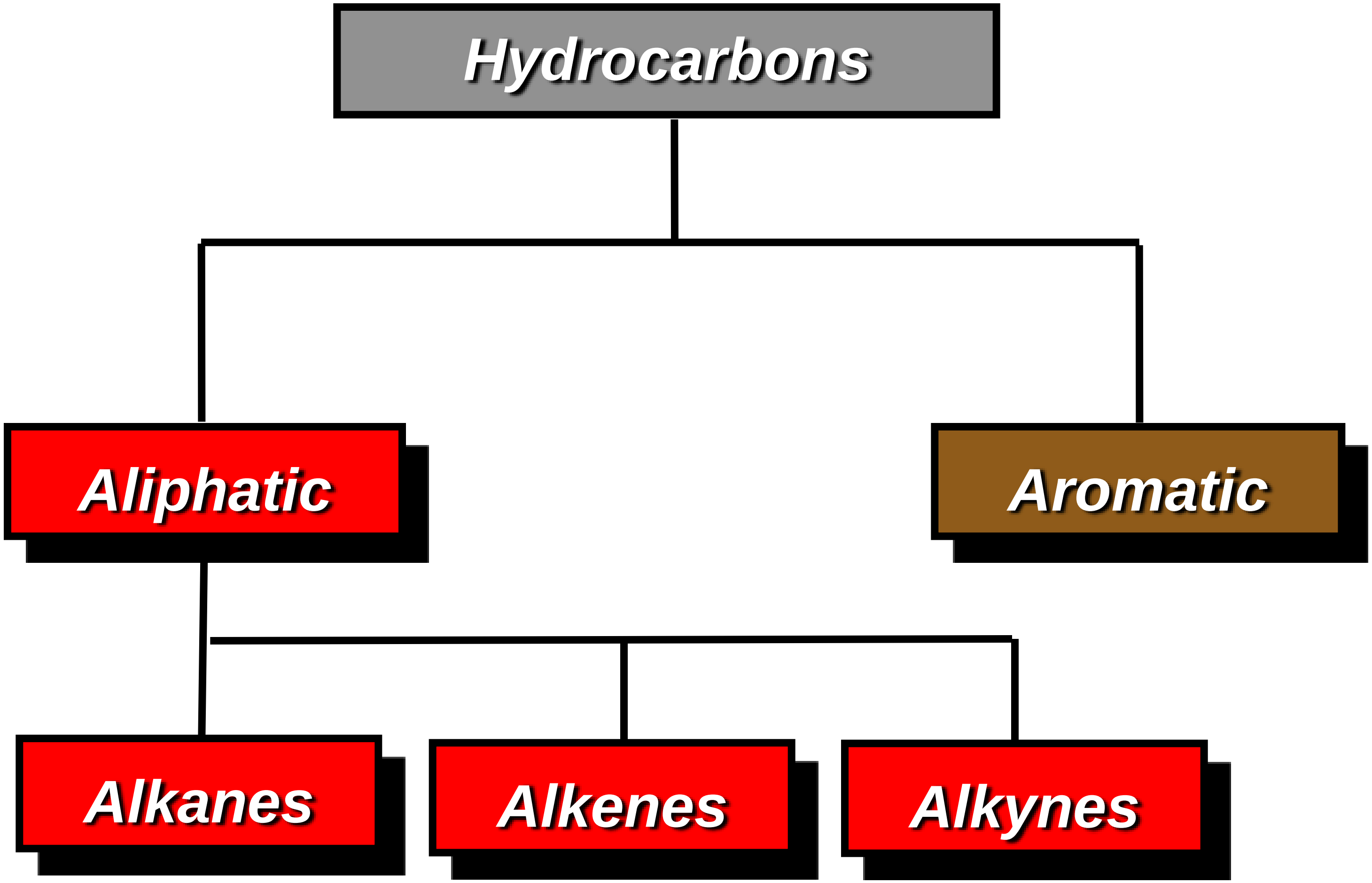
Stratification

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





Classes of Hydrocarbons

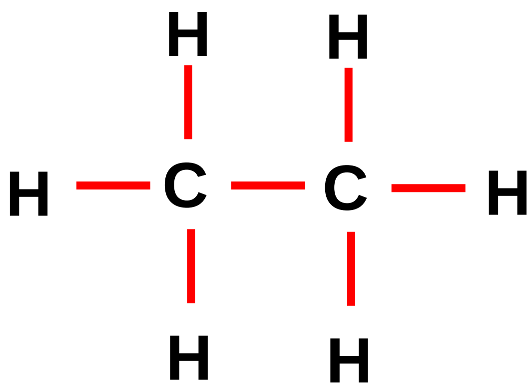


Hydrocarbons

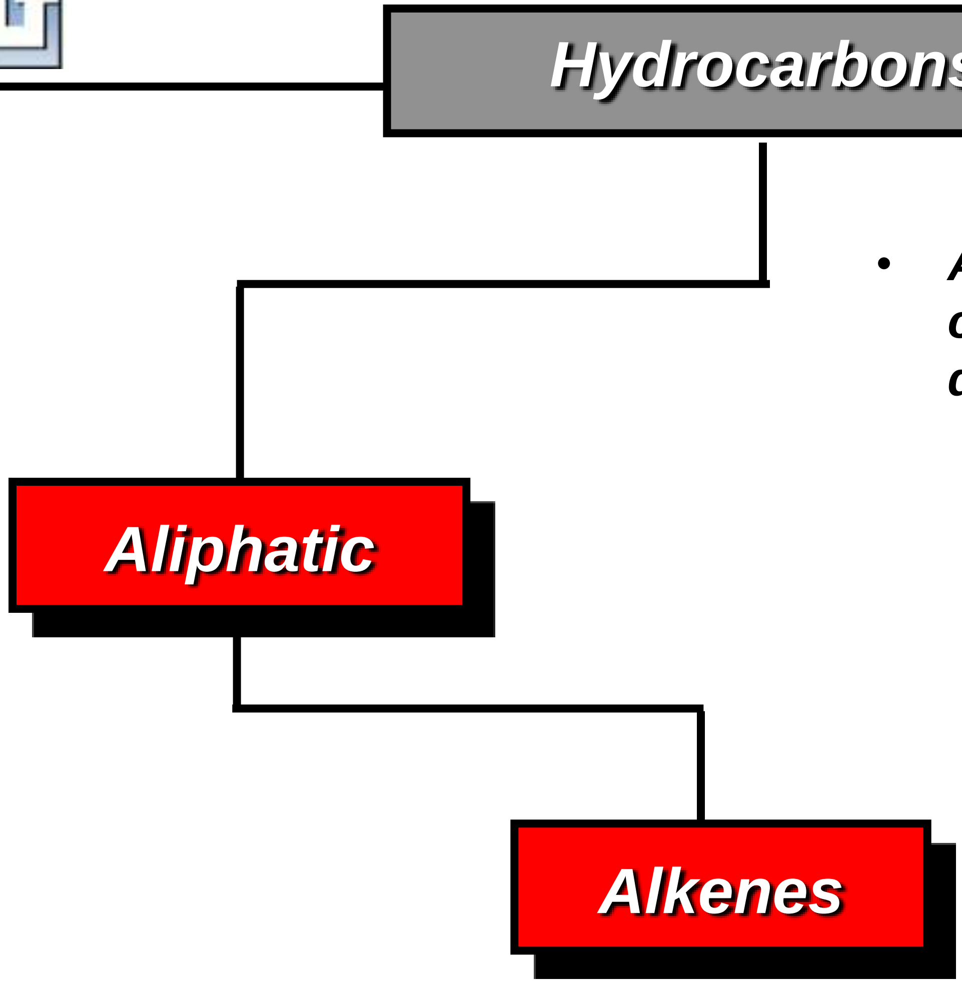
Aliphatic

Alkanes

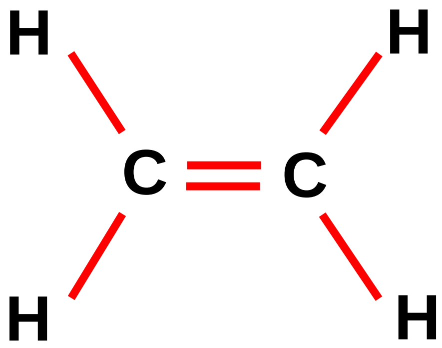
- ***Alkanes are hydrocarbons in which all of the bonds are single bonds***



GfG Instrumentation



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



Hydrocarbons

Aliphatic

Alkynes

- ***Alkynes are hydrocarbons that contain a carbon-carbon triple bond***

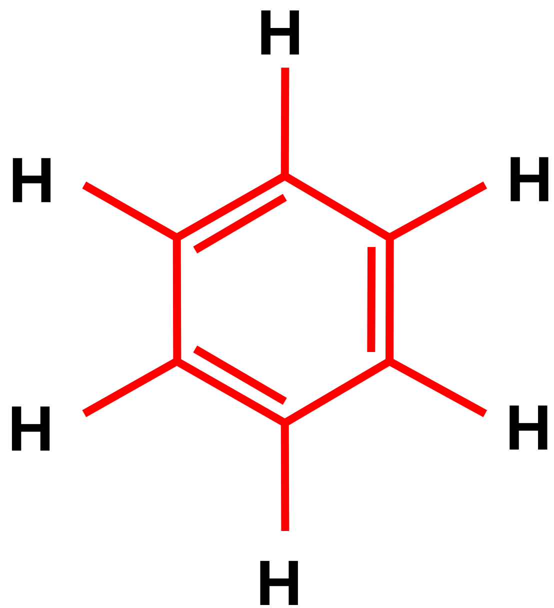
$$HC \equiv CH$$

GfG Instrumentation

Hydrocarbons

Aromatic

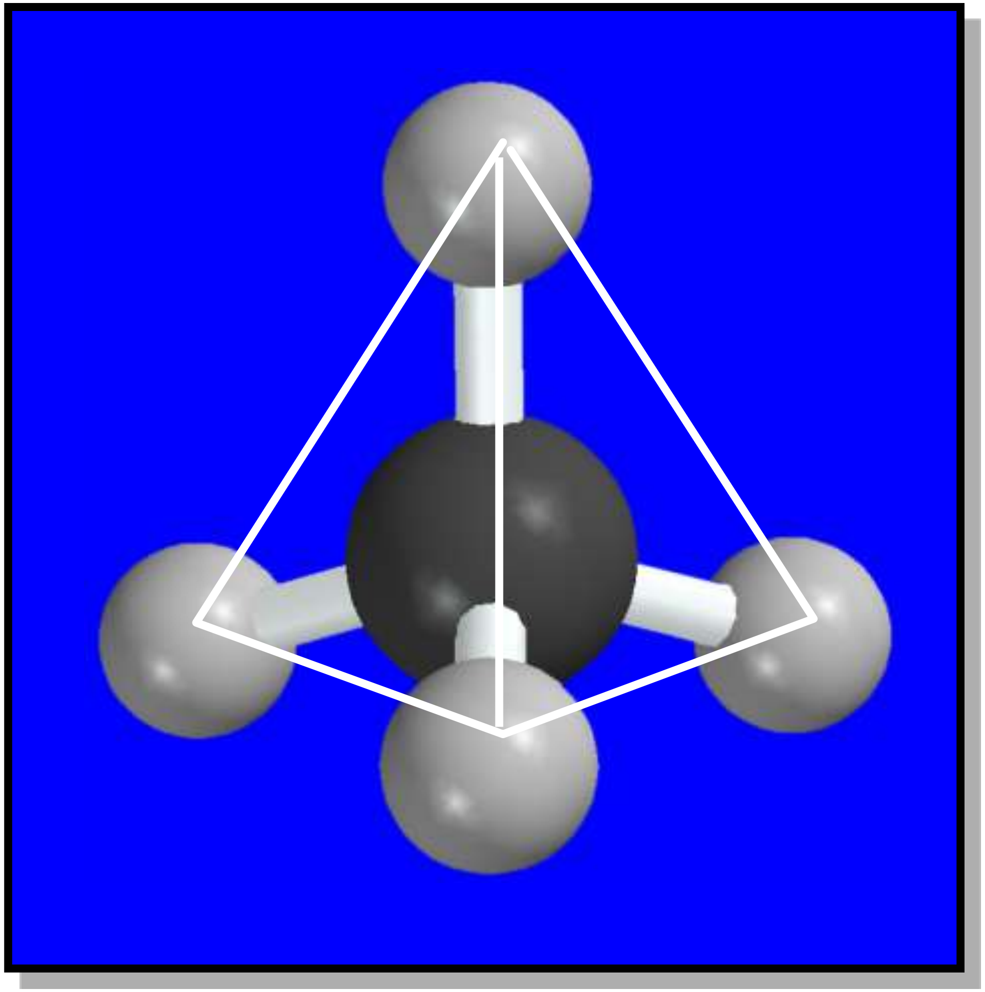
- ***The most common aromatic hydrocarbons are those that contain a benzene ring***



GfG Instrumentation

Chemical structure of Methane

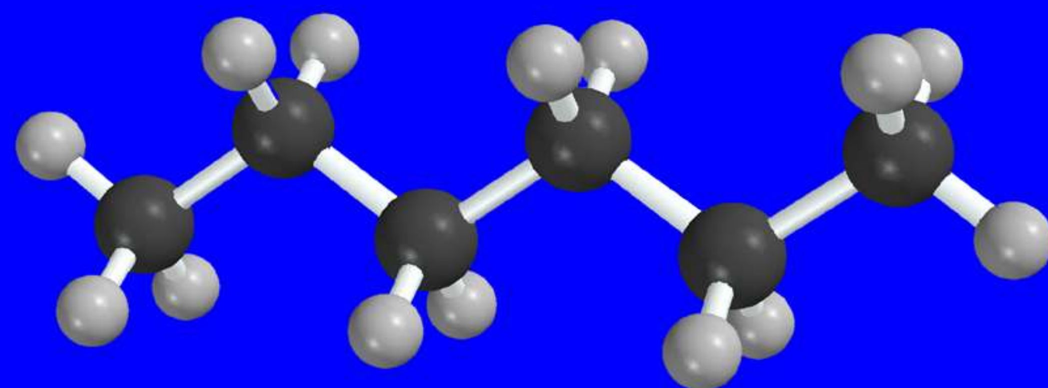
- *Tetrahedral geometry*
- *Each H—C—H angle = 109.5°*



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

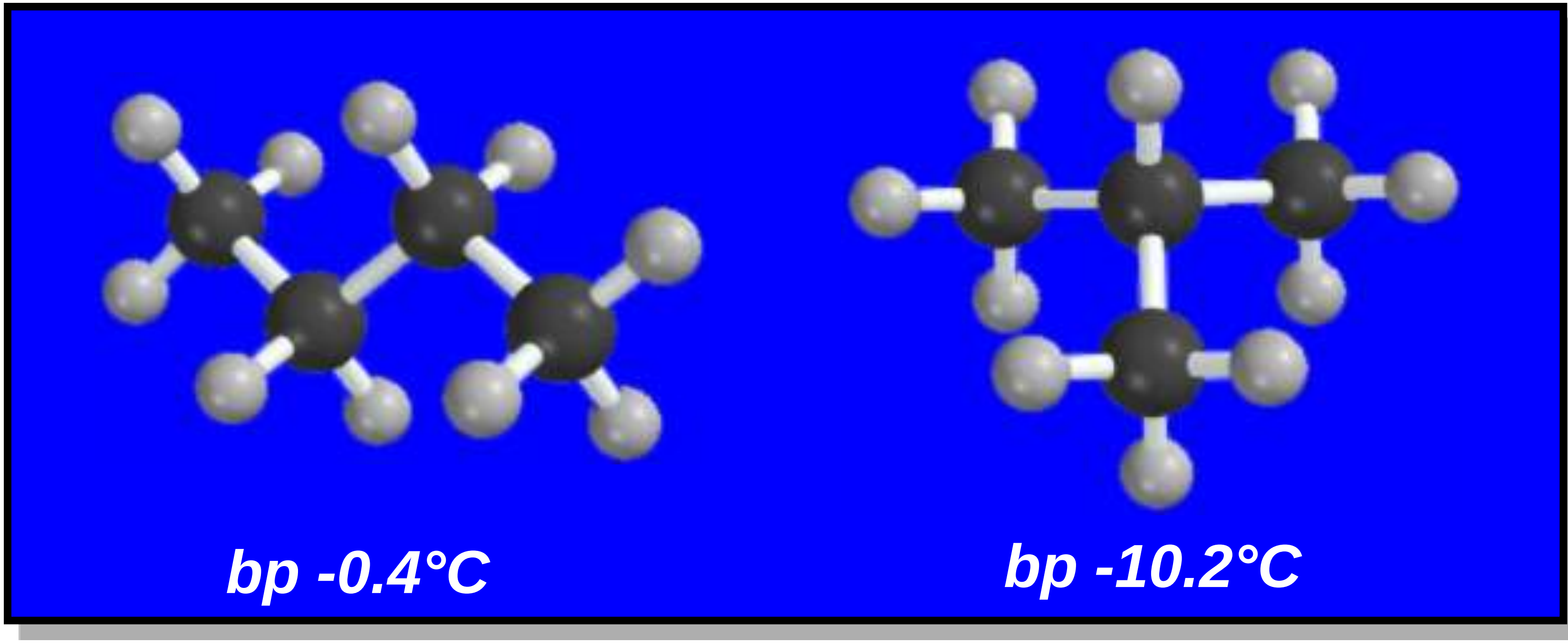
- ***The most stable conformation of unbranched alkanes (designated "n")***



n-Hexane

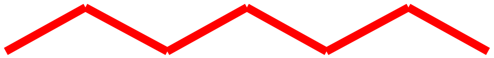
Isomeric Alkanes: Butanes C_4H_{10}

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



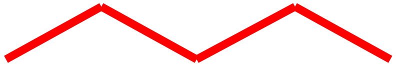
$CH_3CH_2CH_2CH_2CH_3$ ***n-Pentane***

$CH_3CH_2CH_2CH_2CH_2CH_3$ ***n-Hexane***

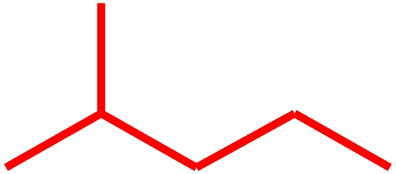


$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ ***n-Heptane***

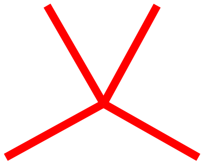
The C_5H_{12} Isomers



$CH_3CH_2CH_2CH_2CH_3$ **n-Pentane**



$(CH_3)_2CHCH_2CH_3$ **Isopentane**

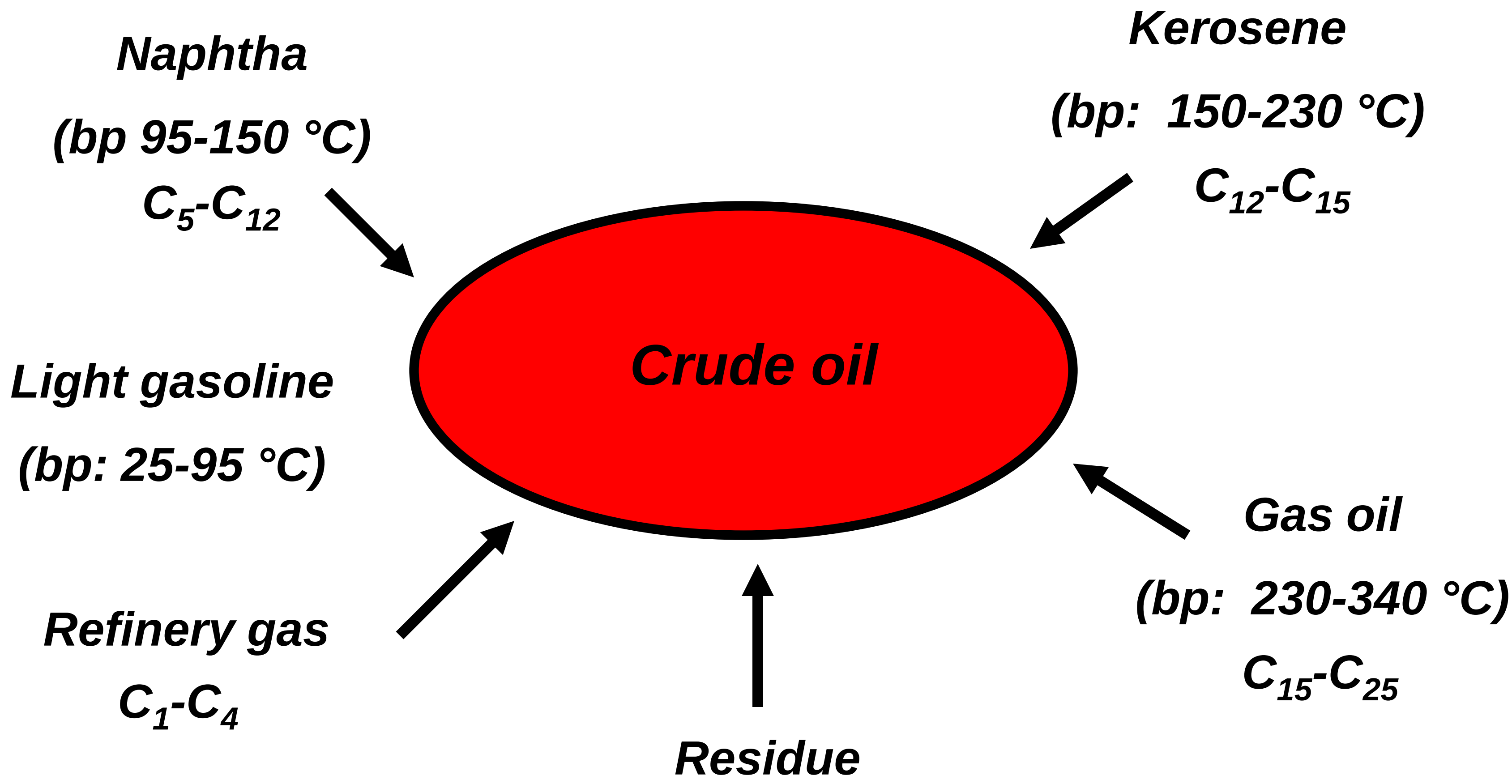


$(CH_3)_4C$ **Neopentane**

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

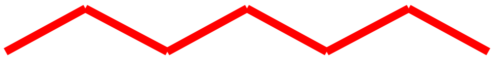


- ***Cracking***
  - ***Converts high molecular weight hydrocarbons to more useful, low molecular weight ones***
- ***Reforming***
  - ***Increases branching of hydrocarbon chains***
  - ***Branched hydrocarbons have better burning characteristics for automobile engines***

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***

Heptane



4817 kJ/mol

654 kJ/mol

Octane

5471 kJ/mol

654 kJ/mol

Nonane

6125 kJ/mol

Stoichiometric formulas

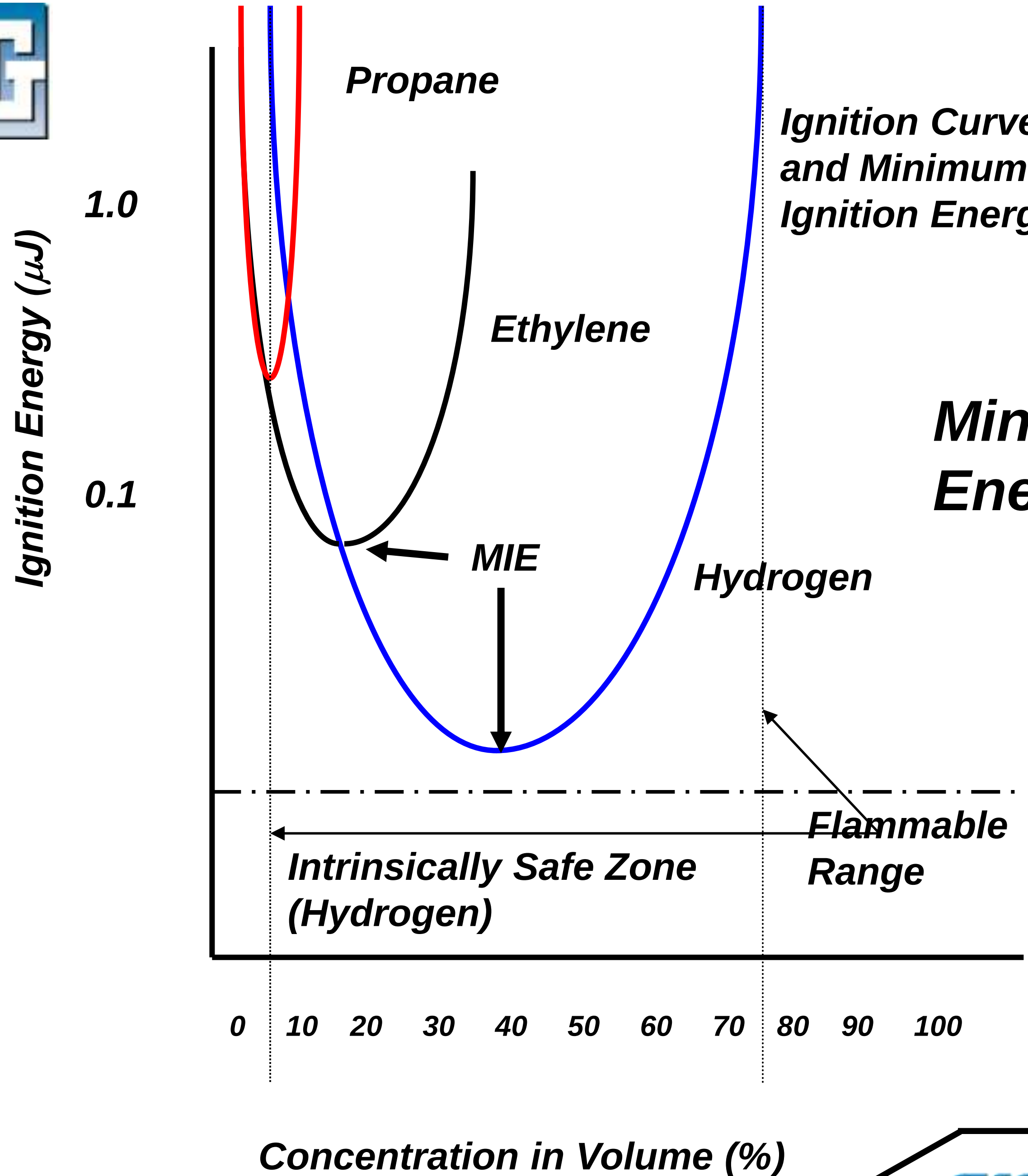
- ***Stoichiometric is not an imported vodka***
- ***Describes correct mixture of ingredients in a chemical reaction***
- ***After the reaction is over, no surplus ingredients will be left***
- ***In combustion, the stoichiometric ratio also is called the correct, ideal or perfect ratio:***

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

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***

Minimum Ignition Energy



GfG Instrumentation

Combustible sensor electrical safety and performance requirements

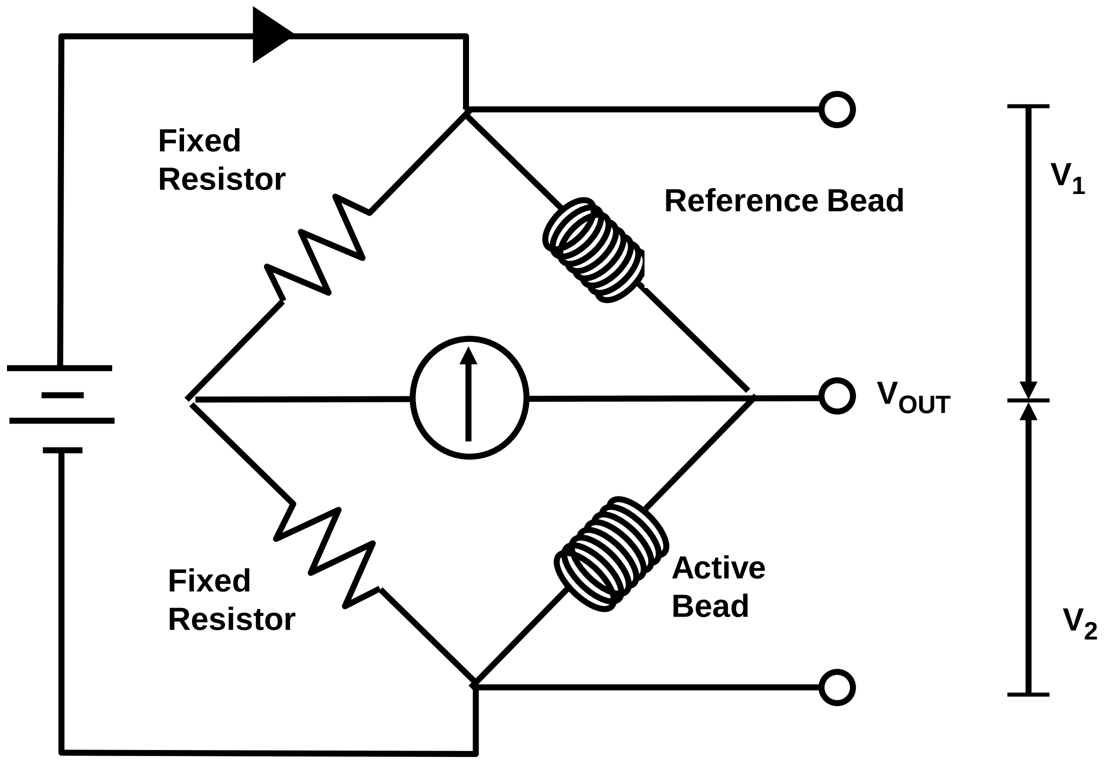
- *Important standards defining combustible sensor performance:*
  - *Canadian requirements: CSA 22.2*
  - *United States: UL 913*
  - *ATEX: EN50018*
  - *Harmonized IECEx: IEC60079-1*

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!***

Simplified Balanced Wheatstone Bridge



Catalytic "Hot Bead" Combustible Sensor

- ***Detects combustible gas by catalytic oxidation***
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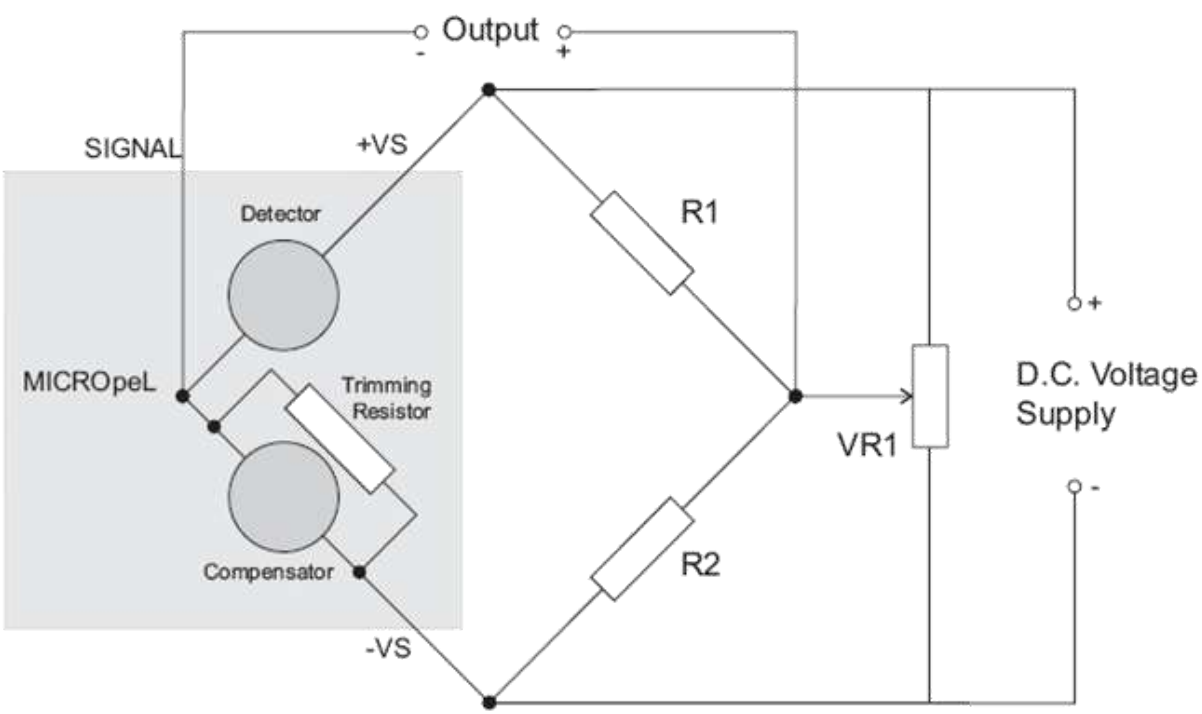
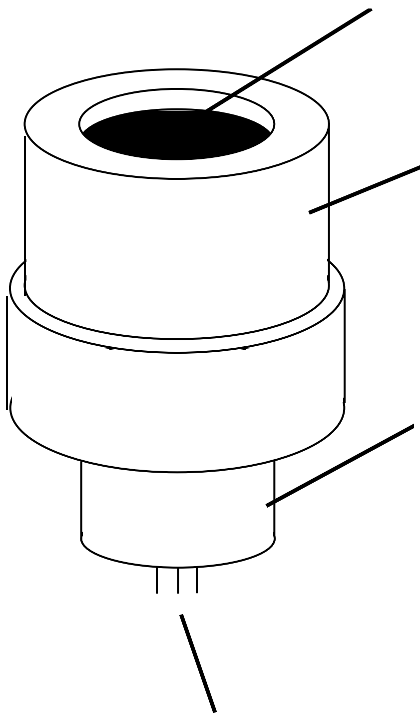
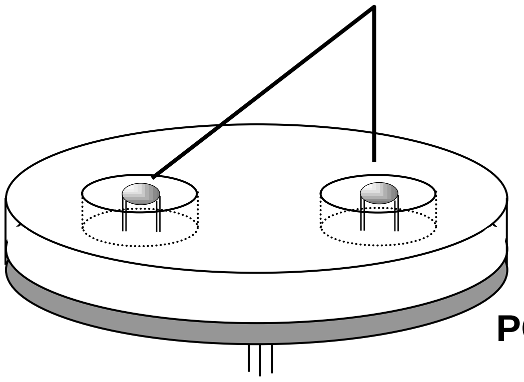


GfG Instrumentation

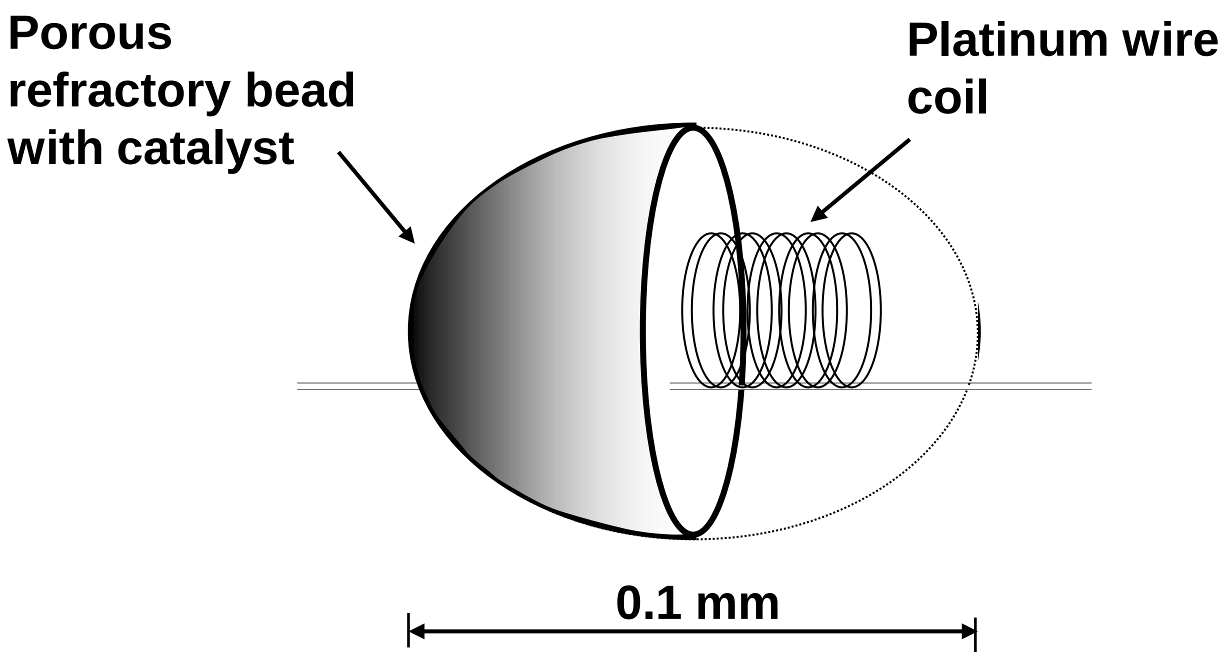
Combustible sensors detect gas by catalytic combustion



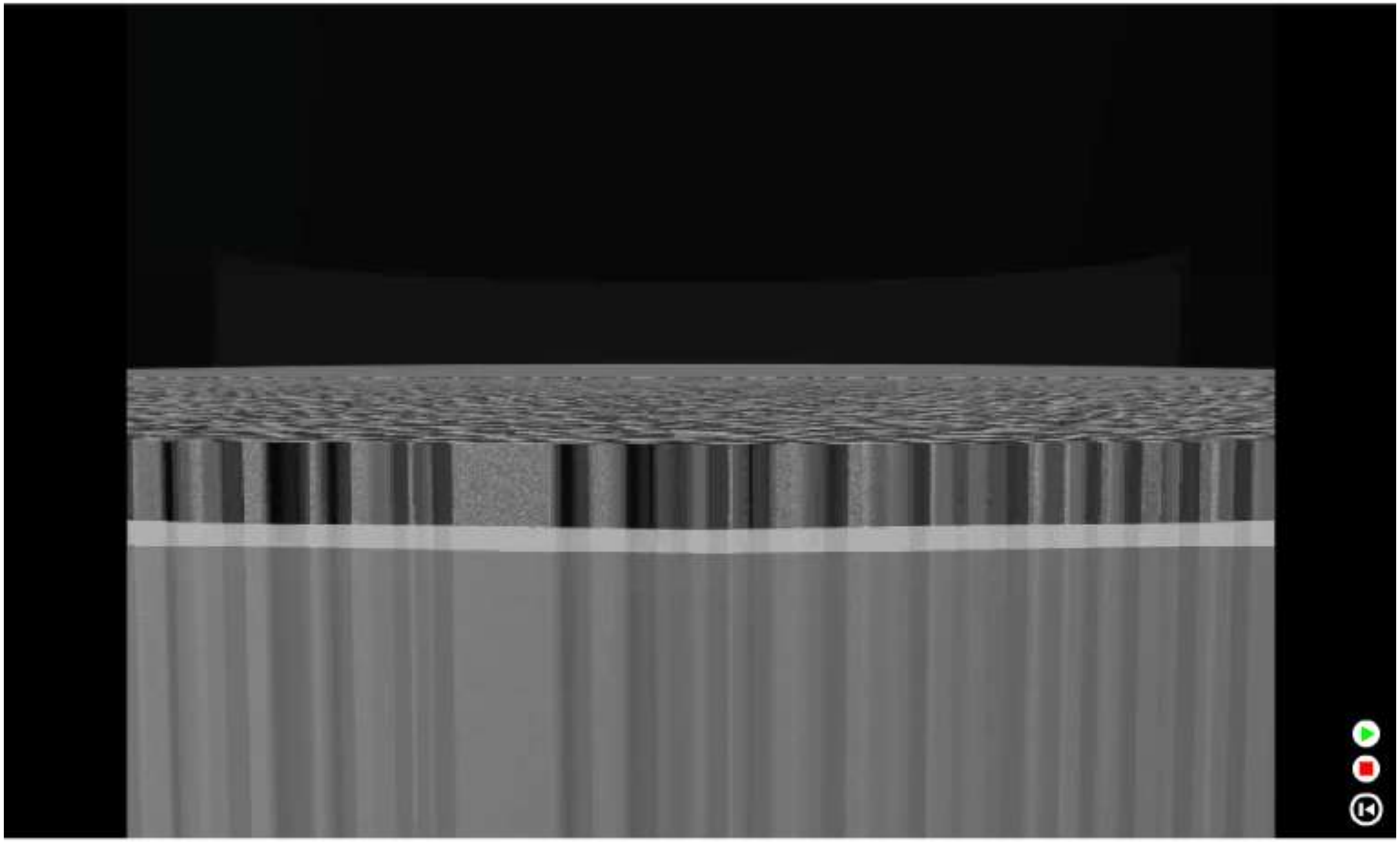


PELLISTOR HEADER DETAIL

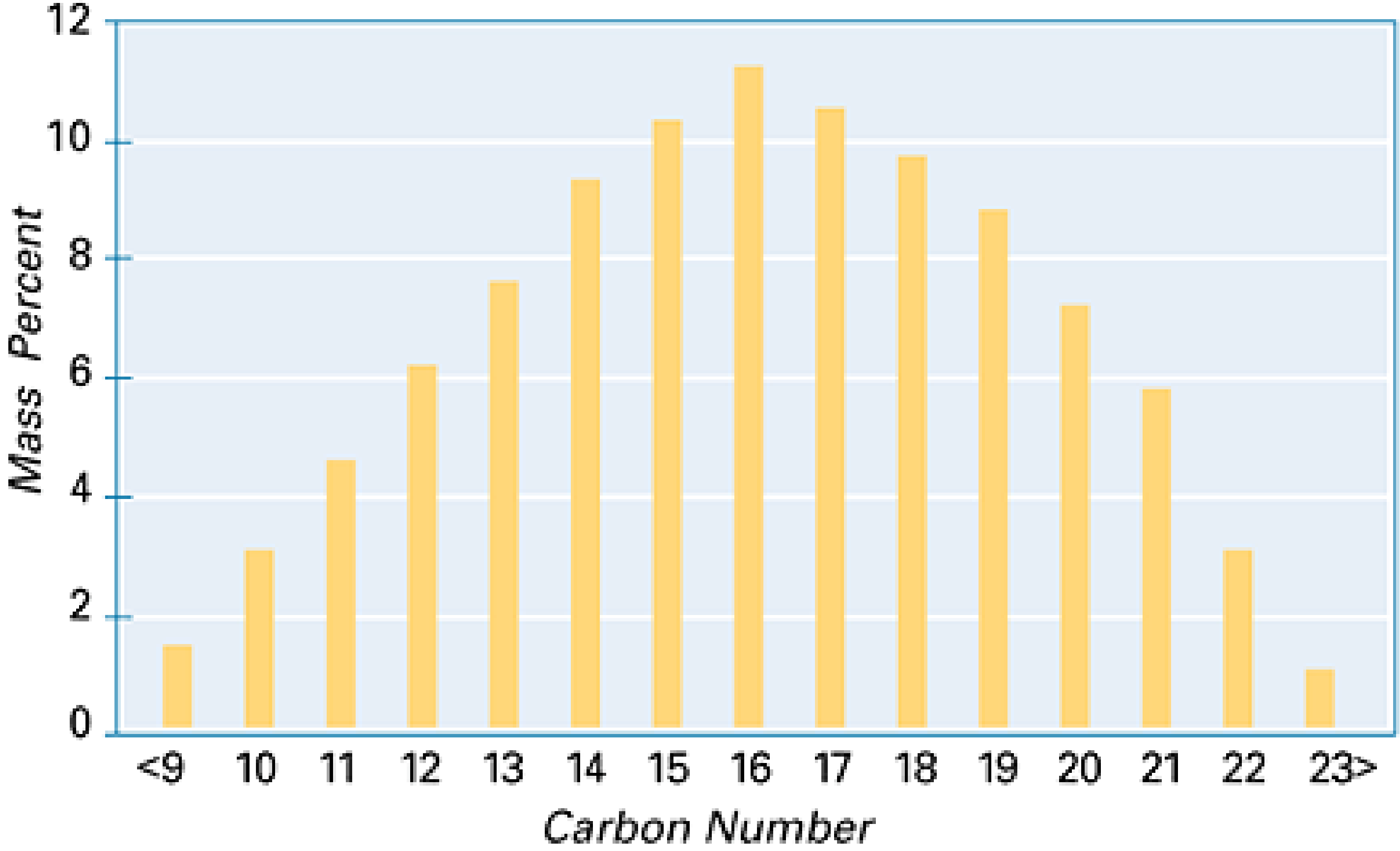
GfG Instrumentation


Porous refractory bead with catalyst
Platinum wire coil
0.1 mm

Catalytic Sensor Structure



Typical Carbon Number distribution in No. 2 Diesel Fuel



GfG Instrumentation

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

GfG Instrumentation

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

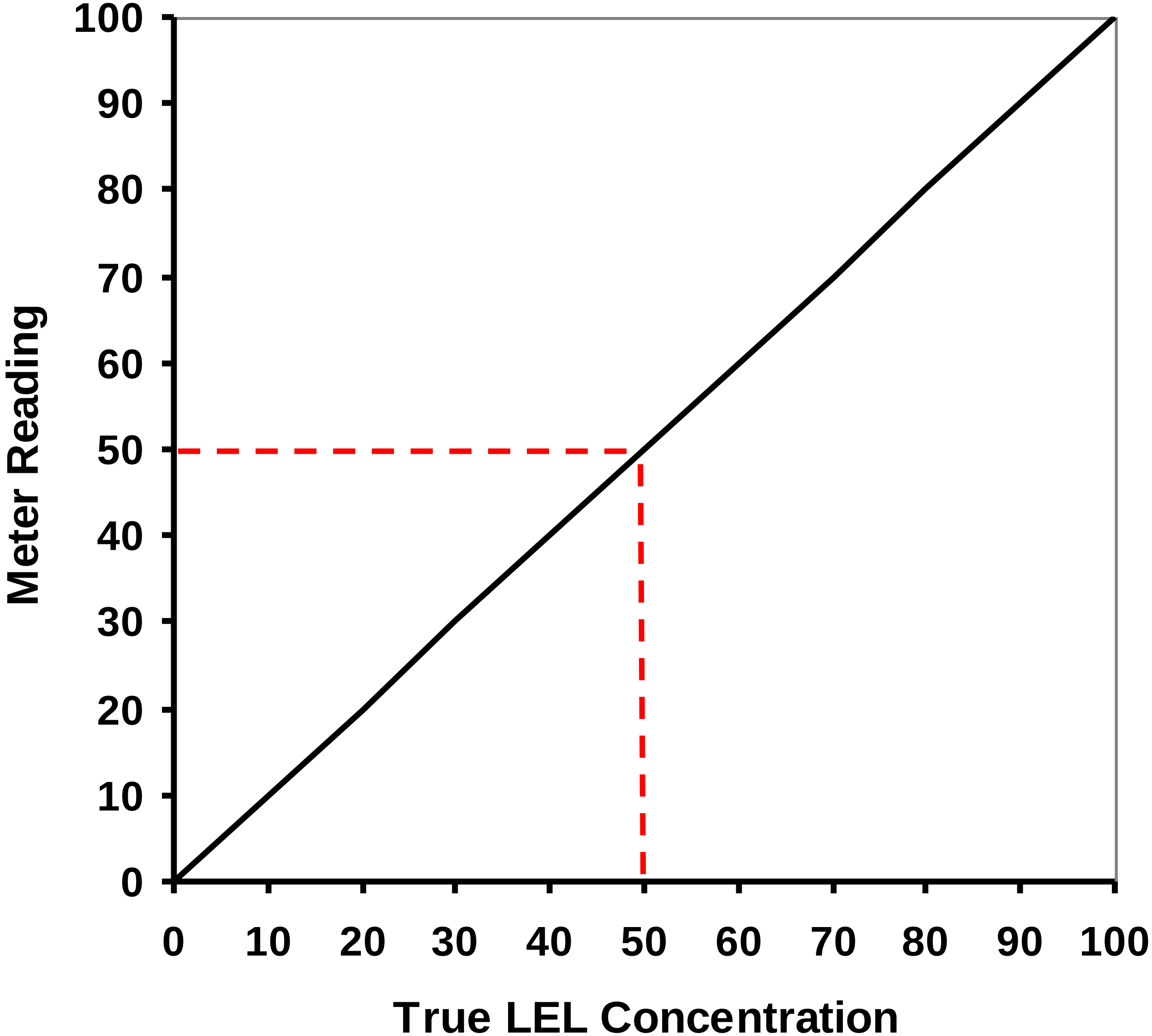
Combustible gas / vapor	Correction factor when sensor is calibrated on pentane	Correction factor when sensor is calibrated on propane	Correction factor when sensor is calibrated on methane
Hydrogen	0.45	0.59	0.9
Methane	0.5	0.67	1.0
Propane	0.77	1.0	1.54
n-Butane	0.83	1.12	1.67
n-Pentane	1.0	1.34	2.0
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

Correction Factors

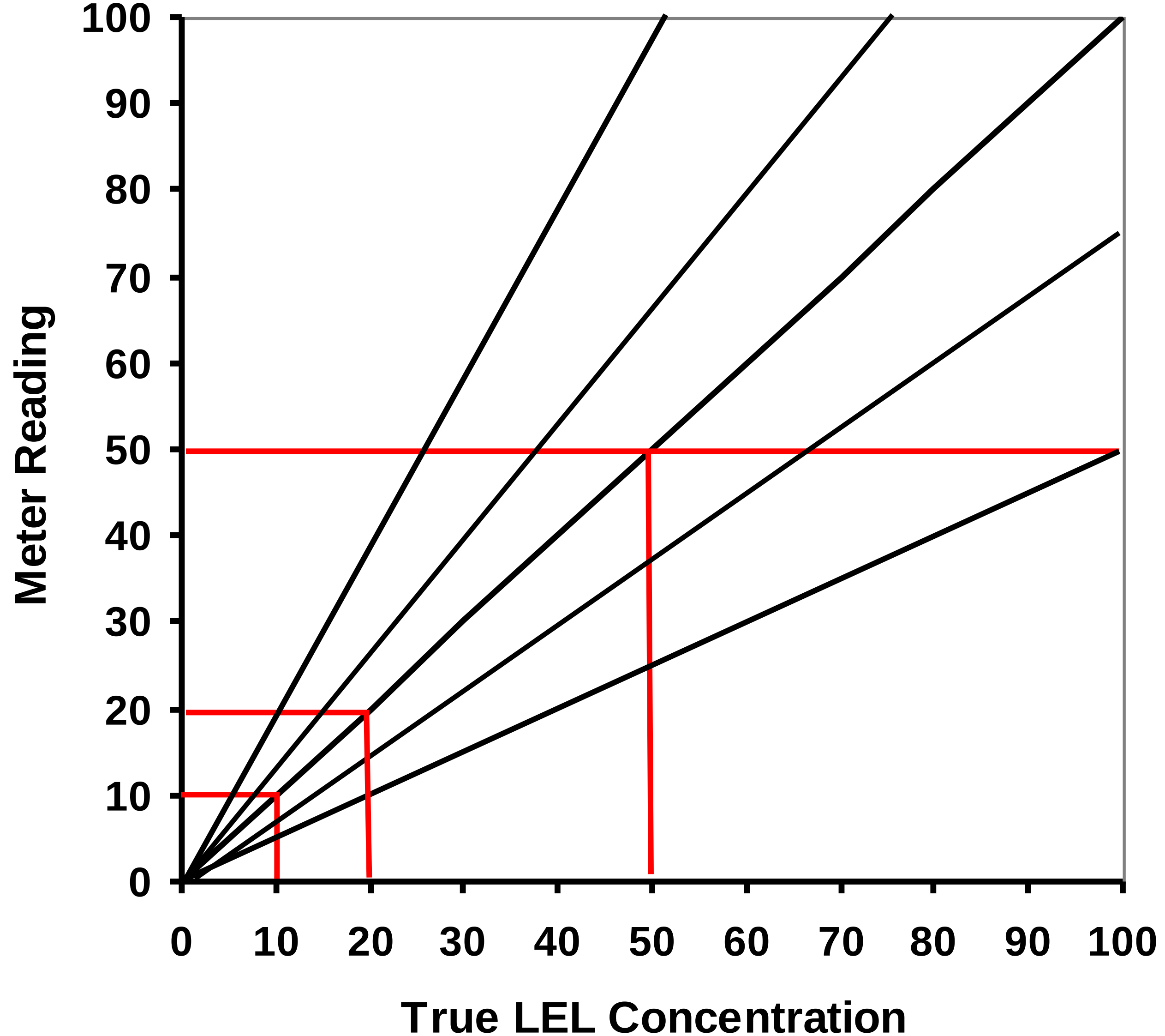
- ***Multiplying the instrument reading by the correction factor for ethanol provides the true concentration***
- ***Given a correction factor for ethanol of 1.25, and an instrument reading of 40 per cent LEL, the true concentration would be calculated as:***

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

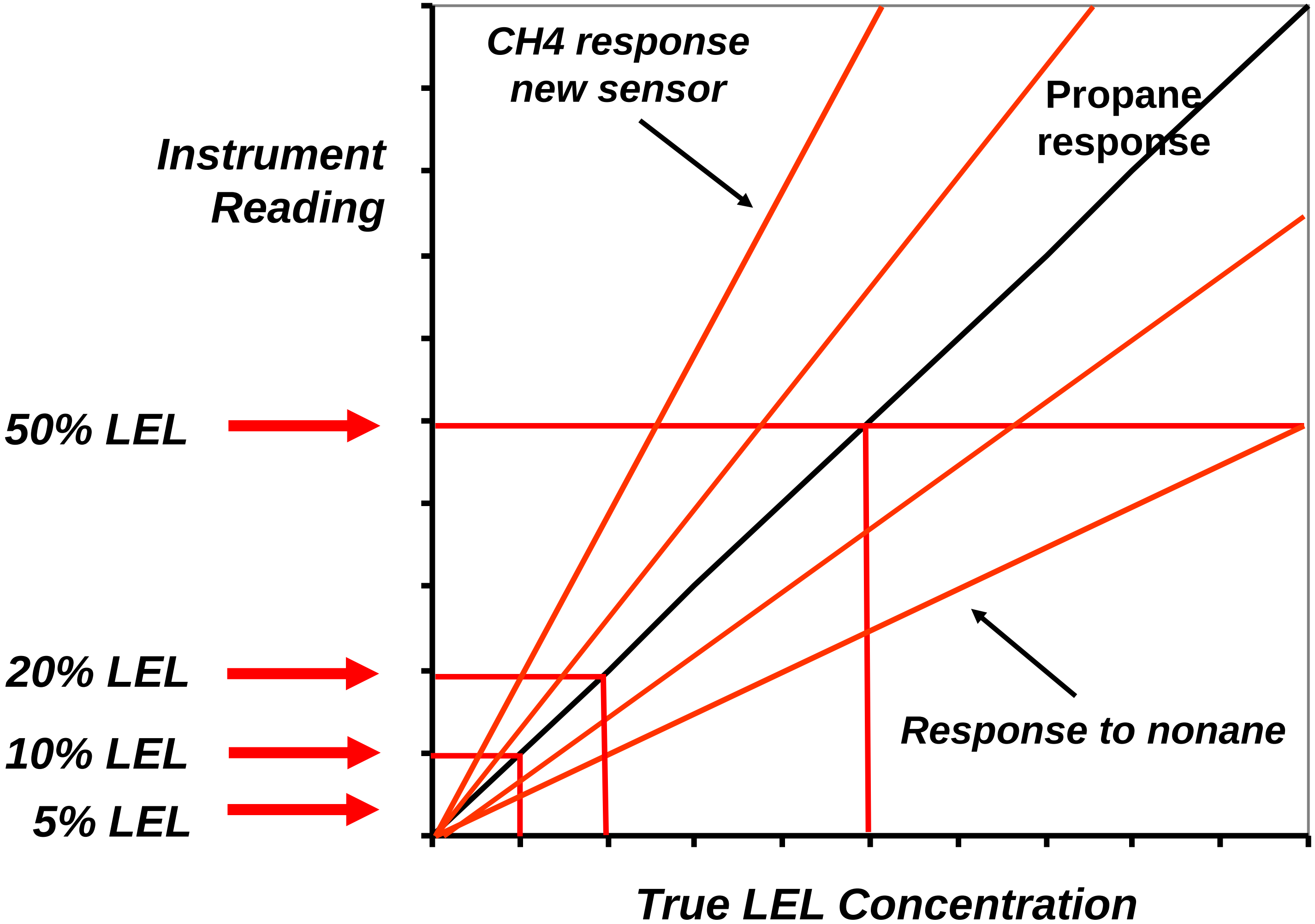
Linear Response Curve (Calibration Standard)



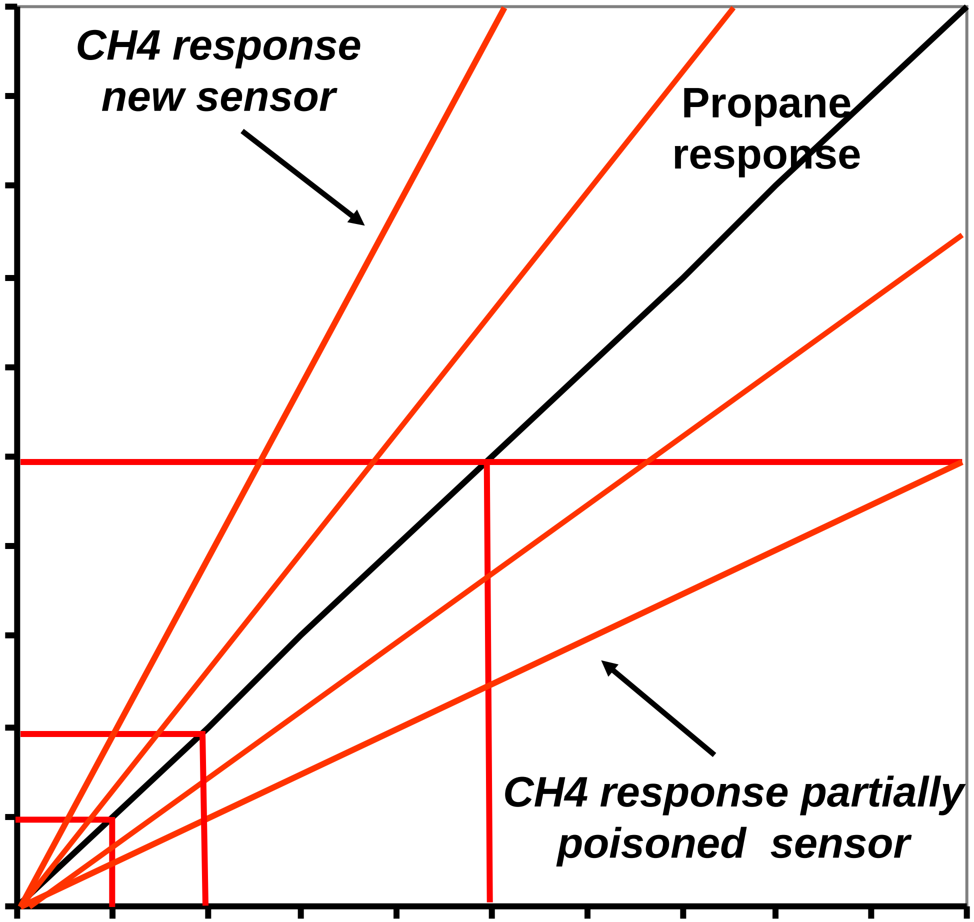
Relative Response Curves

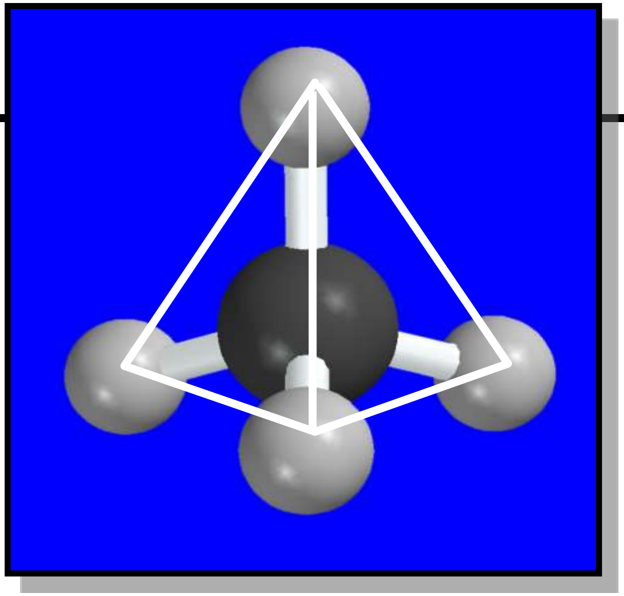


Using a lower alarm setting minimizes effect of relative response on readings



Response to methane over life of sensor





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

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

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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*

GfG Instrumentation

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 concentra-tion 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)***

GfG Instrumentation

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***

Limitations of catalytic pellistor LEL sensors

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

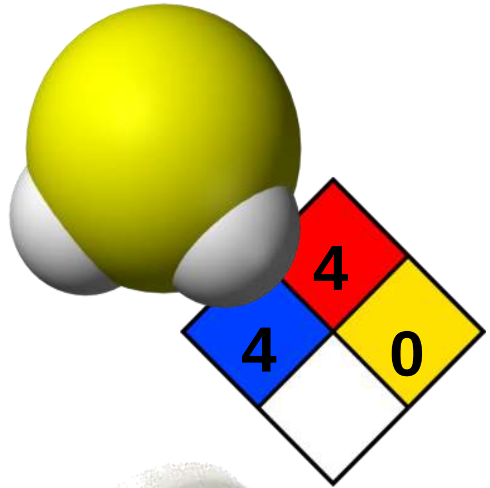
GfG Instrumentation

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.)***

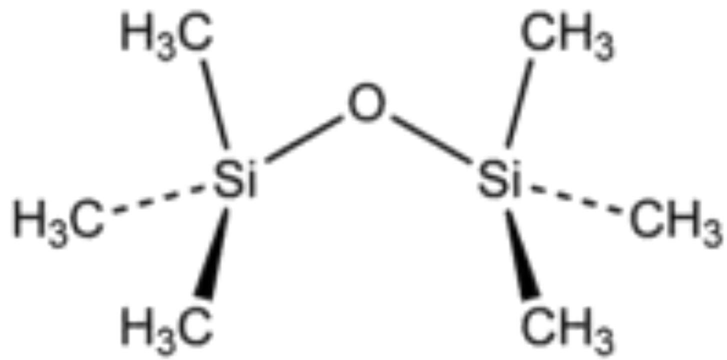
Effects of H2S on combustible gas sensors

- *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***



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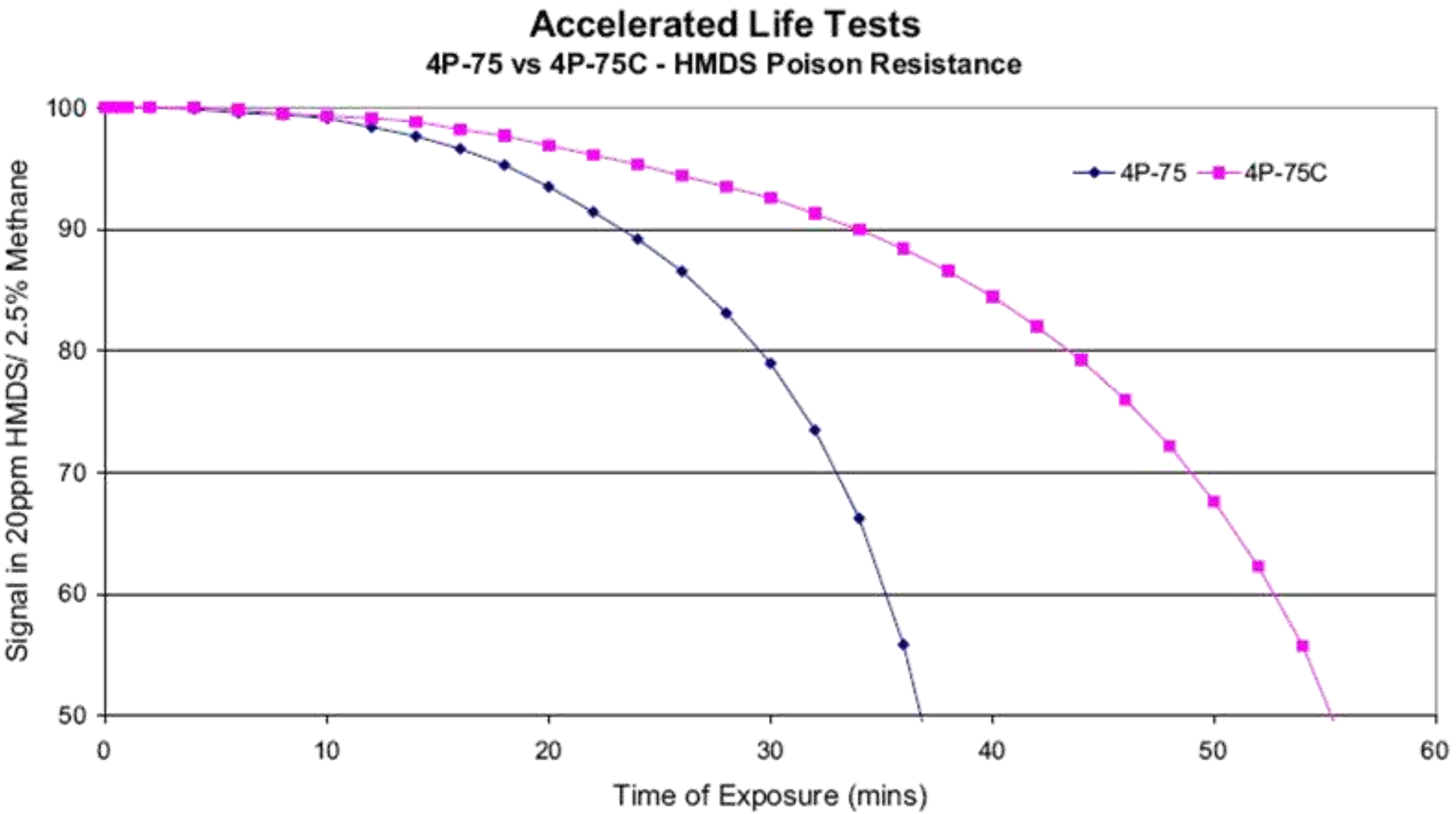
Effects of hexamethyldisiloxane (HMDS) on pellistor sensor



GfG Instrumentation

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*

Low-power pellistor issues

- *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 much easier to poison.*
  - *Silicones*
  - *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.)*

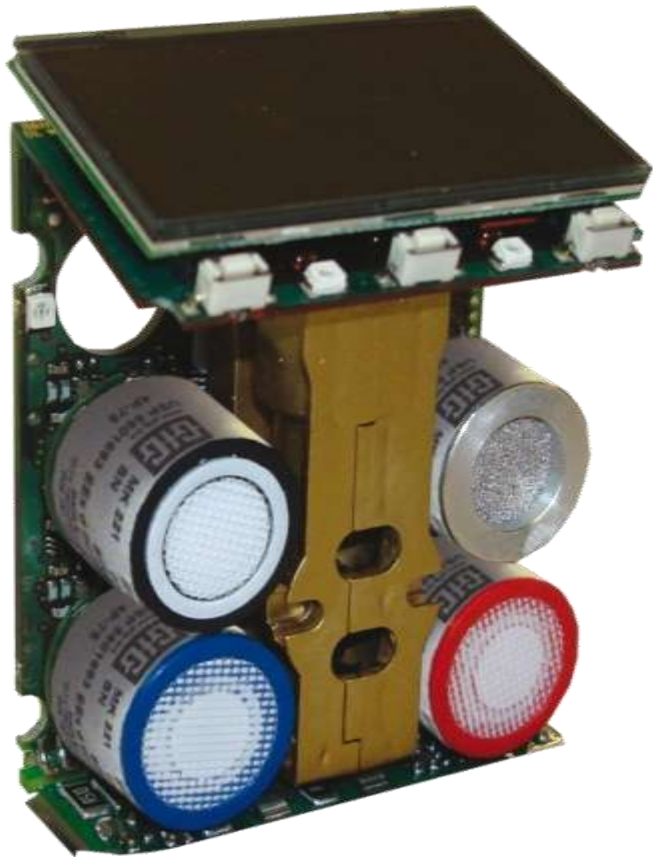
Low-power pellistor advice

- *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 avoids all of these issues!



GfG Instrumentation

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***
  - ***Even when atmosphere contains 0 % oxygen, diluting with an equal volume of fresh air produces an O_2 concentration of at least 10 % at the combustible sensor***

GfG Instrumentation

Dilution Fitting Limitations

- ***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!***

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***

Thermal Conductivity Sensors

- *Sensor contains two beads on opposite arms of balanced Wheatstone Bridge circuit*
- *Neither bead receives a catalyst coating*
- *Reference bead isolated from the air being monitored in a sealed chamber, while active bead exposed to atmosphere being sampled*
- *Detection depends on "air conditioning" effect of high concentrations of gas on the active bead*

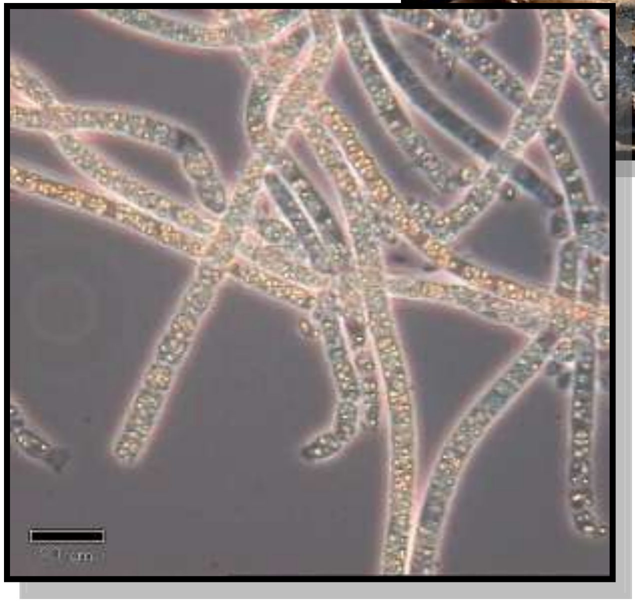
Use of Oxygen Readings to Determine High Range Concentrations of Combustible Gas

- *At high levels of gas, oxygen concentration drops*
- *Amount of gas inversely proportional to oxygen concentration*
- *Volume percent oxygen used to calculate and display volume percent methane*

Toxic Gases and Vapors

Toxic atmospheres can come from:

- *Microbial action*
- *Products or chemicals being used or stored*
- *Work being performed*
- *Areas adjacent to work area*



USA Permissible Exposure Limit (PEL)

- *Determined by the United States Occupational Safety and Health Administration (OSHA)*
- *Sets limits for legal unprotected worker exposure to a listed toxic substance*
- *Force of law in USA!*
- *Individual states free to enact stricter, but never less conservative limits*
- *Given in "Parts-per-Million" (ppm) concentrations*
  - *1 % = 10,000 ppm*

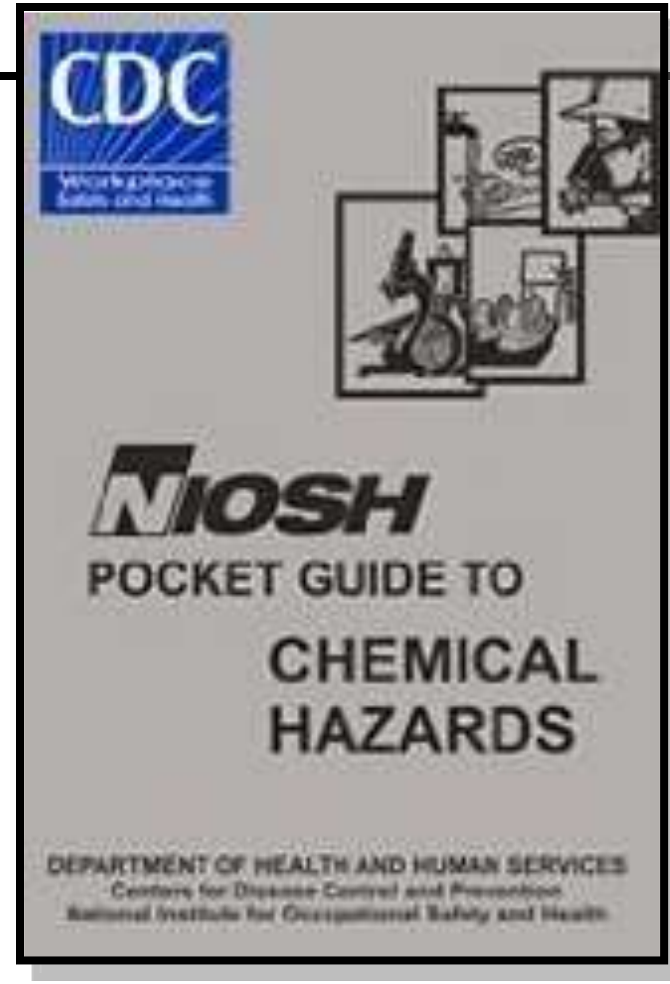
GfG Instrumentation

- *“Parts-per-Million” (ppm) concentrations*
  - *1.0 ppm the same as:*
    - *One automobile in bumper-to-bumper traffic from Cleveland to San Francisco*
    - *One inch in 16 miles*
    - *One minute in two years*
    - *One ounce in 32 tons*
    - *One cent in $10,000*

- ***"Parts-per-Billion" (ppb) concentrations***
  - ***1.0 ppb the same as:***
    - ***One silver dollar in a roll of silver dollars stretching from Detroit to Salt Lake City***
    - ***One kernel of corn in a 45-foot high, 16-foot diameter silo***
    - ***One sheet in a roll of toilet paper stretching from New York to London***
    - ***One second of time in 32 years***

NIOSH Recommended Exposure Limit (REL)

- ***Determined by USA National Institute of Occupational Safety and Health (NIOSH)***
- ***<u>Guidelines</u> for control of potential health hazards***
- ***Usually more conservative than Federal OSHA exposure limits***
- ***Intended as recommendation but incorporated by adoption in many states with OSHA approved safety and health plans***
- ***Force of law in these states***



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Threshold Limit Value (TLV ®)

- ***Determined by American Conference of Governmental Industrial Hygienists (ACGIH)***
- ***<u>Guidelines</u> for control of potential health hazards***
- ***Intended as recommendation***
- ***Usually more conservative than Federal OSHA PEL, frequently more conservative than NIOSH REL***

GfG Instrumentation

What are TLVs®, and why do they matter?

- ***In the United States which toxic exposure limits apply depends on:***
  - ***The state in which the workplace is located***
  - ***The type of work being performed (e..g. shipyard confined space entry versus general industry permit confined space entry)***
  - ***Requirements that apply to a specific employer (e.g. US Coast Guard, Navy, Air Force, MSHA regulated worksites, etc.)***
  - ***Corporate health and safety policies***

GfG Instrumentation

What are TLVs®, and why do they matter?

- *The three most widely referenced toxic exposure limits for workers in the United States are:*
  - *United States Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs)*
  - *United States National Institute of Occupational Safety and Health (NIOSH) Recommended Exposure Limits (RELs)*
  - *American Conference of Governmental Industrial Hygienists (ACGIH ®) Threshold Limit Values TLVs®*

TLVs® Incorporated by Reference in:

- *NFPA 306 – Control of Gas Hazards on Vessels*
- *US Coast Guard regulations (OSHA PEL or TLV®, whichever is lower)*
- *US Army (OSHA PEL or TLV®, whichever is lower, or specific Army OEL)*
- *Some individual state health and safety plans (e.g. California)*
- *Many international standards and regulations (e.g. Canada)*
- *Many consensus standards (e.g. ANSI, NFPA)*
- *Many corporate health and safety plans*
- *Mine Safety and Health Administration (MSHA) regulations*

GfG Instrumentation

Corporate Toxic Exposure Limit Strategy

- Given the potential for lawsuits, large USA companies with "deep pockets" have to follow the most conservative exposure limit standards

- Since ACGIH ® TLV ® recommendations are frequently more conservative than OSHA PELs; many corporations use the ACGIH TLVs®

- Most oil companies in the United States and Canada (where they have no choice) strictly follow the TLVs

GfG Instrumentation

Exposure Limits defined in three ways:

- ***Time Weighted Average (TWA)***
- ***Ceiling***
- ***Short Term Exposure Limit (STEL)***

TWA is projected value

- ***When monitoring session less than eight hours, TWA projected for the full eight hour shift.***
- ***When monitoring session more than 8 hours, TWA calculated on an "equivalent" 8 hour shift basis***

TWA is Projected Value

According to OSHA cumulative TWA exposures for an eight hour work shift are calculated as follows:

$$E = (C_a T_a + C_b T_b + \cdots C_n T_n) / 8$$

Where:

- ***E is the equivalent exposure for the eight hour working shift***
- ***C is the concentration during any period of time T where the concentration remains constant***
- ***T is the duration in hours of the exposure at concentration C***

TWA Calculation

Exposure	Concentration	TWA
4 hours	100 ppm	50 ppm
8 hours	100 ppm	100 ppm
12 hours	100 ppm	150 ppm

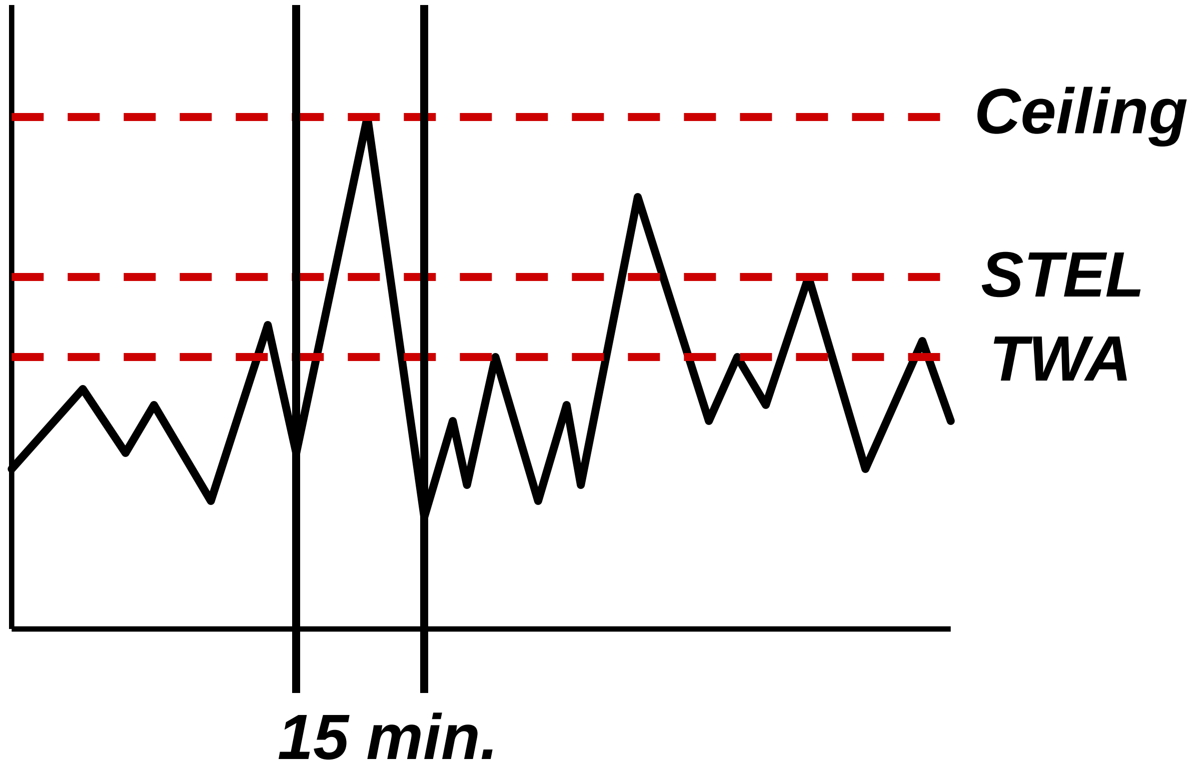
Ceiling Limit

- ***Ceiling is the maximum concentration to which an unprotected worker may be exposed***
- ***Ceiling concentration should never be exceeded even for an instant***

Short Term Exposure Limit (STEL)

- *Some gases and vapors have an allowable maximum Short Term Exposure Limit which is higher than the 8 hour TWA*
- *STEL values usually calculated as 15 minute, or in some cases, as 5 minute or 10 minute time weighted averages*

STEL vs. TWA and Ceiling



How are these calculations affected by the choice of datalogging interval?

- *They're not!*
  - *PEL calculations are continuously updated by the instrument*
  - *The datalogging interval simply specifies how often the instrument stores a "snap shot" of the current readings for the purposes of generating a printed report or database file of test results*

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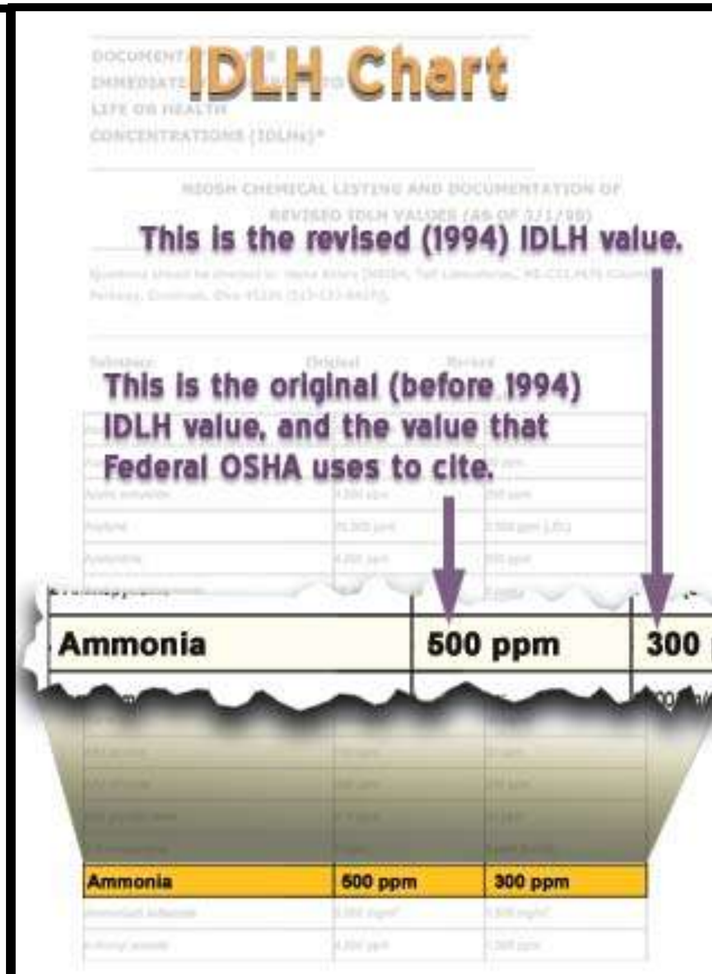
Immediately Dangerous to Life and Health

- ***IDLH is not part of PEL***
  - ***IDLH is maximum concentration from which it is possible for an unprotected worker to escape without suffering injury or irreversible health effects during a maximum 30-minute exposure***
  - ***Primarily used to define the level and type of respiratory protection required***
  - ***Unprotected workers may NEVER be deliberately exposed to IDLH or ANY concentrations which exceed the PEL***

Exposure limits for ammonia

	8-Hr TWA	STEL	Ceiling
Federal USA OSHA PEL	50	NA	NA
State OSHA (1989) PEL (NIOSH REL)	25 ppm	35 ppm	NA
TLV	25 ppm	35 ppm	NA



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Converting PPM to mg/m^3

- ***ACGIH / NIOSH use following formulae:***

TLV in mg/m^3 =

$$\frac{\text{(gram molecular weight of substance)} \times \text{(TLV in ppm)}}{24.45}$$

TLV in ppm =

$$\frac{24.45 \times (\text{TLV in mg/m}^3)}{\text{(gram molecular weight of substance)}}$$

- ***So for chlorine:***

Cl_2 gram molecular weight = 70.9 g/mole

Cl_2 TLV = 0.5 ppm

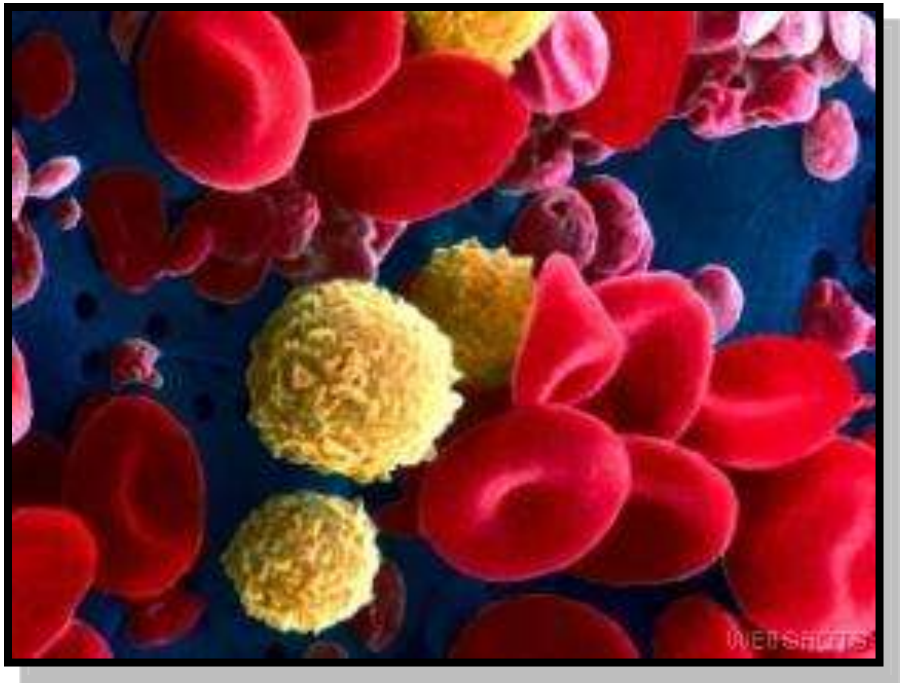
TLV in mg/m^3 calculated:

$$\frac{(70.9\ \text{g/mole}) \times (0.5\ \text{ppm})}{24.45} = 1.45\ \text{mg/m}^3$$

Carbon Monoxide

- ***Produced as a by product of incomplete combustion***
- ***Associated with internal combustion engine exhaust***
    - ***Vehicles***
    - ***Pumps***
    - ***Compressors***

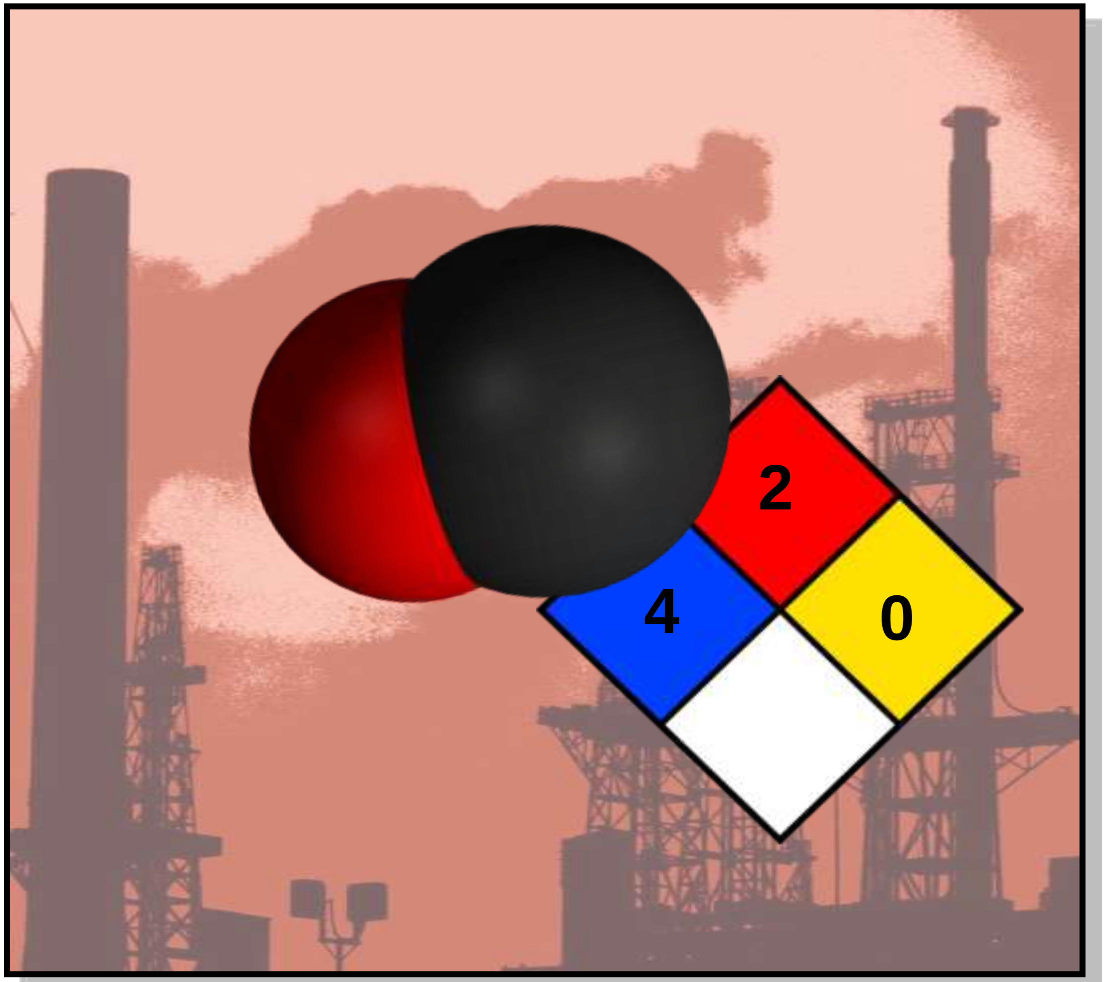
- ***Bonds to hemoglobin in red blood cells***
- ***Contaminated cells can't transport O_2***
- ***Chronic exposure at even low levels harmful***




Effects of Carbon Monoxide CO
As oxygen enters the lungs, capillaries allow it to come into contact with red blood cells. Oxygen then enters these cell to be carried to other cells throughout the body.
O2

Characteristics of Carbon Monoxide

- *Colorless*
- *Odorless*
- *About the same weight as air*
- *Flammable (LEL is 12.5 %)*
- *Toxic!*



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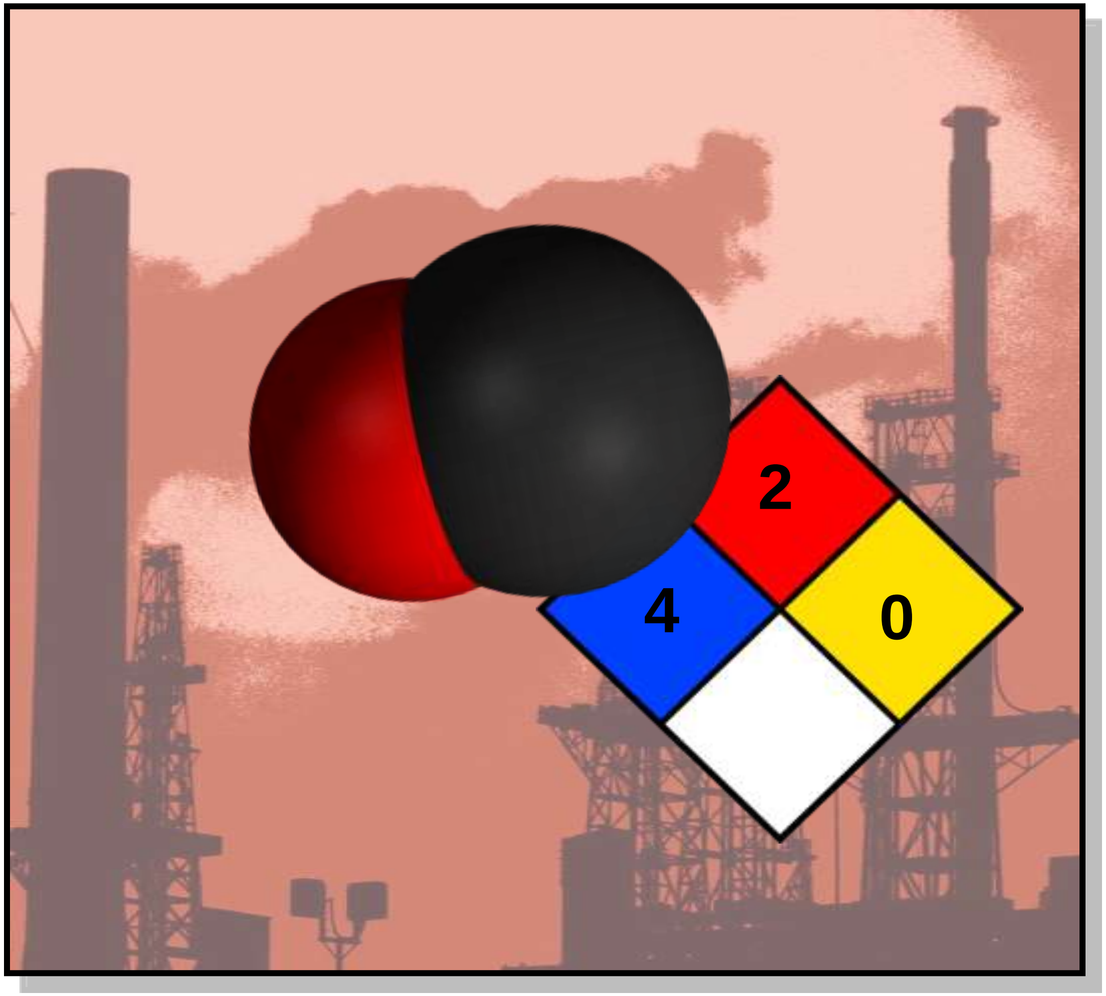
Symptoms of Carbon Monoxide Exposure

- *Headaches*
- *Fatigue*
- *Nausea and other "Flu-like" symptoms*
- *Loss of consciousness*
- *Brain damage*
- *Coma*
- *Death*



Toxic Effects CO

- *Concentration of only 1,600 ppm fatal within hours*
- *Even lower level exposures can result in death if there are underlying medical conditions, or when there are additional factors (such as heat stress)*

Levels of Carbon Monoxide (CO)

10,000 ppm	Immediate unconsciousness, death in one minute
6400 ppm	Death in 10 to 15 minutes
1600 ppm	Headache, dizziness, nausea in 20 minutes, death in 1.5 to 2 hours
1500 ppm	IDLH (from NIOSH Pocket Guide, June 1990)
500 ppm	Death in four hours
200 ppm	Slight headache
50 ppm	OSHA's PEL

GfG Instrumentation

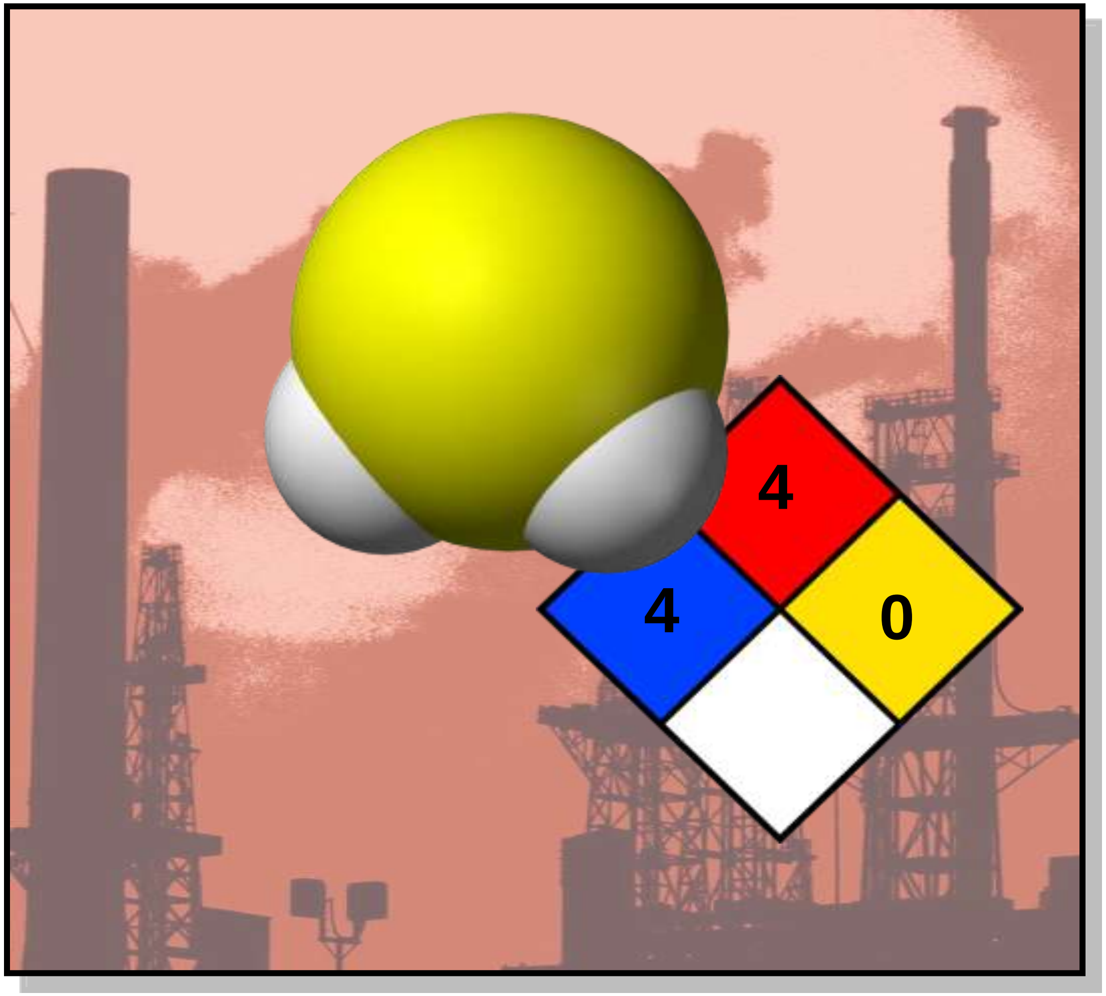
Exposure Limits for Carbon Monoxide

	8-Hr TWA	STEL	Ceiling
Federal USA OSHA PEL	50 ppm	NA	NA
NIOSH REL	35 ppm	NA	200 ppm
TLV	25 ppm	NA	NA
UK OEL	30 ppm	200 ppm	NA
French VL	50 ppm	NA	NA
DFG MAK	30 ppm	60 ppm peak for any 15-min period, (as average value), maximum 4 per shift separated by at least 1-hour	

GfG Instrumentation

Characteristics of Hydrogen Sulfide

- *Colorless*
- *Smells like "rotten eggs" (at low concentrations)*
- *Heavier than air*
- *Corrosive*
- *Flammable (LEL is 4.3 %)*
- *Soluble in water*
- *Extremely toxic!*



Hydrogen Sulfide

- *Produced by anaerobic sulfate-reducing bacteria*
- *Especially associated with:*
  - *Raw sewage*
  - *Crude oil*
  - *Marine sediments*
  - *Tanneries*
  - *Pulp and paper industry*

GfG Instrumentation

Characteristics of Hydrogen Sulfide

- *Half-life in air = 12 to 37 hours*
- *Eventually breaks down in sunlight*
- *During very cold and dry conditions, half-life can exceed 37 hours*
- *Particularly dangerous in oil production areas subject to cold winter temperatures*
- *Collects in pits, within protective berms, or in other low lying areas*

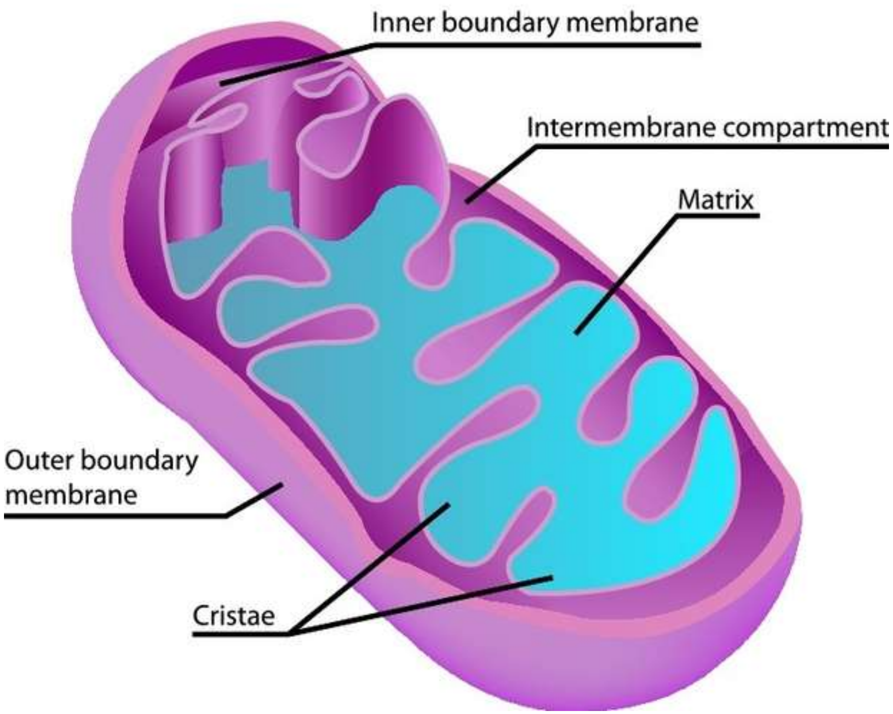
Characteristics of Hydrogen Sulfide

- *Mitochondrial poison that prevents utilization of oxygen during cellular respiration, shutting down power source for many cellular processes*

- *Also binds to hemoglobin in red blood cells, interfering with oxygen transport*

- *Exposure primarily by inhalation, but can also occur by ingestion (contaminated food) and skin (water and air)*

- *Once in body, rapidly distributed to central nervous system, lungs, liver, muscle and other organs*




Effects of Hydrogen Sulphide H_2S
At low concentrations, as low as 150 ppm, hydrogen sulphide deadens the sense of smell. At higher concentrations the phrenic nerve, which controls the contractions of the diaphragm, is neutralised, causing breathing to stop.
The phrenic nerve travels down the neck into the chest cavity, supplying the diaphragm with electrical impulses that control breathing. When neutralized, breathing stops.

Toxic effects H_2S

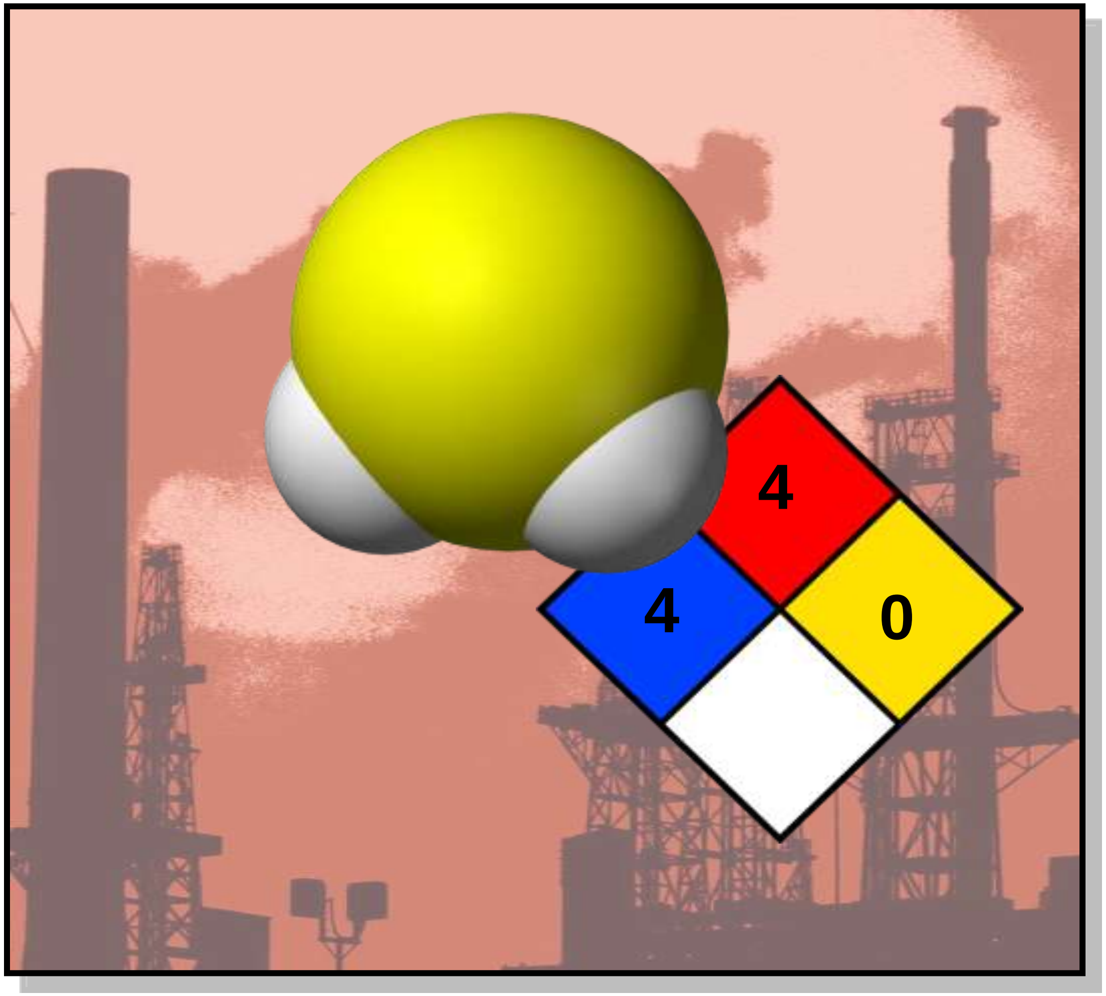
>1.0 PPM	*Smell*
100 PPM	*Rapid loss of smell*
200 – 300 PPM	*Eye inflammation, respiratory tract irritation after 1 hour, loss of consciousness with time*
500 – 700 PPM	*Death in 30 min. – 1 hr.*
1000 PPM	*Immediate respiratory arrest, loss of consciousness, followed by death*

Exposure limits for H_2S

Federal USA OSHA PEL	8-Hour TWA	STEL	Acceptable Ceiling Concentration	Acceptable Max Peak Above Ceiling for an 8-Hour Shift	
				Concentration	Maximum Duration
	NA	NA	20 ppm	50 ppm	10-minutes once only if no other measurable exposure occurs during shift
REL	10 ppm	15 ppm	NA	NA	NA
TLV (NIC)	10 ppm 1 ppm	15 ppm 5 ppm	NA	NA	NA
UK OEL	10 ppm	15 ppm	NA	NA	NA
FR VL	5 ppm	10 ppm	NA	NA	NA
DFG MAK	10 ppm	NA	20 ppm peak in any 10-min period, (as momentary ceiling value), maximum 4 per shift		

Exposure limits for H_2S

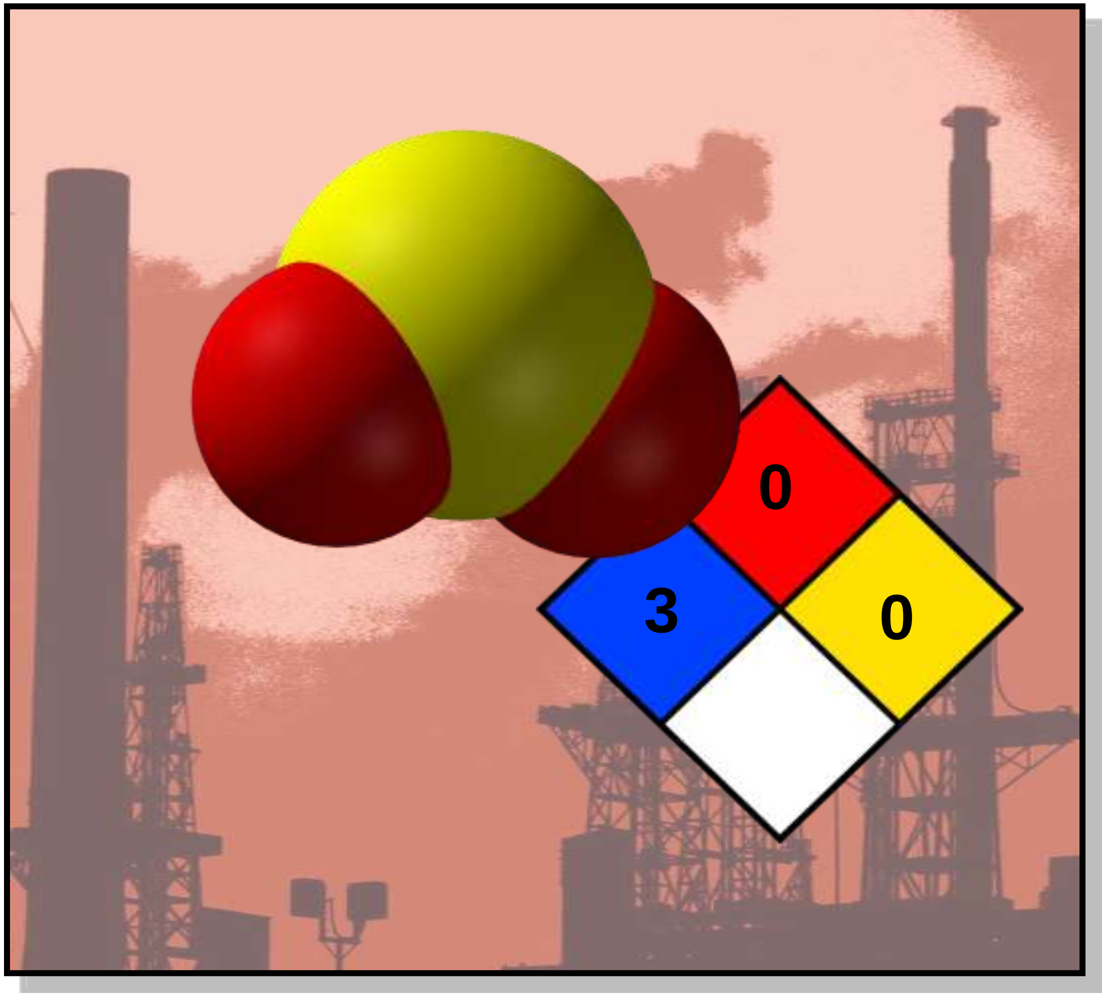
- ***TLV Currently:***
  - ***TWA = 10 ppm***
  - ***STEL = 15 ppm***
- ***NIC:***
  - ***TWA = 1.0 ppm***
  - ***STEL = 5.0 ppm***



GfG Instrumentation

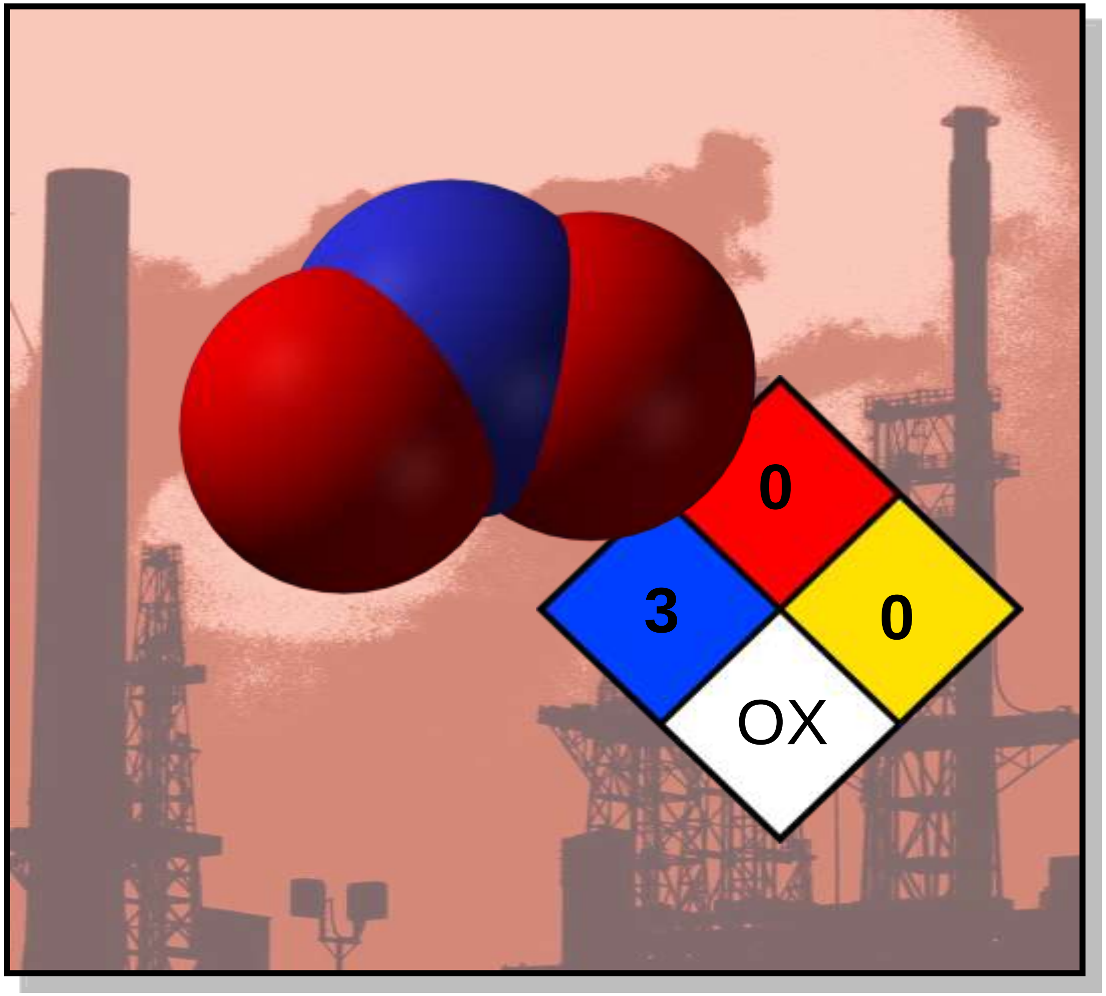
Exposure limits for SO2

- *TLV Currently:*
  - *TWA = 2 ppm*
  - *STEL = 5 ppm*
- *NIC: STEL = 0.25 ppm*



Exposure limits for NO2

- *TLV:*
  - *8 hr. TWA = 3 ppm*
  - *15 min. STEL = 5 ppm*
- *US OSHA PEL:*
  - *Ceiling = 5 ppm*
- *US NIOSH REL:*
  - *15 min. STEL = 1 ppm*



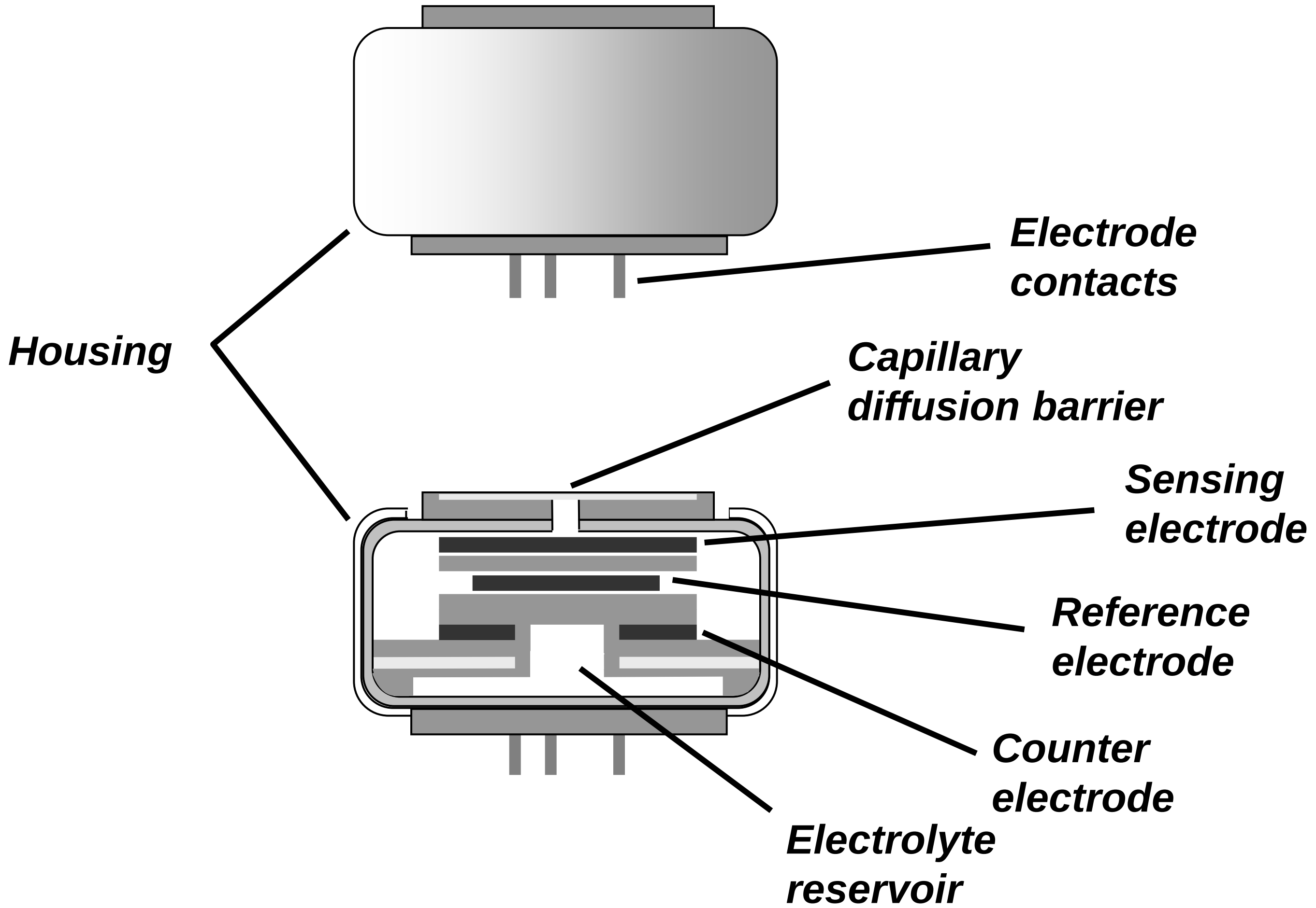
Typical factory default alarm settings

Factory Default Alarm Set-points	TWA	STEL	Low	High
Hydrogen sulfide	10 ppm	15 ppm	10 ppm	15 ppm
Sulfur dioxide	2 ppm	5 ppm	2 ppm	5 ppm
Hydrogen cyanide	4.7 ppm	10 ppm	4.7 ppm	10 ppm
Carbon monoxide	35 ppm	200 ppm	35 ppm	200 ppm
Chlorine	0.5 ppm	1.0 ppm	0.5 ppm	1.0 ppm
Nitrogen dioxide	2 ppm	5 ppm	2 ppm	5 ppm
Ammonia	25 ppm	35 ppm	25 ppm	50 ppm
Phosphine	0.3 ppm	1.0 ppm	0.3 ppm	1.0 ppm
Ethylene oxide	1 ppm	5 ppm	1 ppm	5 ppm
Chlorine dioxide	0.1 ppm	0.3 ppm	0.1 ppm	0.3 ppm
Ozone	25 ppm	25 ppm	25 ppm	25 ppm
Oxygen	NA	NA	19.5%	23.5%

Substance-specific electrochemical sensors

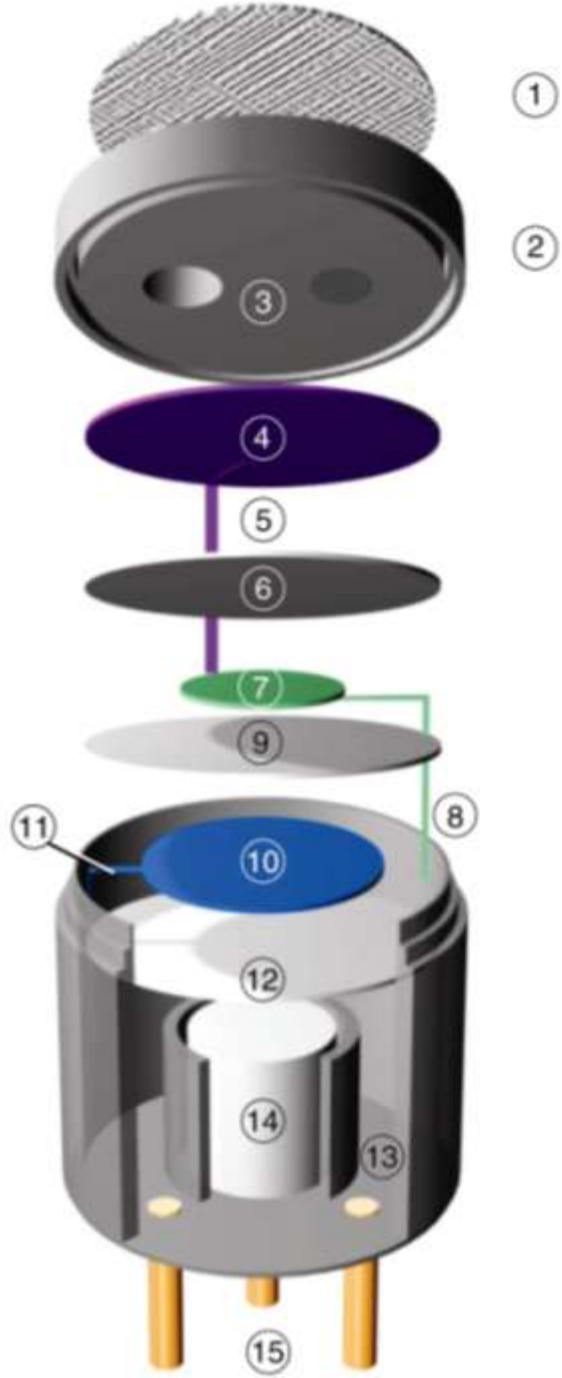
- ***Gas diffusing into sensor reacts at surface of the sensing electrode***
- ***Sensing electrode made to catalyze a specific reaction***
- ***Use of selective external filters further limits cross sensitivity***

Three electrode electrochemical toxic sensor



GfG Instrumentation

Major Components of Electrochemical H2S Sensor



1. External Moisture Barrier
2. Diffusion Barrier
3. Diffusion Capillary
4. H_2S Sensing Electrode
5. Current Collector (sensing)
6. Separator
7. Reference Electrode
8. Current Collector (reference)
9. Separator
10. Counter Electrode
11. Current Collector (counter)
12. Separator
13. Electrolyte Reservoir
14. Wick
15. Connector Pins

Electrochemical CO Sensor Detection Mechanism

Carbon monoxide is oxidized at the sensing electrode:

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-$$

The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:

$$1/2O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

And the overall reaction is: $CO + ½O_2 \longrightarrow CO_2$

4CF Signal Output: 0.07 μA / ppm CO

Electrochemical H_2S Sensor Detection Mechanism

Hydrogen sulfide is oxidized at the sensing electrode:

$$H_2S + 4H_2O \longrightarrow H_2SO_4 + 8H^+ + 8e^-$$

The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen present in the air to water:

$$2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$$

And the overall reaction is: $H_2S + 2O_2 \longrightarrow H_2SO_4$

4HS Signal Output: 0.7 μA / ppm H2S

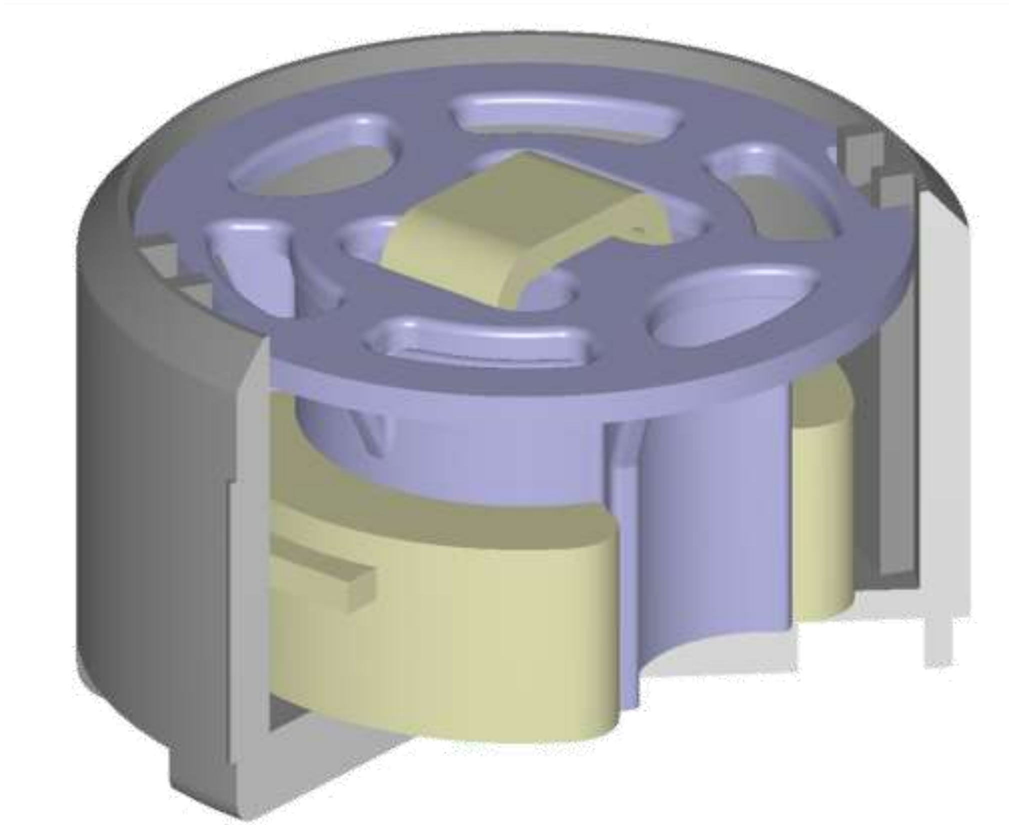
MicroCel versus 4 Series H2S and CO Sensors

- ***Same "non consuming" chemistry as 4 Series sensors BUT:***
  - ***MicroCel CO sensor has better internal filter, less cross sensitivity to VOCs than CO channel of COSH sensor***
  - ***MicroCel H2S sensor based on the 4HS-LM "low methanol" electrode system (less cross sensitivity to interfering gases and VOCs)***

GfG Instrumentation

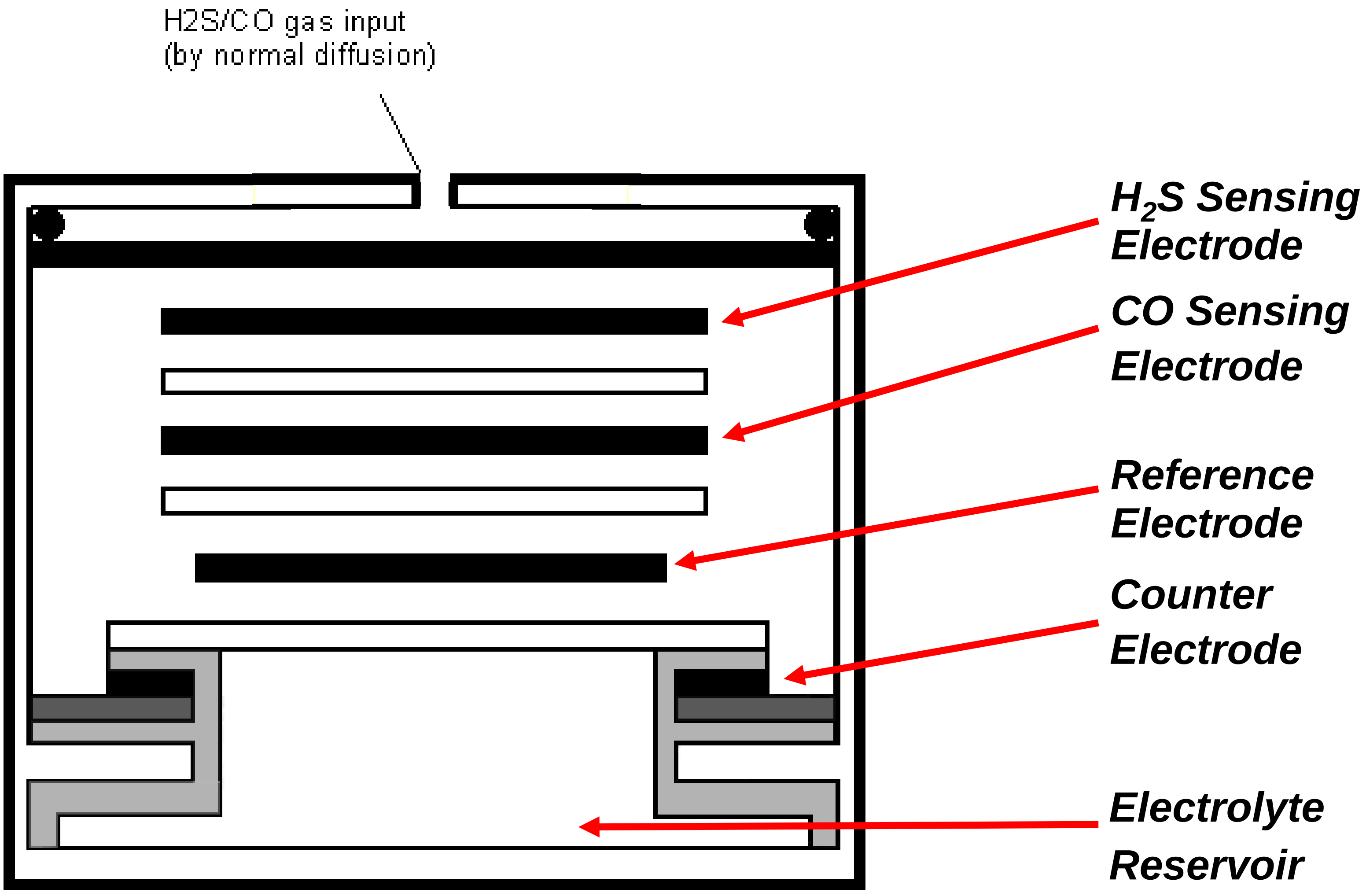
City Technology 4 COSH Sensor

- Dual channel "COSH" sensor
- Single housing
- Two independent outputs for H2S and CO measurement
- Gas path through H2S first, CO 2nd



GfG Instrumentation

City Technology 4 COSH Sensor



GfG Instrumentation

City Technology 4 COSH Sensor

H_2S Gas Reaction:

H_2S Sensing Electrode Reaction: $H_2S + 4H_2O \longrightarrow H_2SO_4 + 8H^+ + 8e^-$

H_2S Counter Electrode Reaction: $2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$

Overall reaction: $H_2S + 2O_2 \longrightarrow H_2SO_4$

CO Gas Reaction:

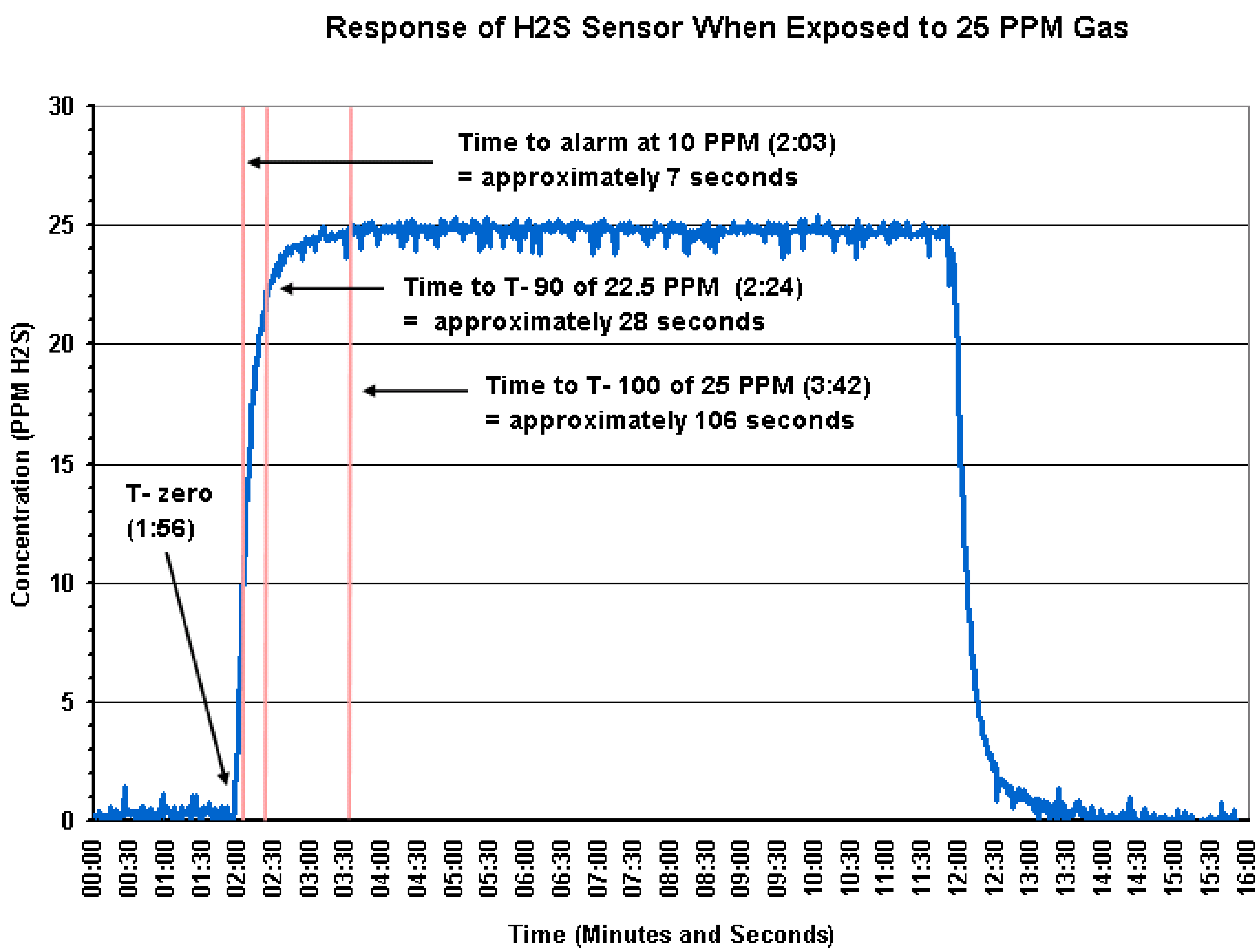
CO Sensing Electrode Reaction: $CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-$

CO Counter Electrode Reaction: $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

Overall reaction: $CO + \frac{1}{2}O_2 \longrightarrow CO_2$

H_2S signal output: 775 nA / ppm

CO signal output: 80 nA / ppm



Response of H2S Sensor When Exposed to 25 PPM Gas
Time to alarm at 10 PPM (2:03)
= approximately 7 seconds
Time to T- 90 of 22.5 PPM (2:24)
= approximately 28 seconds
Time to T- 100 of 25 PPM (3:42)
= approximately 106 seconds
T- zero
(1:56)
Concentration (PPM H2S)
30
25
20
15
10
5
0
00:00
00:30
01:00
01:30
02:00
02:30
03:00
03:30
04:00
04:30
05:00
05:30
06:00
06:30
07:00
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08:00
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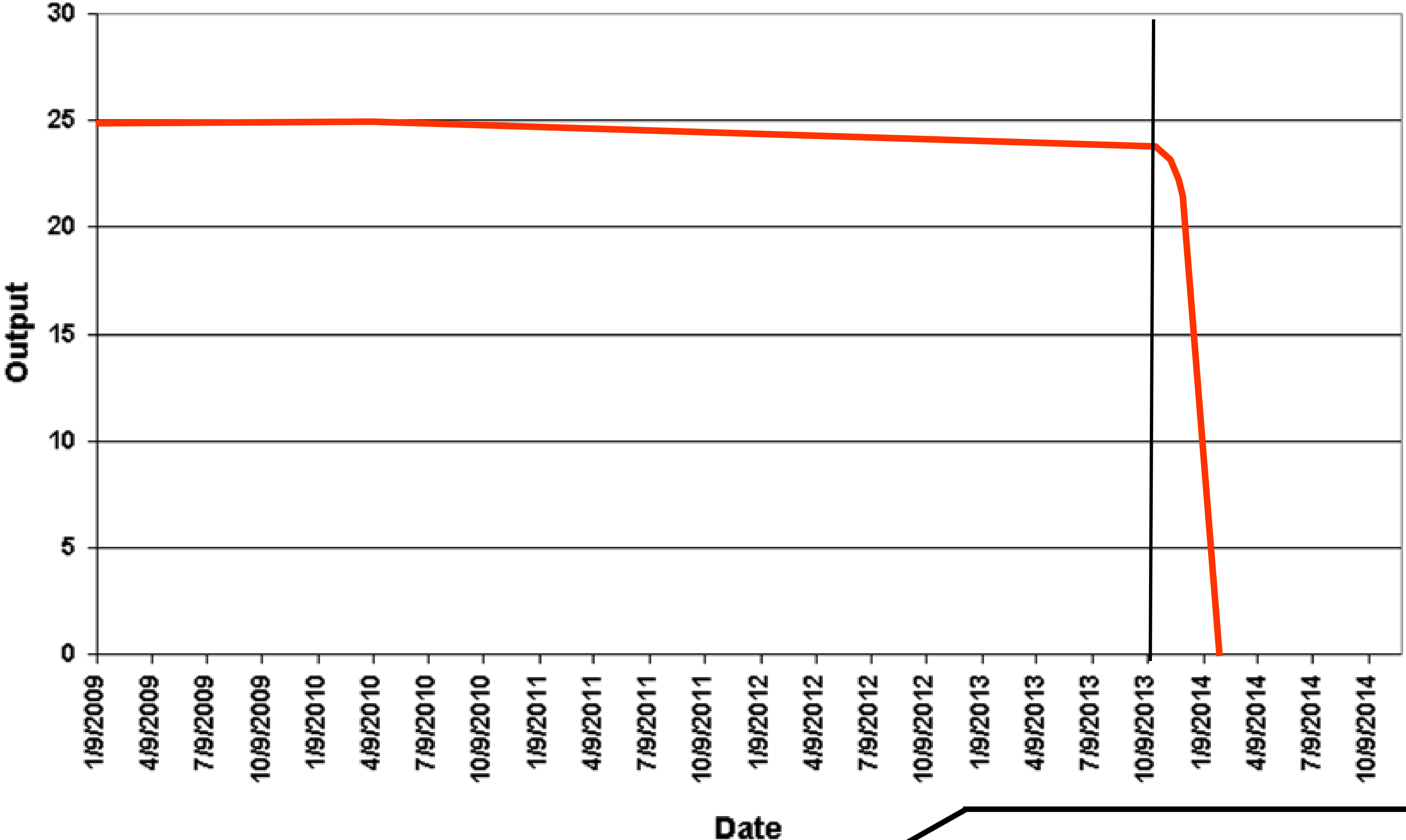
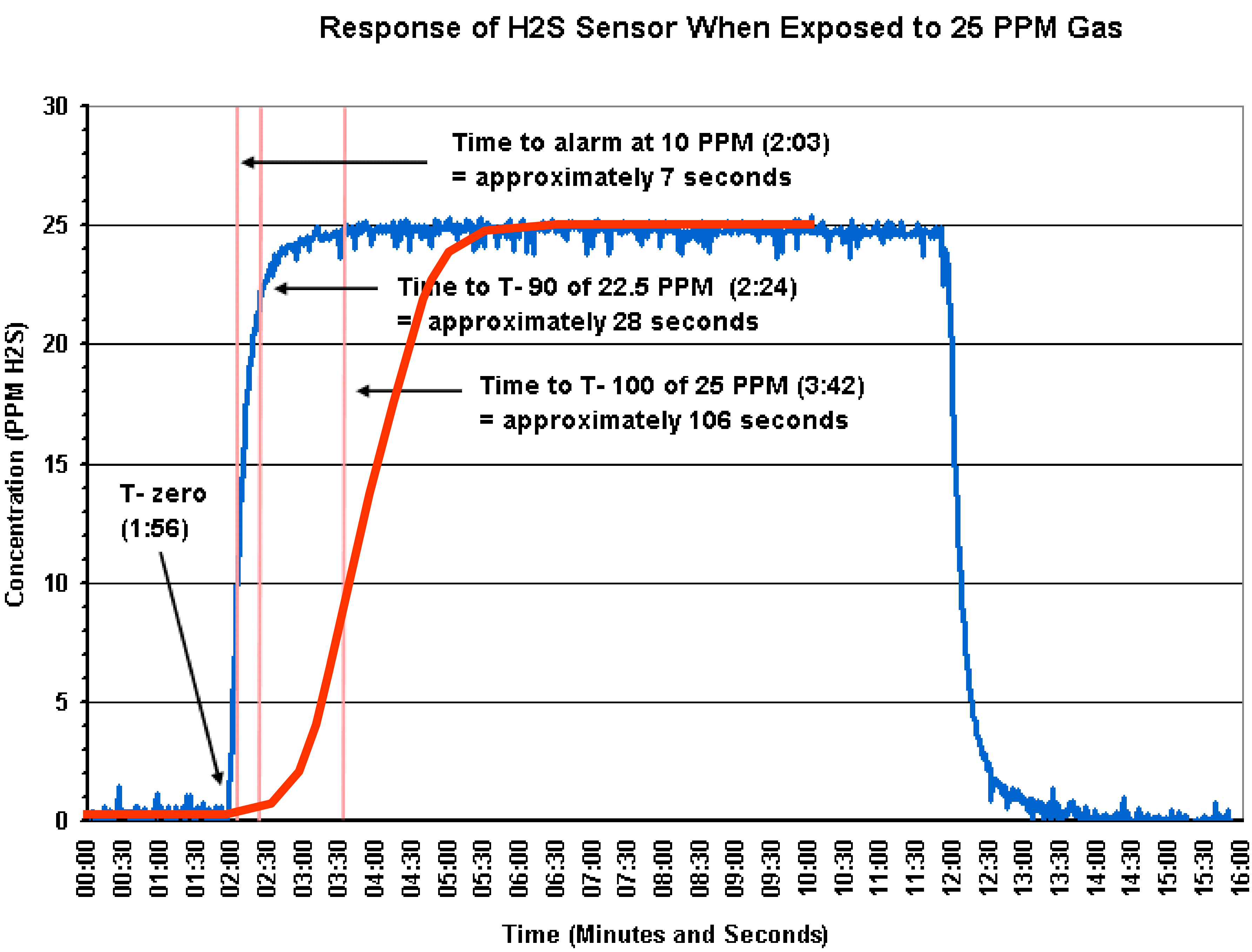
09:00
09:30
10:00
10:30
11:00
11:30
12:00
12:30
13:00
13:30
14:00
14:30
15:00
15:30
16:00
Time (Minutes and Seconds)

Typical signal output over lifespan of sensor



GfG Instrumentation



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= approximately 7 seconds
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= approximately 28 seconds
Time to T- 100 of 25 PPM (3:42)
= approximately 106 seconds
T- zero
(1:56)
Concentration (PPM H2S)
0
5
10
15
20
25
30
00:00
00:30
01:00
01:30
02:00
02:30
03:00
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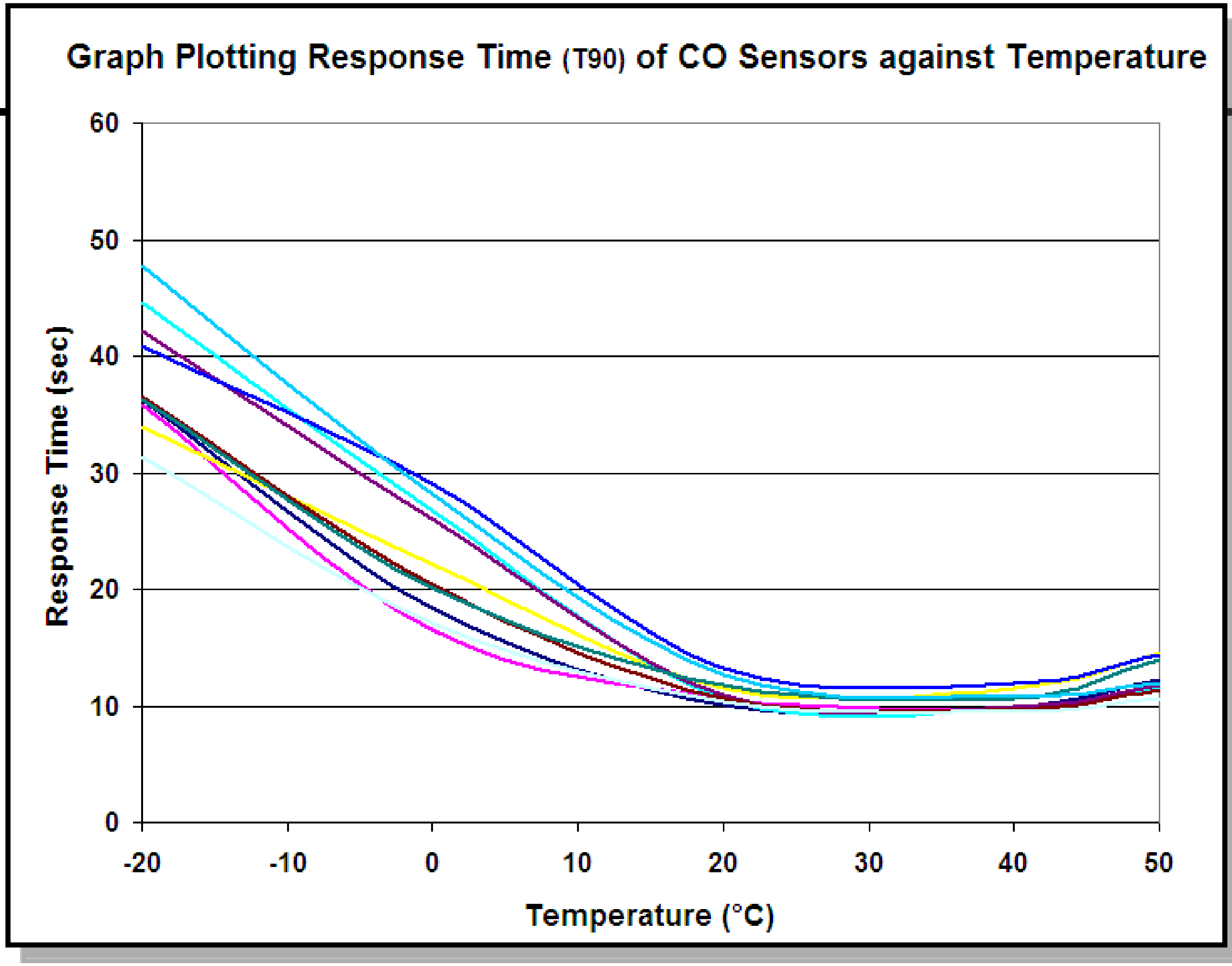
12:00
12:30
13:00
13:30
14:00
14:30
15:00
15:30
16:00
Time (Minutes and Seconds)

Electrochemical sensor performance

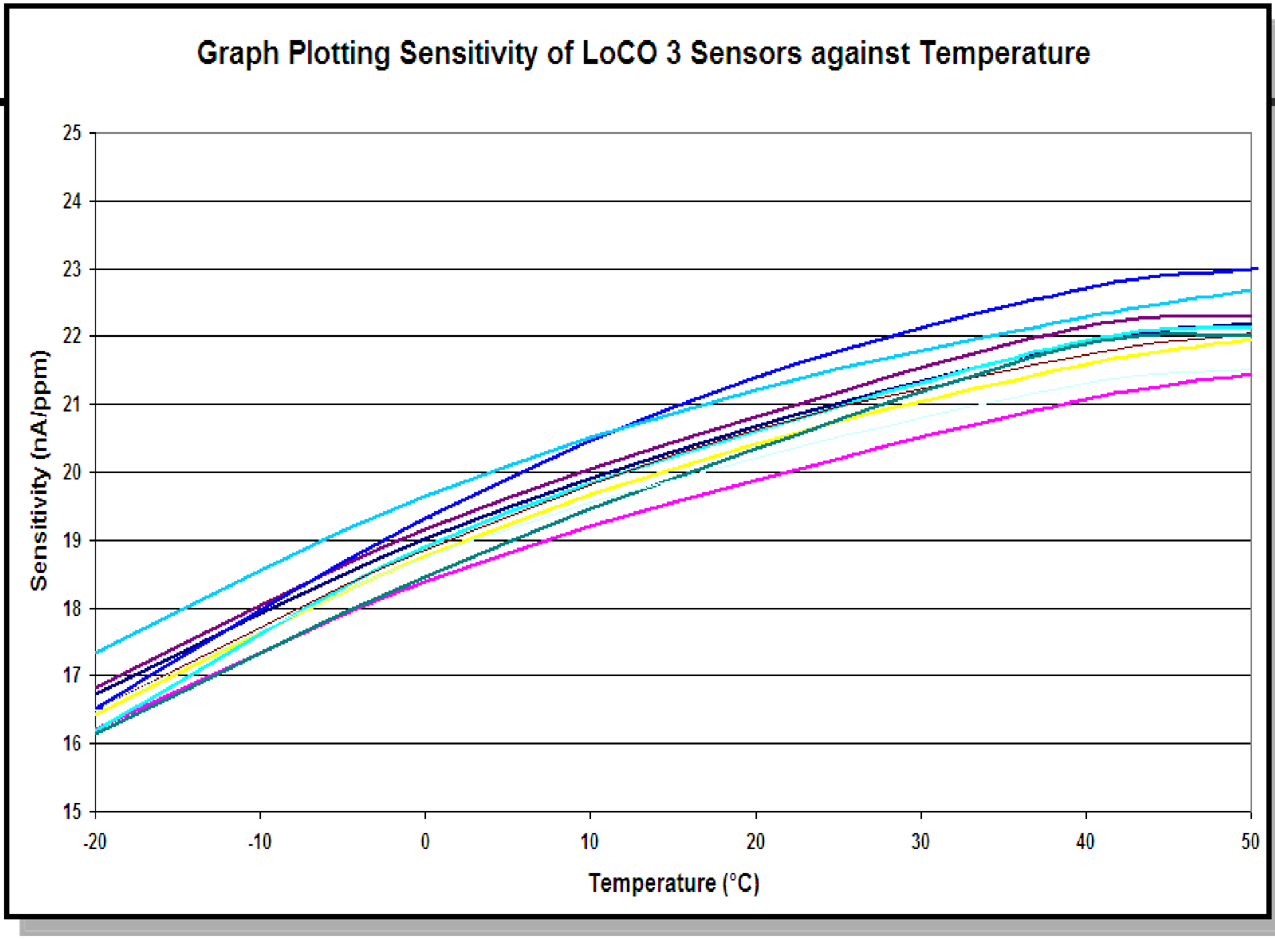
- ***Sensor performance is affected by temperature***
- ***Effects mathematically predictable, but may vary between sensors***
- ***In general, response (T_{90}) slower in very cold temperatures***



GfG Instrumentation

Electrochemical sensor performance

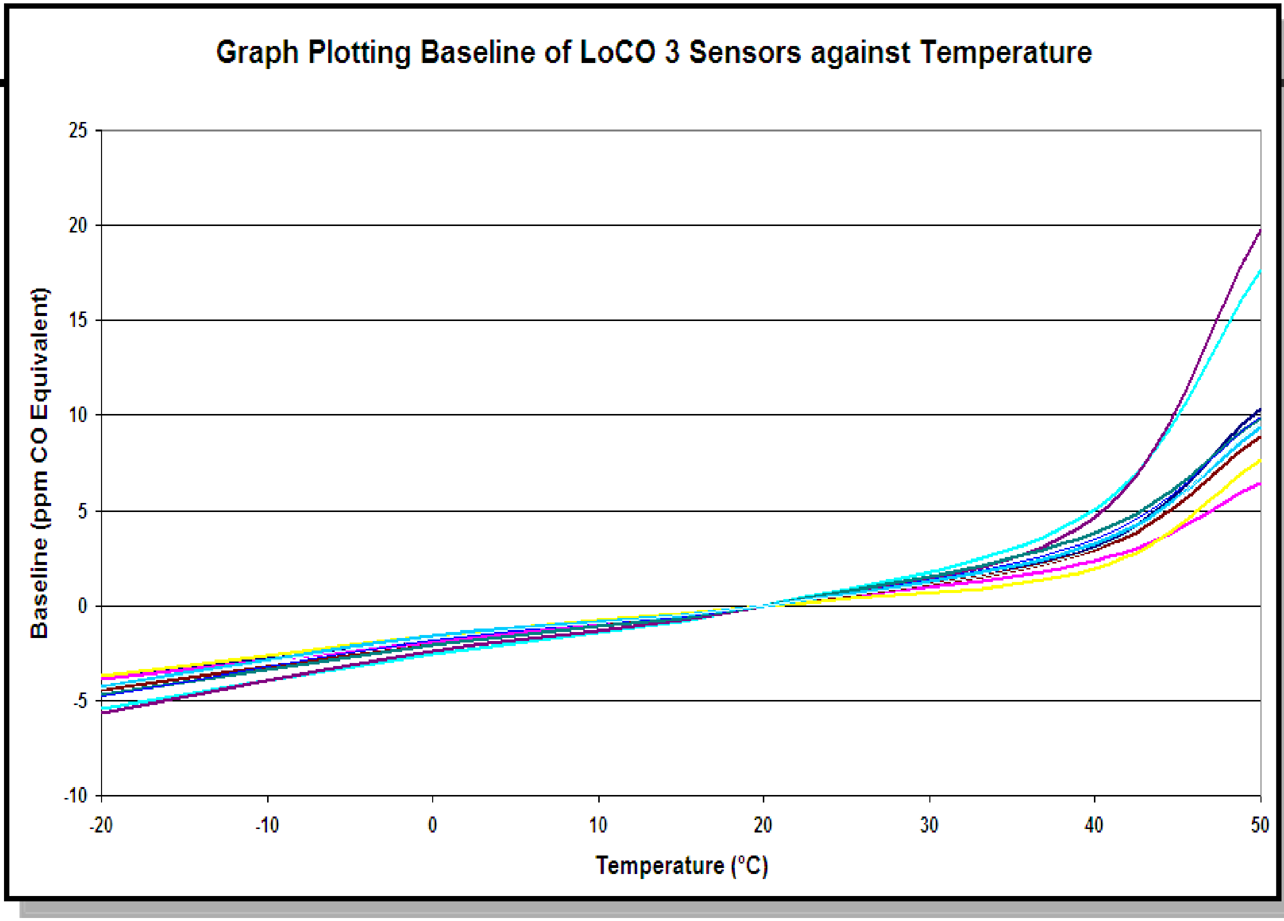
- *EC sensor sensitivity is generally lower in cold temperatures; higher in hot temperatures*
- *Most instruments have temperature compensation that automatically corrects readings as a function of temperature*
- *Can also correct readings by calibrating instrument near temperature in which it will be used*



GfG Instrumentation

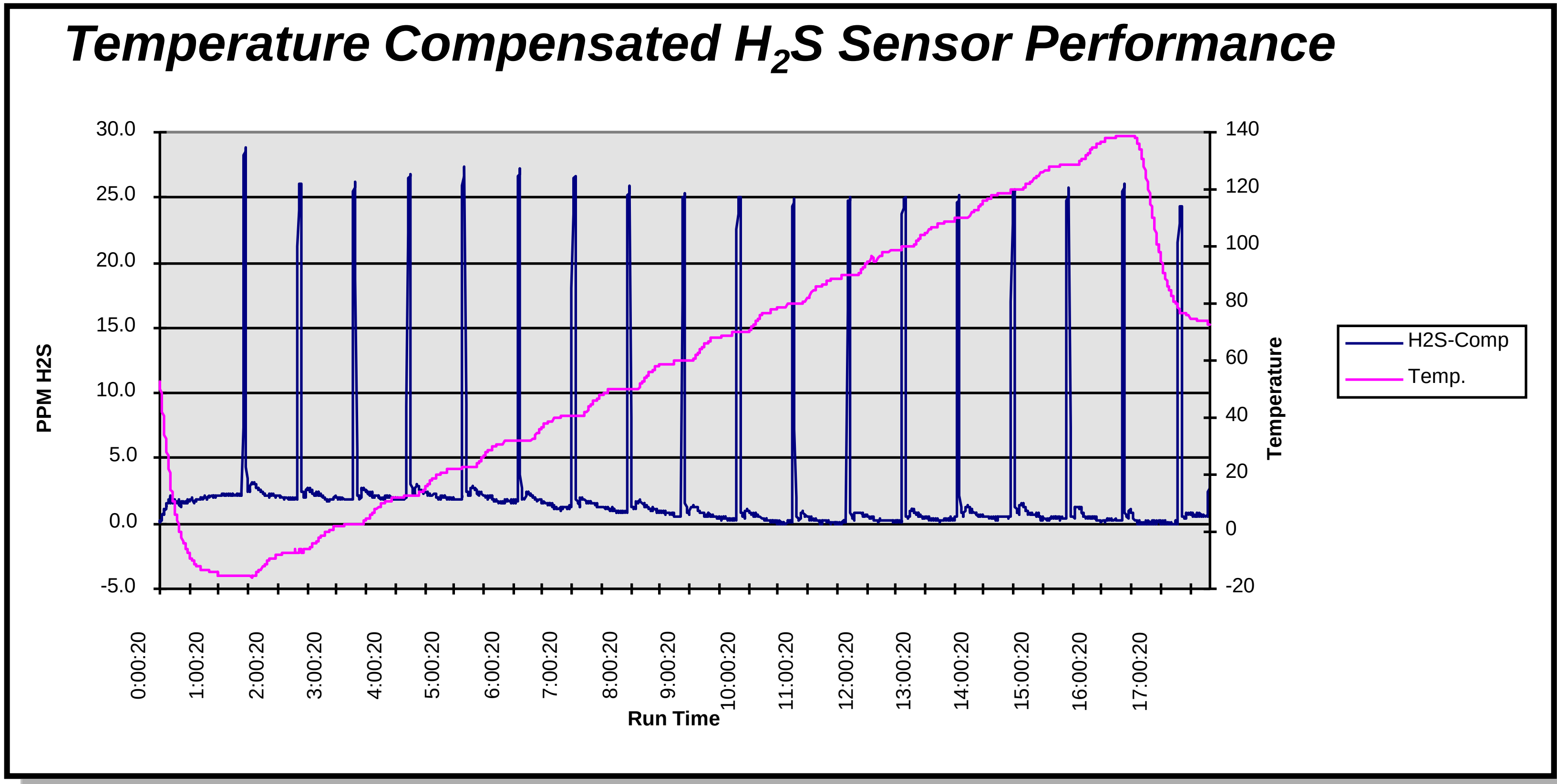
Electrochemical sensor performance

- *In general, uncorrected "zero" (baseline) output of sensor is lower in cold temperatures; higher in hot temperatures*
- *Effects mathematically predictable; can be corrected by means of temperature compensation*



GfG Instrumentation

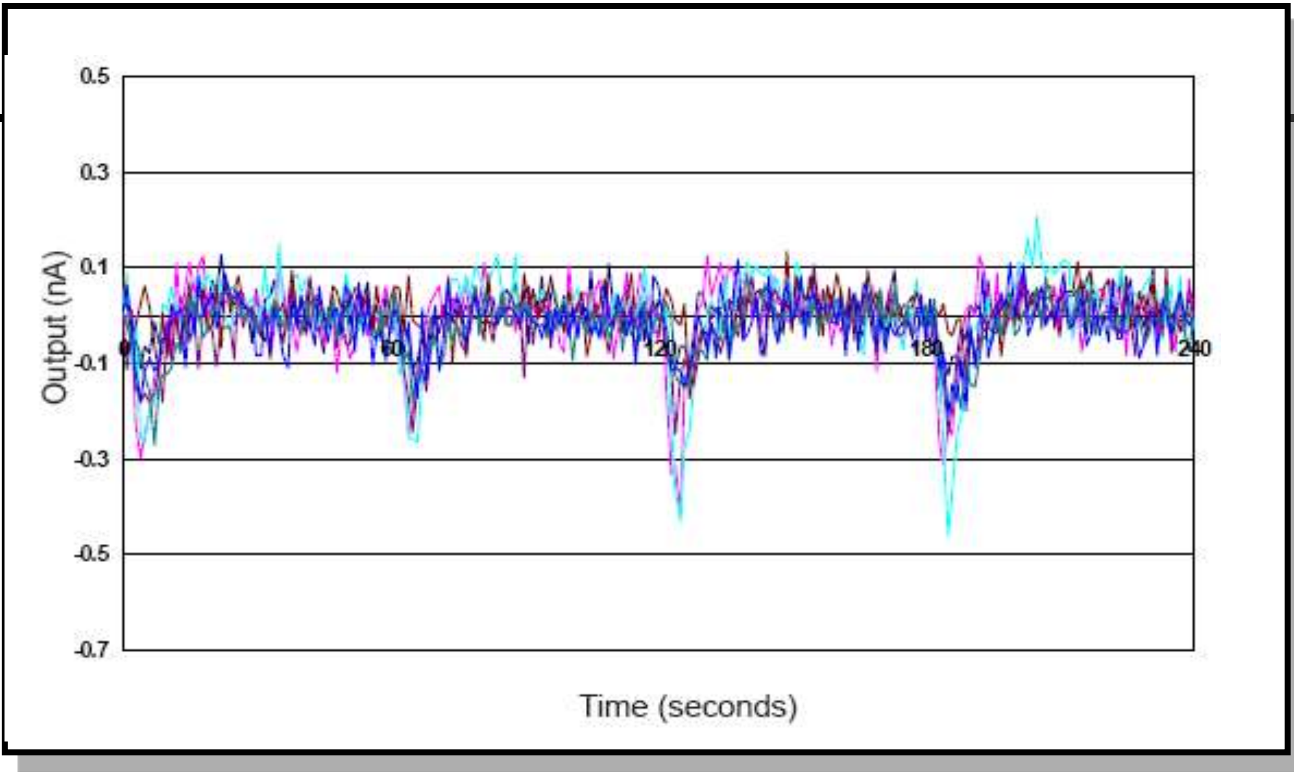
Performance after electronic temperature compensation



GfG Instrumentation

Effects of humidity on EC sensors

- *Sudden changes in humidity can cause "transientys" in readings*
- *Sensor generally stabilizes rapidly*
- *Avoid breathing into sensor or touching with sweaty hand*



GfG Instrumentation

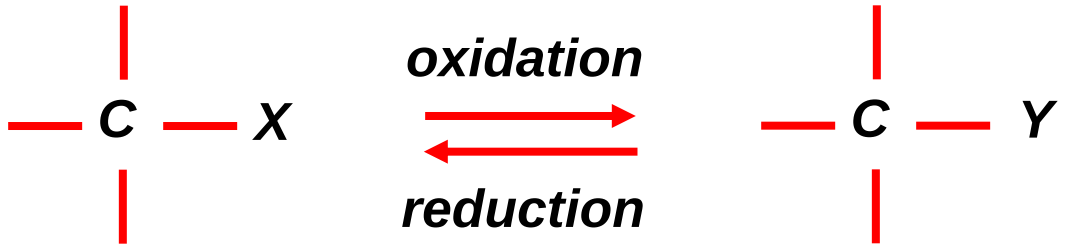
Commonly Available Toxic Sensors

Gas	Formula	Sensor
Ammonia	NH_3	NH_3
Arsine	AsH_3	AsH_3
Carbon Monoxide	CO	CO
Chlorine	Cl_2	Cl_2
Chlorine Dioxide	ClO_2	ClO_2
Diborane	B_2H_6	AsH_3
Fluorine	F_2	F_2
Germane	GeH4	GeH4
Hydrazine	N_2H_4	N_2H_4
Hydrogen Bromide	HBr	HCl
Hydrogen Chloride	HCl	HCl
Hydrogen Fluoride	HF	HF
Hydrogen Sulfide	H_2S	H_2S
Nitric Oxide	NO	NO
Nitrogen Dioxide	NO_2	NO_2
Ozone	O_3	O_3
Phosgene	$COCl_2$	$COCl_2$
Phosphine	PH_3	PH_3/ AsH_3
Silane	SiH_4	SiH_4

GfG Instrumentation

Oxidation reduction reactions

- *Oxidation occurs when a bond between an atom which is less electronegative is replaced by a bond to an atom that is more electronegative. The reverse process is reduction*



X is less electronegative

Y is more electronegative

Oxidizing vs. reducing gases

- ***Reducing gases:***
  - ***H_2S***
  - ***CO***
  - ***SO_2***
  - ***PH_3***
- ***Oxidizing gases:***
  - ***Cl_2***
  - ***NO_2***
  - ***O_3***

Reducing vs. oxidizing sensor reactions

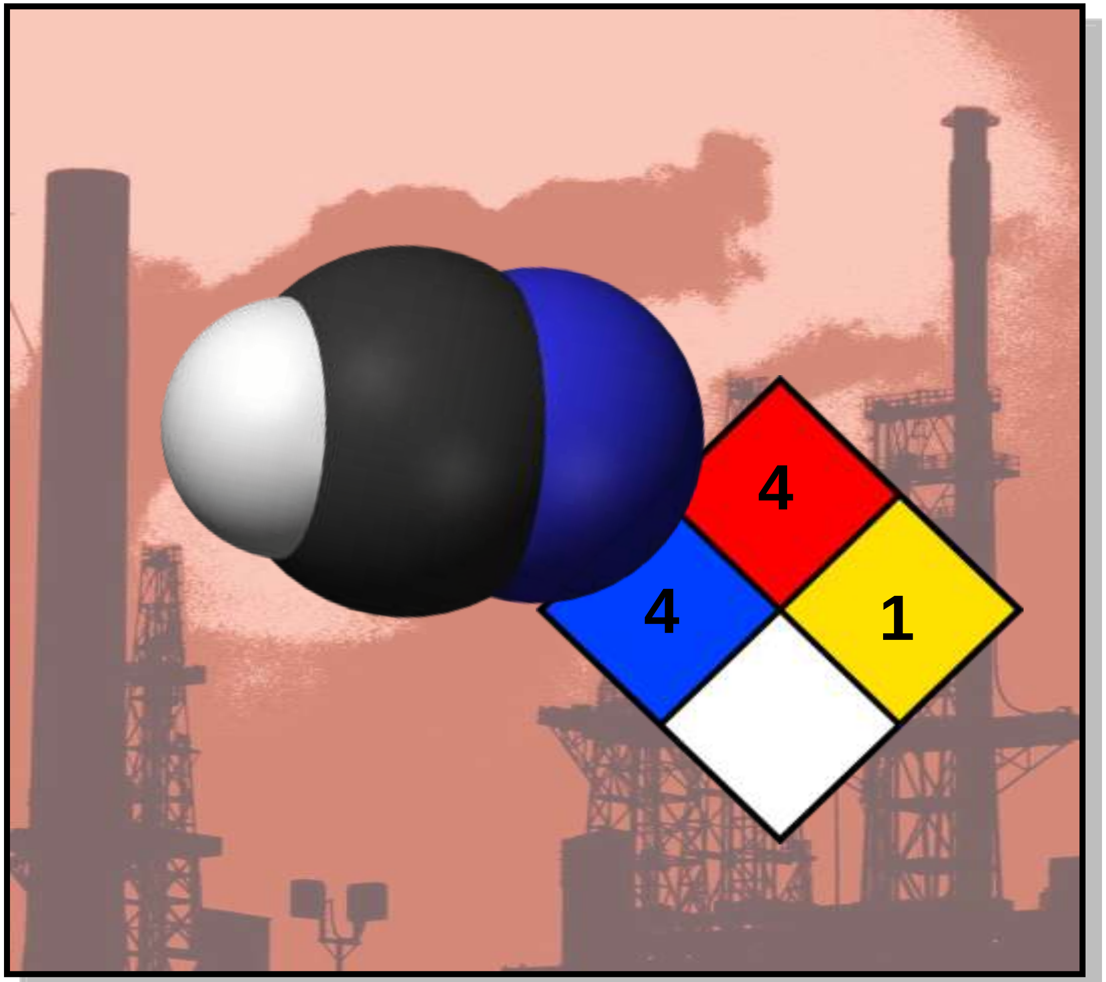
- ***Reducing gas sensor:***
  - $H_2S + 2O_2 \longrightarrow H_2SO_4$
  - $CO + \frac{1}{2}O_2 \longrightarrow CO_2$
- ***Oxidizing gas sensor reaction:***
  - $Cl_2 + H_2 \longrightarrow 2HCl$

GfG Instrumentation

	Sensor Type and Percentage Response to Interfering Gas											
Interfering Gas	***CO***	***H_2S***	***SO_2***	***NO_2***	***Cl_2***	***ClO_2***	***HCN***	***HCl***	***PH_3***	***NO***	***H_2***	***NH_3***
Carbon Monoxide (CO)	100	2	1	0	0	0	0	0	0	0	20	0
Hydrogen Sulfide (H_2S)	10	100	1	-8	-3	-25	400	60	3	10	20	130
Sulfur Dioxide (SO_2)	0	10	100	0	0	0	-	40	-	0	0	70
Nitrogen Dioxide (NO_2)	-20	-20	-100	100	12	-	-120	-	-	30	0	0
Chlorine (Cl_2)	-10	-20	-25	-100	100	20	-20	6	-10	0	0	-50
Chlorine Dioxide (ClO_2)	-	-	-	-	20	100	-	-	-	-	-	-
Hydrogen Cyanide (HCN)	15	10	50	1	0	0	100	35	1	0	30	5
Hydrogen Chloride (HCl)	3	0	0	0	2	0	0	100	0	15	0	0
Phosphine (PH_3)	-	-	-	-	-	-	0	300	100	-	-	-
Nitric Oxide (NO)	10	1	1	0	-	-	-90	-	-	100	30	50
Hydrogen (H_2)	60	0.05	0.5	0	0	0	0	0	0	0	100	0
Ammonia (NH_3)	0	0	0	0	0	0	0	0	0	0	0	100

Exposure limits for HCN

- ***US OSHA PEL:***
  - ***TWA = 10 ppm***
- ***US NIOSH REL:***
  - ***15 min. STEL = 4.7 ppm***
- ***TLV:***
  - ***Ceiling = 4.7 ppm***



- ***Example: Sensoric HCN hydrogen cyanide sensor at 20°C***

Gas	Concentration	Reading [ppm]
Alcohols	1000 ppm	0
Ammonia	100 ppm	0
Arsine	0.2 ppm	1
Carbon Dioxide	5000 ppm	0
Carbon Monoxide	100 ppm	1
Chlorine	1 ppm	0
Diborane	0.25 ppm	0.4
Hydrocarbons	% ppm	0
Hydrochloric Acid	5 ppm	0
Hydrogen	10000 ppm	0
Hydrogen Sulfide	10 ppm	0[1]
Nitric Oxide	100 ppm	0
Nitrogen	100 %	0
Nitrogen Dioxide	10 ppm	-19
Ozone	0.25 ppm	0
Sulfur Dioxide	20 ppm	0.04

1) Short gas exposure in minute range; after filter saturation: ca. 40 ppm reading.

H_2S Sensor Cross Sensitivity

Gas	Conc.	Response
CO	300 ppm	≤1.5 ppm
SO_2	5 ppm	about 1 ppm
NO	35 ppm	<0.7 ppm
NO_2	5 ppm	about – 1 ppm
H_2	1000 ppm	≤ 10 ppm
CO2		No response
Methyl sulphide	100 ppm	15 ppm
Ethyl sulphide	100 ppm	10 ppm
Methyl mercaptan	100 ppm	about 45 ppm
Propylene	1000 ppm	about – 0.5 ppm
Isobutylene	1000 ppm	about – 0.3 ppm
Ethylene		No response
Toluene	10000 ppm	No response
Turpentine	3000 ppm	about 70 ppm
MTBE	1000 ppm	≤ 60 ppm

Effect of citrus solvents on H2S and COSH sensors

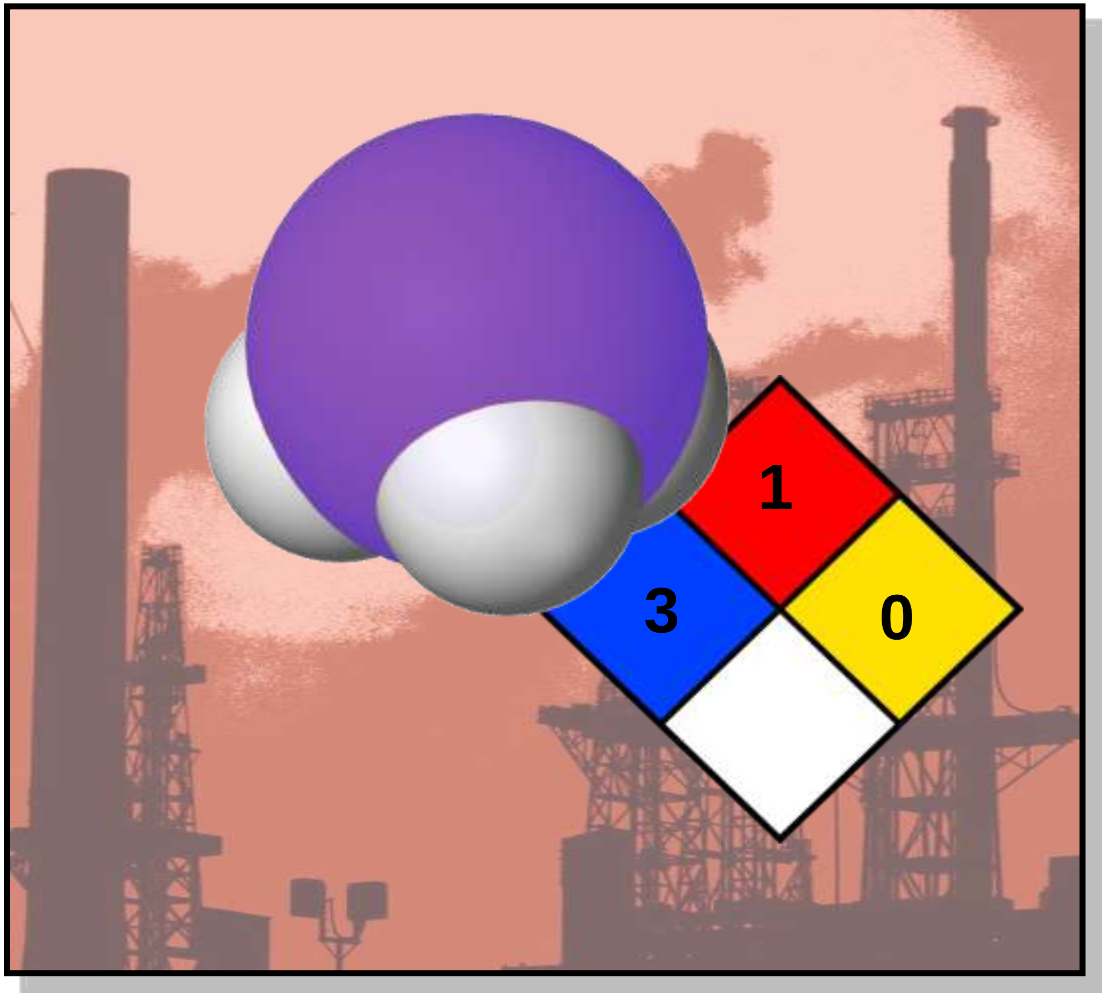
- *Orange peels contain d-limonene, the same "citrus oil" solvent included in many household cleaners*
- *ALL H2S sensors respond to limonene as well as other VOCs like butadiene if the vapors are present in high enough concentrations*
- *Instrument responds by going into alarm, making this a "Fail Safe" alarm condition*
- *Requires high concentration for the H2S sensor to go into alarm*
- *In most cases this is actually a benefit for our customers*
- *Although H2S sensors are not designed to function as general VOC detectors, the fact that they respond to high concentrations of VOC has saved the life of at more than one worker*

Cross sensitivity to VOCs actually benefit to customers

- *Case study example:*
  - *A worker at chemical plant entered production area to remove a bucket of "product" that contained mix of 1,3 butadiene (48%), C6 hydrocarbons (22%), and C5 hydrocarbons (15%)*
  - *Butadiene is an extremely volatile and toxic VOC*
  - *The worker's personal H_2S detector immediately went into alarm, but the worker did not believe that the alarm was valid*
  - *The worker left the area, replaced his H_2S detector with a new one, donned a second detector for SO_2, and went back into the area*
  - *Both new instruments went into alarm but , unfortunately, this time the worker collapsed*
  - *The worker was rescued, but had to spend significant time in the hospital*
  - *The alarms were caused by response of sensors to butadiene*

Exposure limits for NH3

- ***US OSHA PEL:***
  - ***TWA = 50 ppm***
- ***US NIOSH REL:***
  - ***8 hr. TWA = 25 ppm***
  - ***15 min. STEL = 35 ppm***
- ***TLV:***
  - ***8 hr. TWA = 25 ppm***
  - ***15 min. STEL = 35 ppm***



GfG Instrumentation

Different types of ammonia sensors have different limitations!

- *The secret to choosing and installing a trouble free system is understanding the limitations of the sensors*
- *Critical to specify the correct sensors for the locations and conditions in which they will be operated*

GfG Instrumentation

Key factors in NH_3 sensor selection

- ***Understand the environmental factors for each location***
- ***Establish the environmental AND detection requirements:***
  - ***Temperature range of the application***
  - ***Detection range required***
  - ***Typical gas concentrations!***
  - ***Background gases present (cleaning solvents, process gases, and other compounds)***
  - ***Make sure you have all the information to provide the best solution***

Choosing the right NH_3 sensor for the application

- ***Issues that can affect the choice of sensors:***
  - ***Continuous or high exposure levels***
  - ***Cross sensitivity – false alarms***
  - ***Temperature of environment to be monitored***
  - ***No one sensor type suitable for all applications***
  - ***Select the best sensor based on conditions in which the sensor will be used***

GfG Instrumentation

Electrochemical Ammonia Sensors

- ***Electrolyte consumed as gas detected***
- ***Life of sensor rated in "PPM Exposure Hours"***
- ***Higher the ambient concentration of ammonia, the faster sensor will need to be replaced***

GfG Instrumentation

Electrochemical (EC) Ammonia Sensors

Benefits	*Concerns*
• *Highly specific to NH_3* • *Accurate at low ranges (<20/30ppm)* • *Low humidity dependence* • *Linear mA output signals* • *Can be use in inert environments*	• *May require heater or different electrolyte in low temperature applications (< -20°C)* • *Sensor life limited to exposure levels* • *Limited end ranges (0-200 or 1,000 ppm)* • *High concentrations can deplete sensors in minutes* • *Monthly to quarterly calibrations/ testing* • *Slow recovery to completion*

NH_3 Electrochemical (EC) Sensor Applications

- *Best suited for areas where NH3 present only in unusual or emergency circumstances*
- *EC sensor best technology for low detection levels*
- *Stable and accurate detection of NH_3 with lowest amount of cross sensitivity*
- *Use for:*
  - *TLV compliance*
  - *Detection of sudden leaks*

GfG Instrumentation

NH_3 Sensing Technologies: Metal Oxide Semiconductor (MOS)

Benefits	Concerns
• Lower investment price and cost of ownership • Long sensor life • Long calibration intervals • Can be calibrated with low cost calibration gases (CH_4 and CO)	• Very cross sensitive • Fluctuations in humidity and temperature (false alarms) • Not designed to provide quantified readings at low concentrations • Slow reaction and clearing times

GfG Instrumentation

- *Sensing element:*
  - *Tin dioxide (SnO_2) on sintered alumina ceramic*
  - *In clean air electrical conductivity low*
  - *Contact with reducing gases (such as CO or combustibles) increases conductivity*
  - *Sensitivity to specific gases depends on temperature of sensing element*

Applications: MOS Sensors

- ***Typically used as a low cost detection method***
- ***Offer longest expected life but also have the highest degree of cross sensitivity and false alarms***
- ***May be used for:***
  - ***Compressors rooms***
  - ***Vent line***
  - ***Cold storage***

Charge carrier injection (CI) sensors

- ***Depend on the adsorption of ammonia by "charge carrier" molecules in a solid state substrate***
- ***Selectively bind NH_3 with a gas-sensitive material***
- ***By absorbing NH_3 the charge carriers are "injected" into the sensor element, causing change in resistance proportional to the concentration of NH_3***

GfG Instrumentation

Applications: Charge Carrier Injection (CI) Sensors

- ***Best suited for areas where electrochemical sensors are unsuitable due to continuous exposure or extreme environmental conditions***
- ***Use for:***
  - ***Compressor rooms***
  - ***Vent line***
  - ***Blast freezers***
  - ***Cold storage***

Characteristics of CI ammonia sensors

- *In presence of NH3 charge carriers are "injected" into the sensor element, while in fresh air the ammonia is desorbed*
- *Thus, CI sensor is not "consumed" or permanently altered by exposure to ammonia*
- *CI sensors are extremely stable, with operational life spans of five years or even longer*
- *CI sensors are not affected by shifts in humidity, and offer excellent performance in the extreme low humidity associated with flash freezing operations*

GfG Instrumentation

CI sensor limitations

- *Although designed to minimize effects of interfering contaminants, may still respond to:*
  - *VOCs (such as the limonene in citrus oil cleansers)*
  - *High concentrations of carbon monoxide due to engine exhaust*
- *CI sensors optimized for detection at higher concentration ranges*
  - *Should not be used for very low concentration alarms (less than 20 ppm)*

GfG Instrumentation

NH_3 Sensing Technologies
Charge Carrier Injection (CI)

Benefits	Concerns
• Low cross sensitivity compared to solid state	▪ Not suitable for all application
• Sensor life unaffected by exposure levels	▪ No low range detection (<20ppm/<30ppm)
• Long sensor life (expected life >3 years)	▪ High cross sensitivity to alcohol compounds and engine exhaust
• Low maintenance (annual calibration)	▪ Not suitable for inert applications (CA rooms)
• Fast response time (T_{90} response time < 8 sec.)	
• High detection range capabilities (up to 10,000 ppm / 1% volume)	

Photoionization Detectors

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

GfG Instrumentation

- ***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***

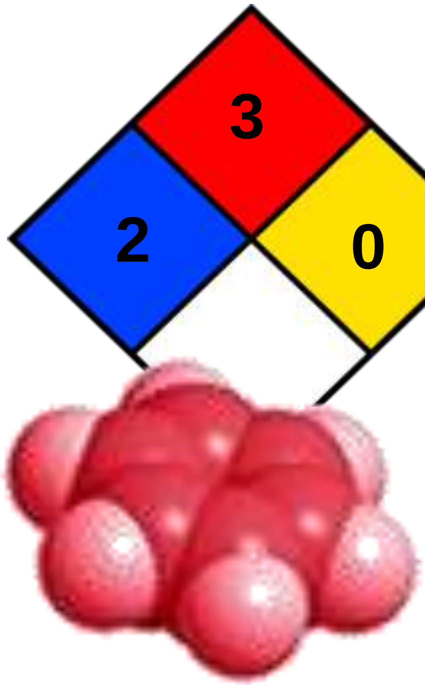
Volatile organic compounds (VOCs)

- ***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*



Toxic Exposure Limits

- *Occupational exposure limits (OELs) designed to protect workers against the health effects of exposure to hazardous substances*
- *OEL is maximum concentration of airborne contaminant to which unprotected worker may be exposed*
- *Unprotected workers may not be exposed to concentration that exceeds the limit*
- *It's up to the employer to determine that these exposure limits are not exceeded*
- *In many cases, a direct reading gas detector is the primary means used to ensure that the OEL has not been exceeded*

VOC Toxicity

- ***Toxic substances produce symptoms in two time frames: acute and chronic***
- ***While some VOCs acutely toxic at low concentrations, most VOCs chronically toxic***
- ***Because of long-term nature of the physiological effects, tendency has been to overlook presence in workplace at OEL concentrations***
- ***Exposure via skin or eye contact with liquid or aerosol droplets, or inhalation of vapors***

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, 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!***

GfG Instrumentation

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 vapours are also toxic, with Occupational Exposure Limit (OEL) values much lower than the 5% or 10% LEL***
- ***Toxic exposure exceeded long before LEL alarm concentration reached***

Limitations of LEL sensor

- ***Percent LEL sensors detect gas by oxidizing the gas on an active bead located within the sensor***
- ***Readings displayed in % LEL increments, with a full range of 0 – 100% LEL***
- ***hazardous condition threshold alarm typically set to 5% or 10% LEL***
- ***Hot-bead pellistor sensors unable to differentiate between different combustible gases***
- ***May be limited or unable to detect vapors of combustible liquids with flashpoint temperatures higher than 38 degrees C***

Limitations of LEL sensor

- ***Percent LEL sensors excellent for gases and vapors that are primarily or only of interest from the standpoint of their flammability (like methane)***
- ***However, many other combustible gases and vapors fall into a different category***
- ***Toxic VOC vapors usually have an OEL that requires taking action at a much lower concentration***

Other Limitations of LEL Sensor

- ***Percent LEL sensors have poor sensitivity to the large molecules found in found in fuels, solvents and other VOCs, with flashpoint temperatures higher than 38ºC (100ºF)***

- ***Because percent LEL detectors are poor indicators for the presence of many VOCs, lack of a reading is not necessarily proof of the absence of hazard***

- ***Reliance on hot-bead type LEL sensors for measurement of VOC vapors means OEL, REL or TLV® exceeded long before the combustible alarm activated***

Toxic VOC Example: Hexane

- *Most standards reference an 8-hour TWA for hexane of 50 PPM*
- *In the United Kingdom, the OEL for hexane is a maximum of only 20 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*

GfG Instrumentation

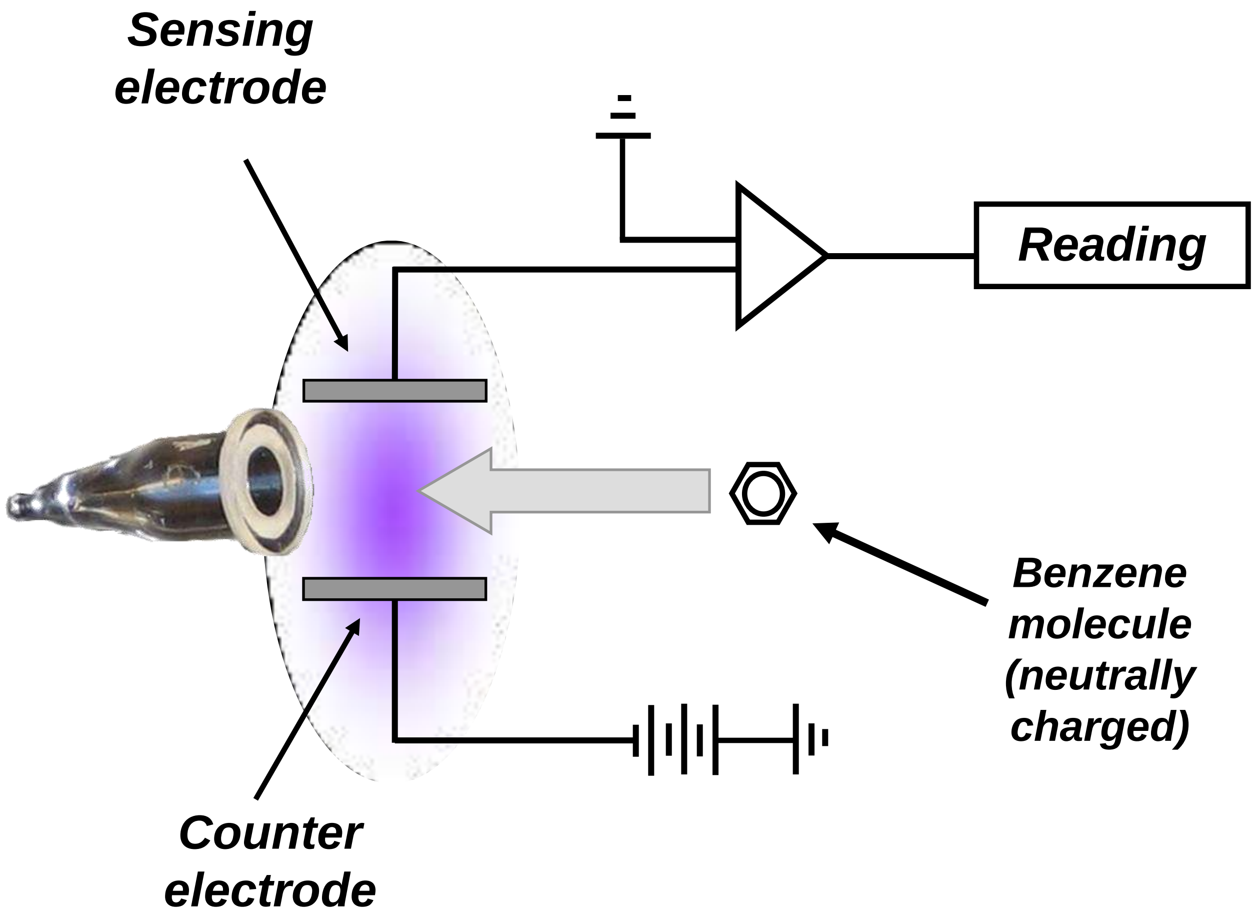
PID - Operating Principle

- ***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:

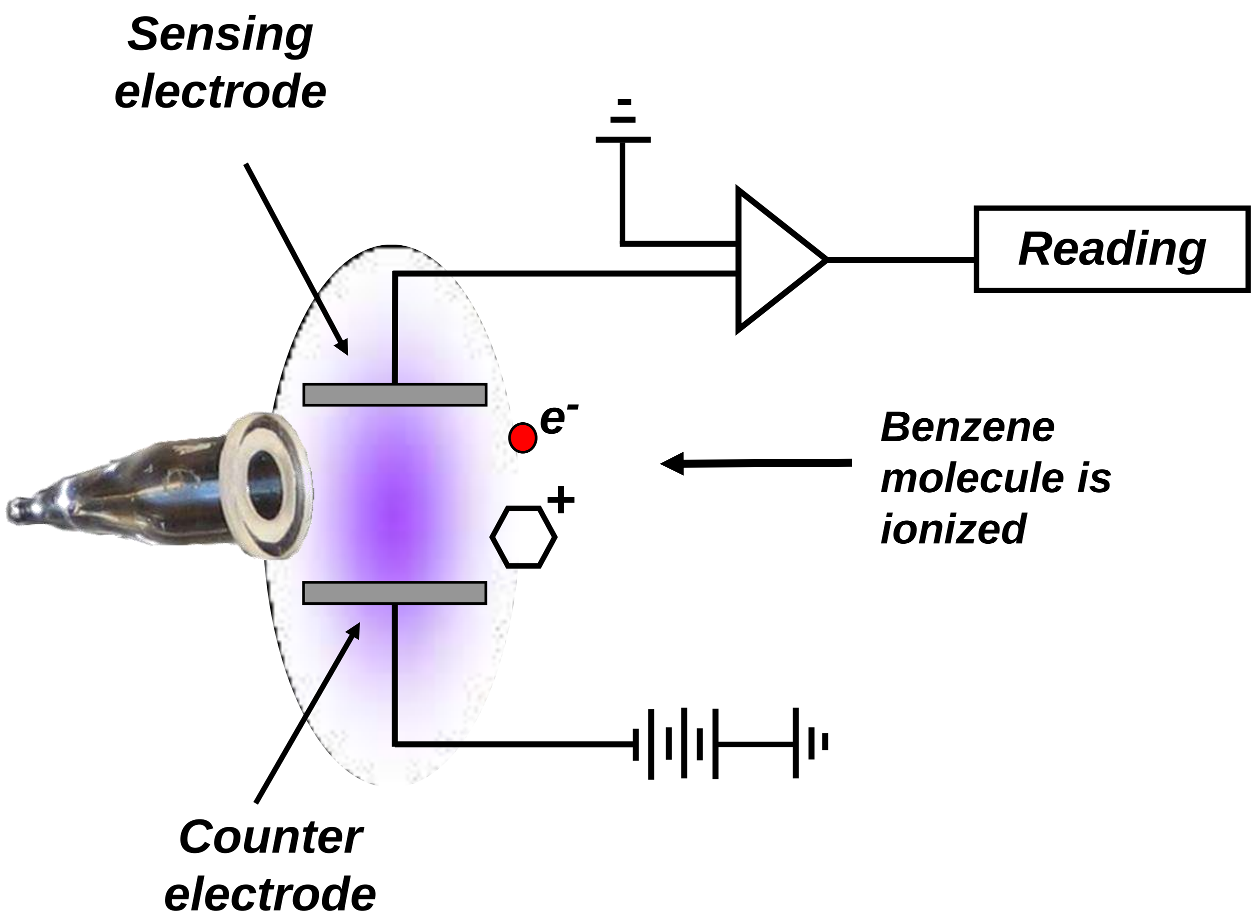
1. Neutrally charged molecule diffuses into glow zone



Operation of PID lamp, sensing and counter electrodes

Detection sequence:

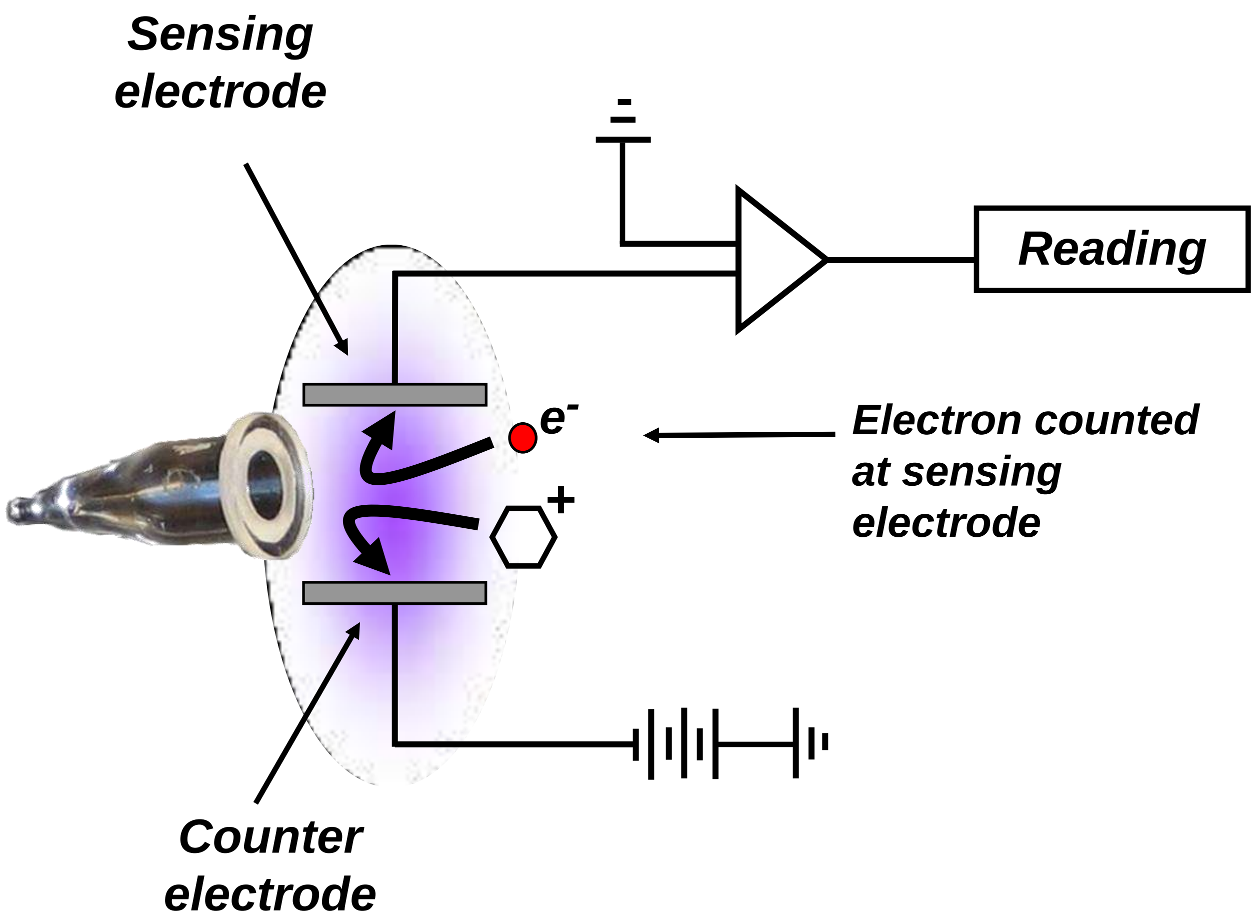
2. Molecule is ionized



Operation of PID lamp, sensing and counter electrodes

Detection sequence:

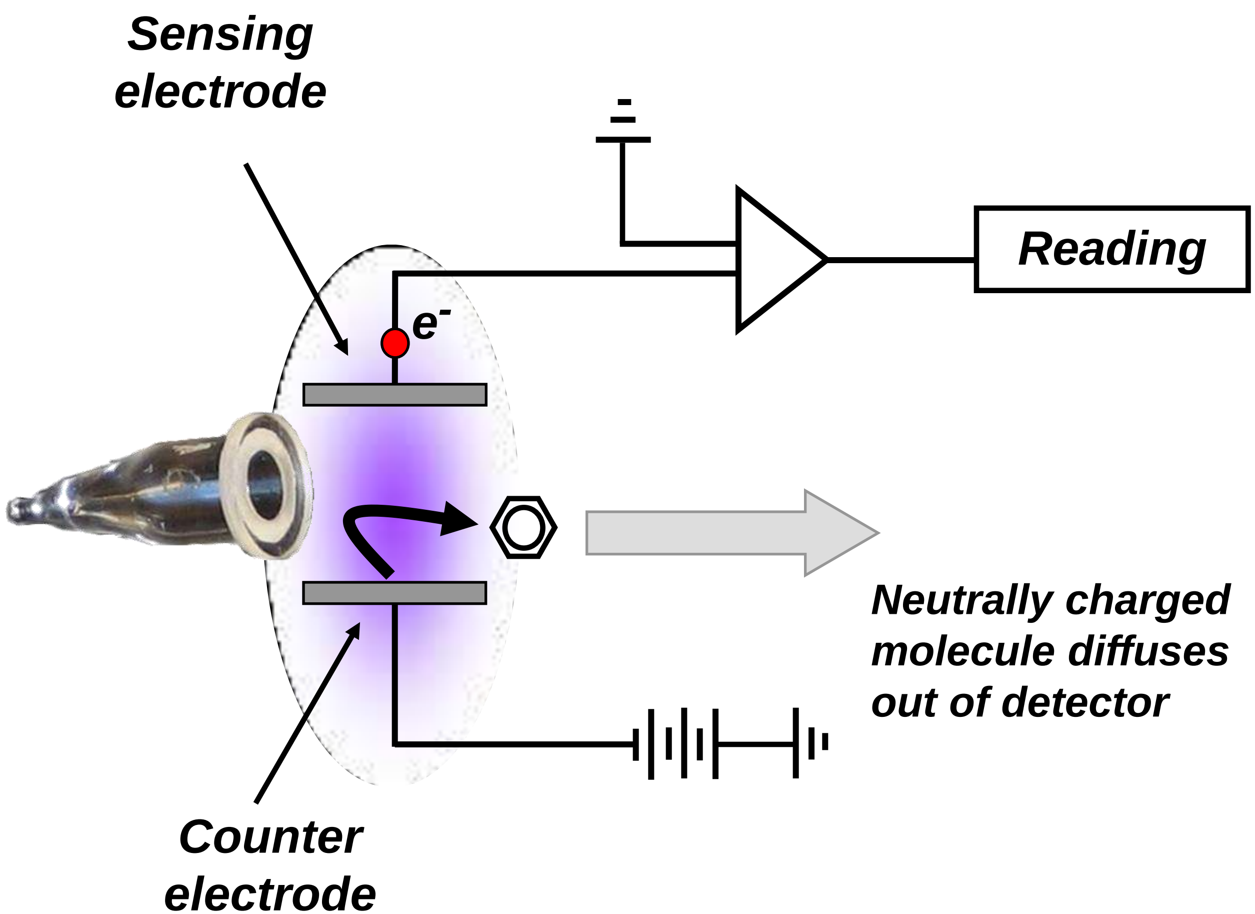
3. *Free electron is electrostatically accelerated to positively charged sensing electrode where it is counted*



Operation of PID lamp, sensing and counter electrodes

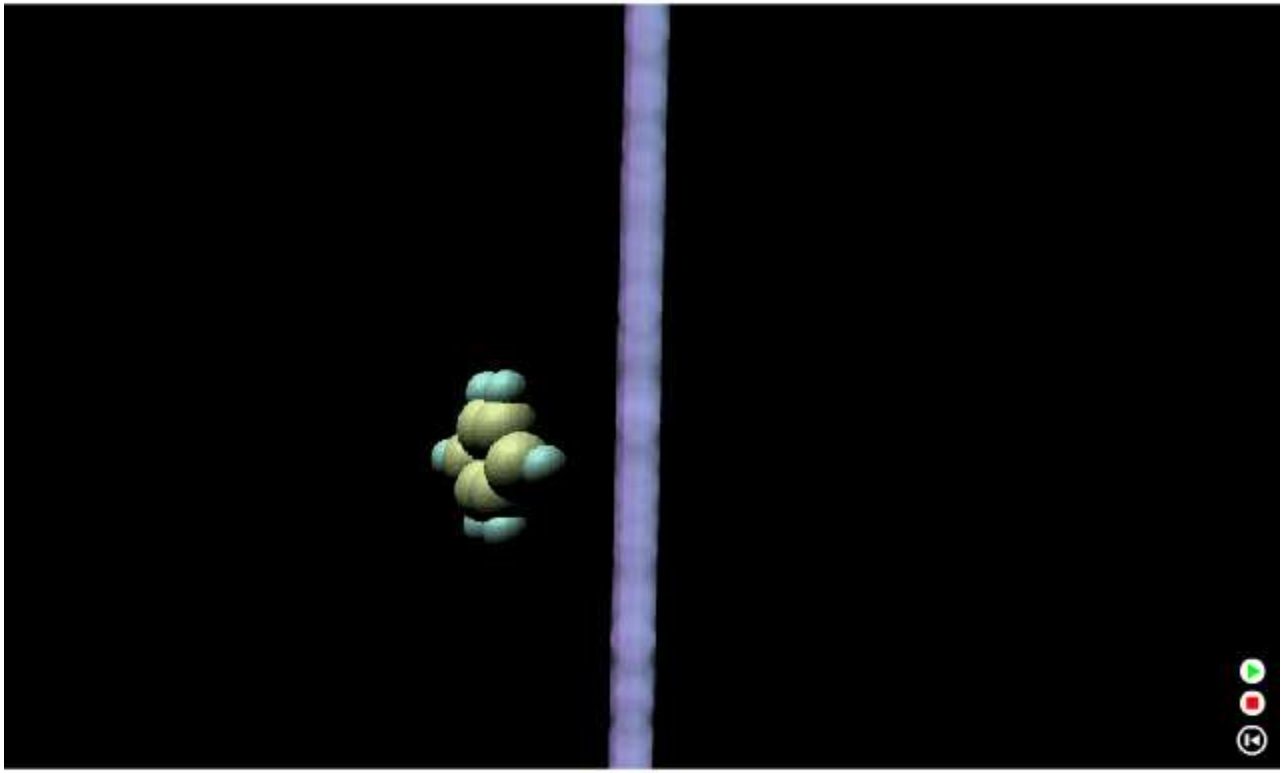
Detection sequence:

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



GfG Instrumentation

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*

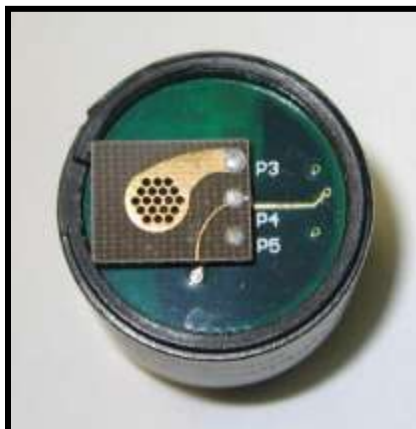
- *Miniaturization*
- *Ruggedness*
- *EMI/RFI resistance*
- *Lower humidity interference*

PID Components

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

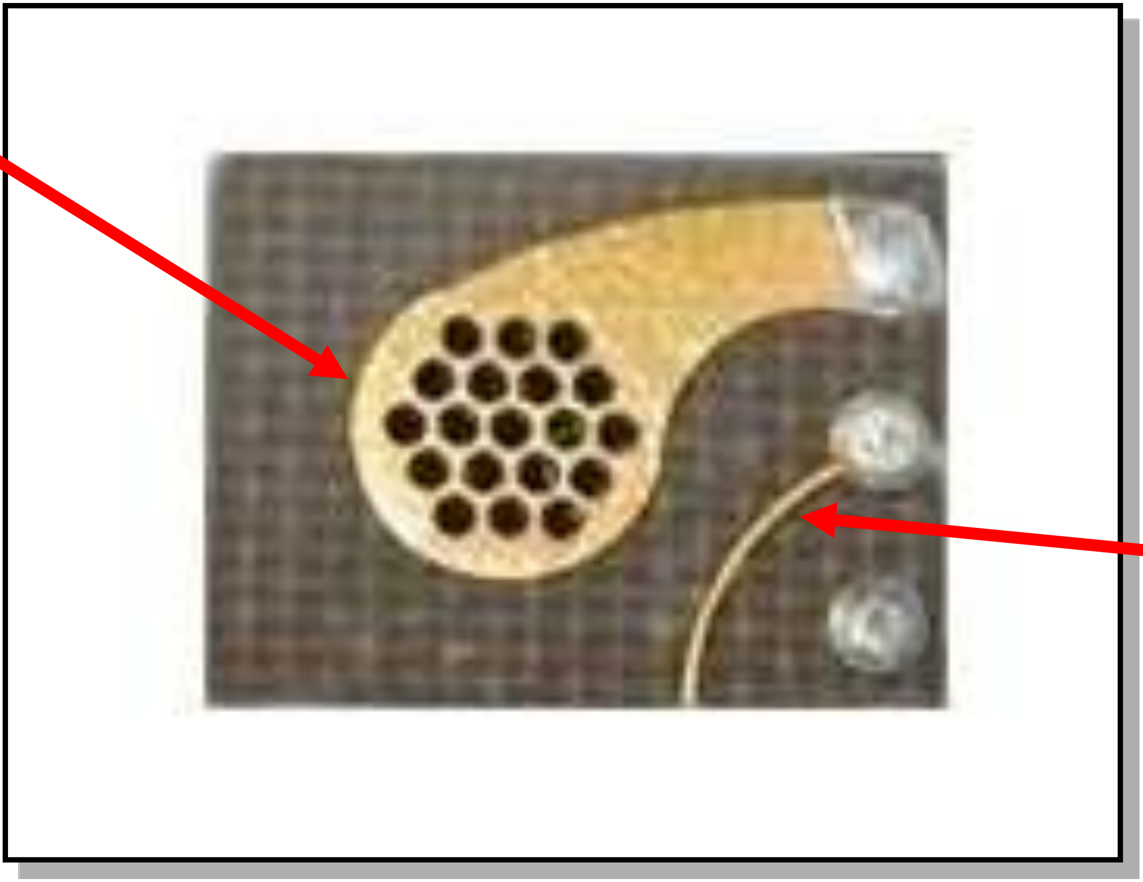






PID Sensing and Counter Electrodes

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*

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

GfG Instrumentation

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***

RAE "3D" PID Design

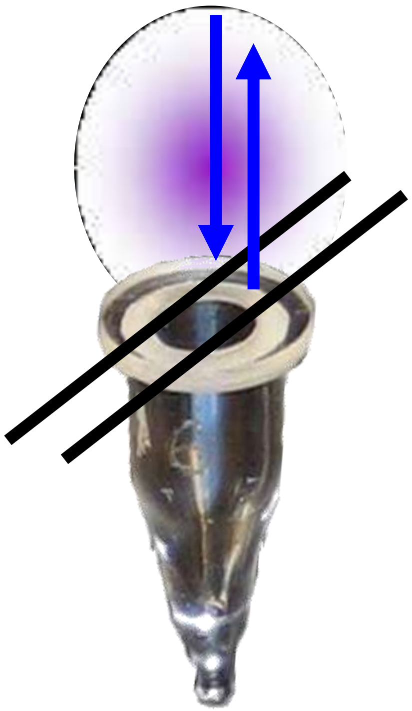
- *Benefits:*
  - *Rapid response and clearing times*
- *Limitations:*
  - *Gap between window and electrodes increases "quenching" effect of water vapor on signal*
  - *Potential for drawing particulate contaminants into sensor*
  - *More ionic fragments left behind to be adsorbed onto electrodes and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

GfG Instrumentation

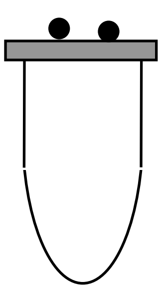
Ion Science (BW) PID Design

- ***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



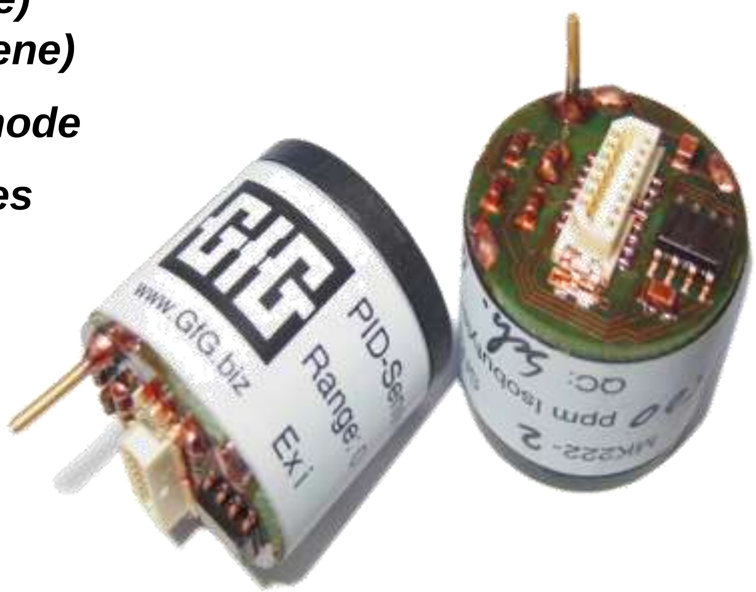
- ***Benefits:***
  - ***No gap at all between electrodes and window***
  - ***Diffusion of molecules into and out of glow zone means no ionic fragments or particulates left behind***
- ***Limitations:***
  - ***Slightly slower response***
- ***Results:***
  - ***Lower sensitivity to water vapor and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



GfG Instrumentation

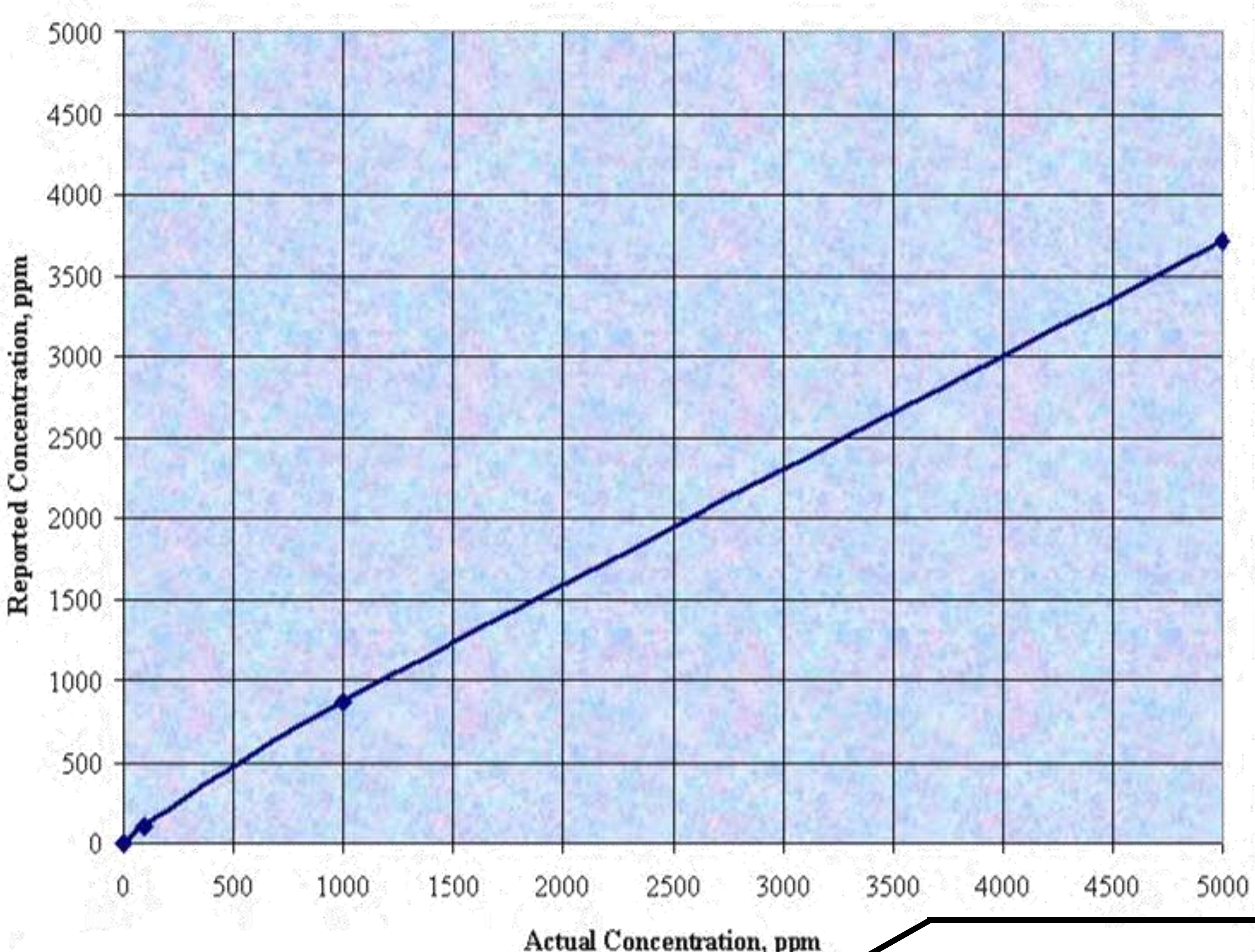
G460 PID Specifications

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™ 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

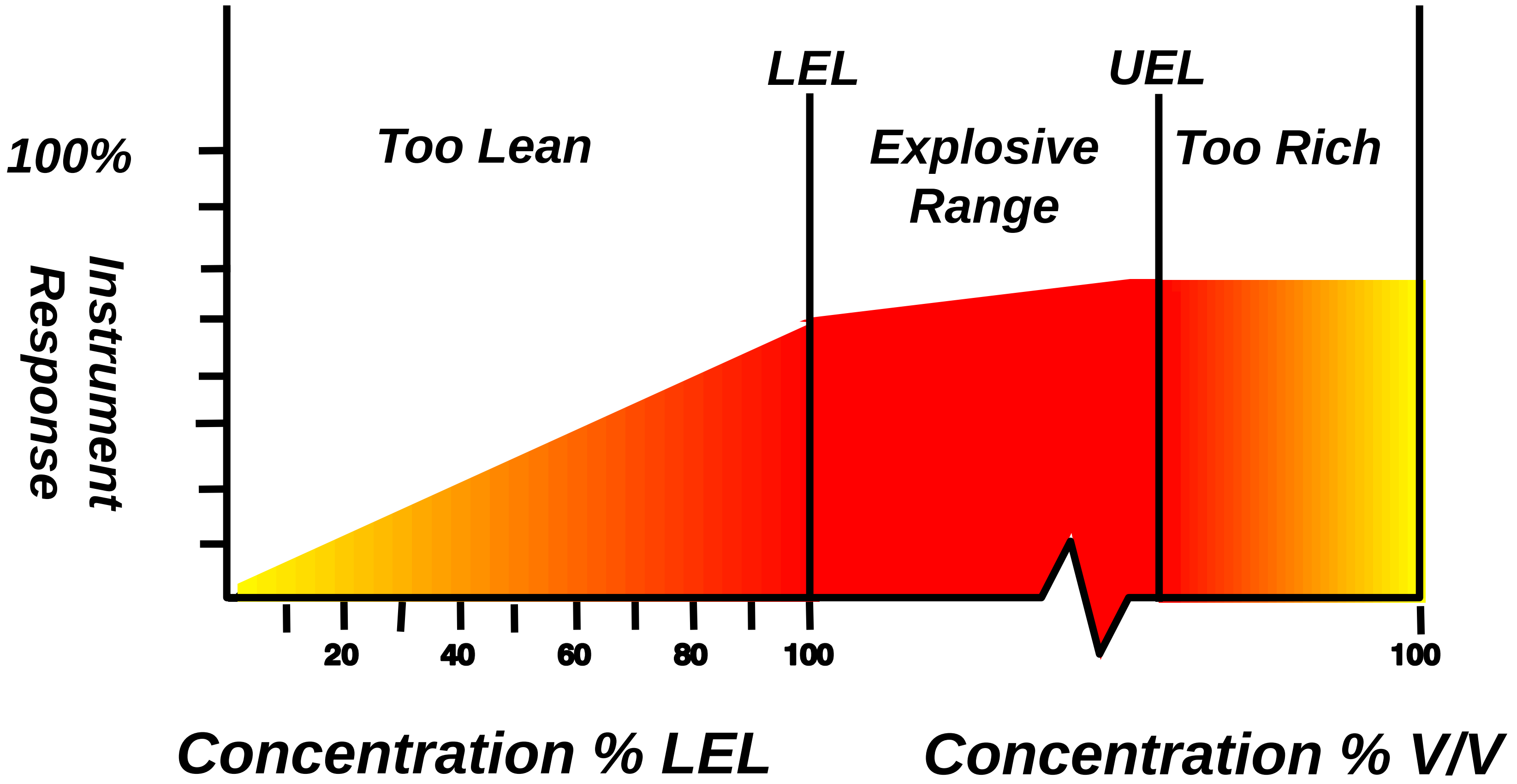


GfG Instrumentation

PID linearity through nominal range



PID Response Curve



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 RH***
        - ***High CH_4***
        - ***High O_2***

Effects of Methane on PID Output

- *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 <200^o C.
  - Vapor Pressures (Pv) > 1.0 mm Hg at 20^o 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

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

GfG Instrumentation

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

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***

PID instruments are nonspecific

- Reading is sum of signals of all detectable substances present, also:
- Reading is function of their varying ionization potentials and other physical properties
- PID readings always relative to gas used to calibrate detector
- Equivalent concentrations of gases other than the one used to calibrate the instrument may not produce equivalent readings!

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

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***

GfG Instrumentation

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***

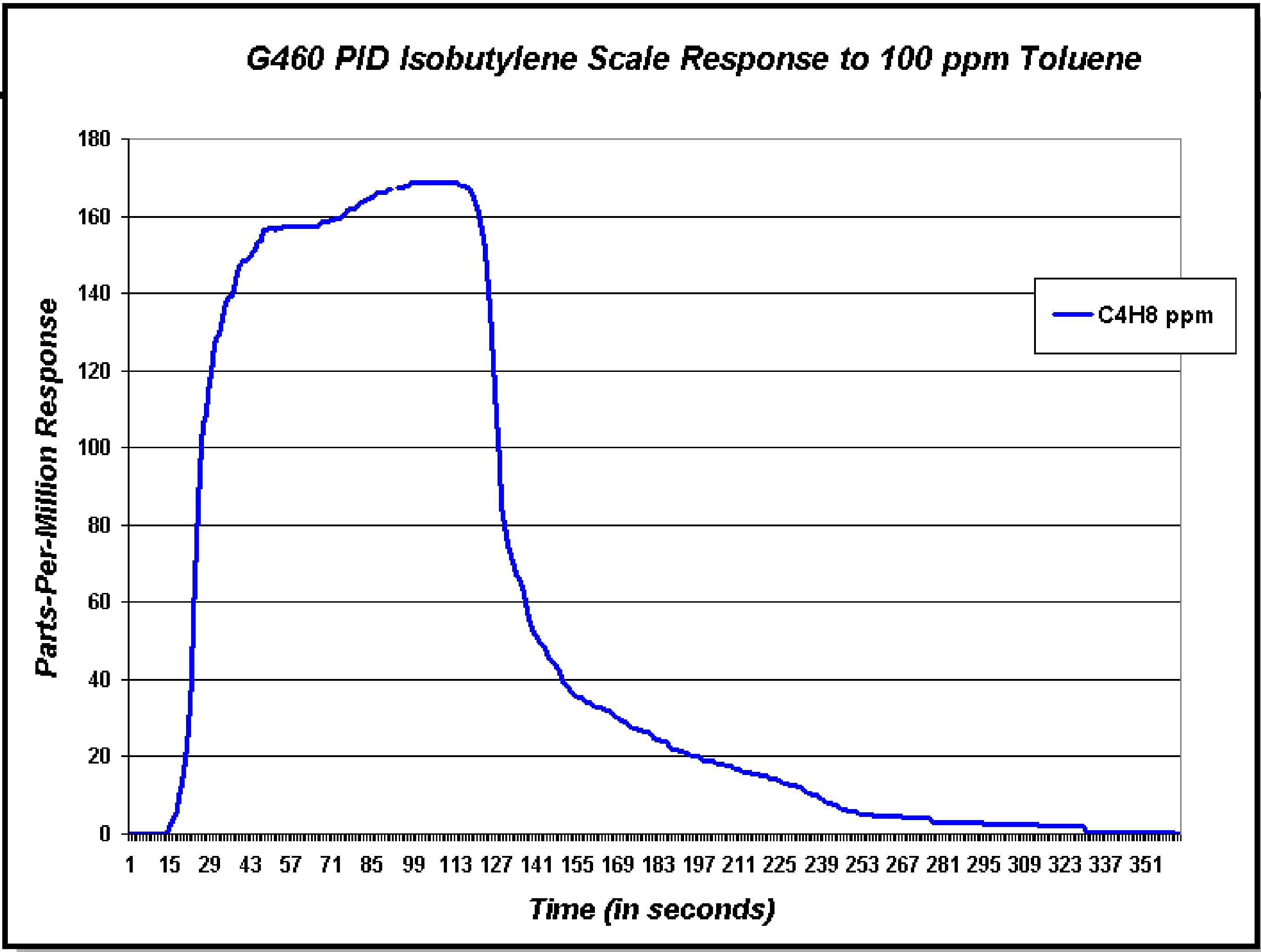
GfG Instrumentation

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*

GfG Instrumentation

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***

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

GfG Instrumentation

Calculating CF and EL for Constant Mixtures

- ***The CORRECTION FACTOR (CF_{mix}) for a mixture is calculated from sum of the fractions (Xi) of each component divided by their respective correction factors (CFi):***
  - ***CFmix = 1 / (X1/CF1 + X2/CF2 + X3/CF3 + ... Xi/CFi)***

- ***The EXPOSURE LIMIT (EL_{mix}) is calculated similarly to the CF_{mix}.***
  - ***When TLV concentrations are used as the exposure limits:***
  - ***ELmix = 1 / (X1/TLV1 + X2/TLV2 + X3/TLV3 + ... Xi/TLVi)***

Paint: 15% Styrene and 85% Xylene

$$CF_{mix} = 1/(0.15/0.4 + 0.85/.6) = 0.56$$

Where:

- ***0.15 is 15% styrene***
- ***0.4 is the CF styrene***
- ***0.85 is 85% xylene***
- ***0.6 is the CF for xylene***

EL_{mix} for Constant Mixtures

Example:

Paint: 15% Styrene and 85% Xylene

$$EL_{mix} = 1/(0.15/50 + 0.85/100) = 87 \text{ ppm}$$

Where:

- ***0.15 is 15% styrene***
- ***50 is the 50 ppm exposure limit for styrene***
- ***0.85 is 85% xylene***
- ***100 is the 100 ppm exposure limit for xylene***

Alarm Limit for Constant Mixtures

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

$$\text{Alarm limit} = \frac{EL_{mix}}{CF_{mix}}$$

- ***In our 15% Styrene and 85% Xylene example:***
  - EL_{mix} = 87 ppm
  - CF_{mix} = 0.56
  - ***Alarm limit = 87 ppm / 0.56 = 155 ppm***

GfG Instrumentation

Constant Mixtures

Continuing with the 15% Styrene and 85% Xylene example:

- ***Say the PID registers reading of 120$_{iso}$ (PID readings in ppm Isobutylene units)***
- ***Multiply by correction factor of 0.56$_{mix}$***
- ***True concentration of mixture = 67.2$_{mix}$ ppm***
- ***This is under the calculated exposure limit of 87$_{mix}$ ppm for the mixture***

GfG Instrumentation

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***

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

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***

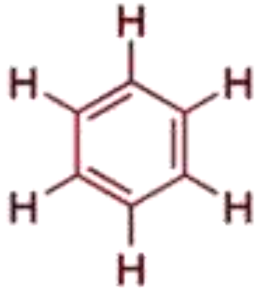
PID Alarms: EL_{iso} & Unknowns

- ***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***



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

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

GfG Instrumentation

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*

GfG Instrumentation

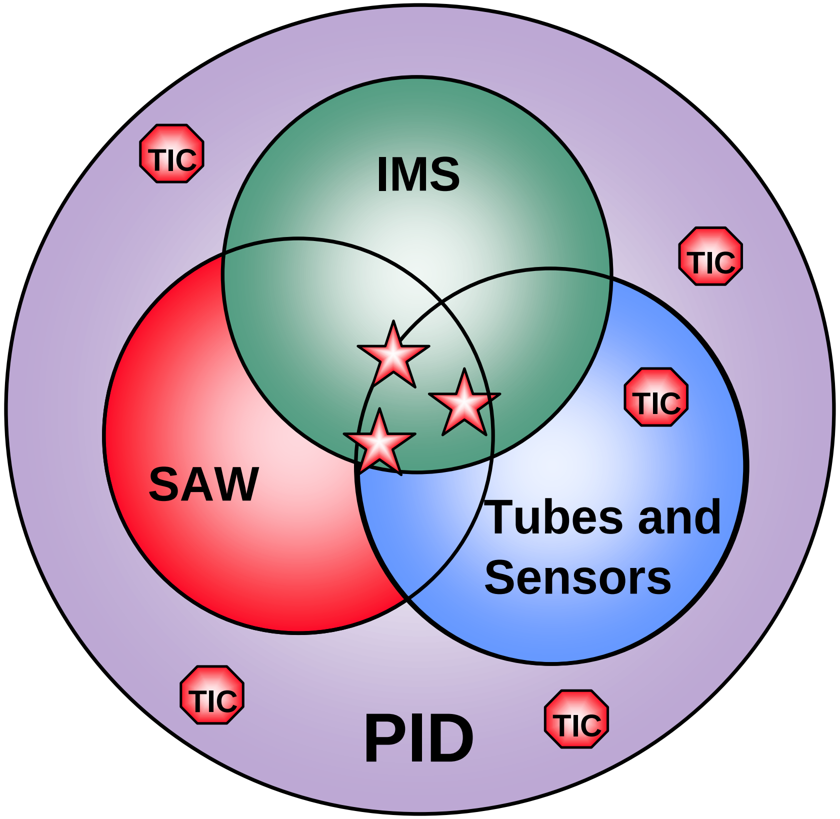
PIDs in WMD and Anti-Terrorist Response

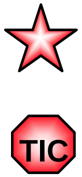
- *Terrorist are not limited to traditional explosives and chemical warfare agents*
- *Weapons of mass destruction (WMD) can be based on:*
  - *Toxic Industrial Chemicals (TICs)*
  - *Chemical Warfare Agents (CWAs)*
  - *Nerve Agents*
  - *Explosives*

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





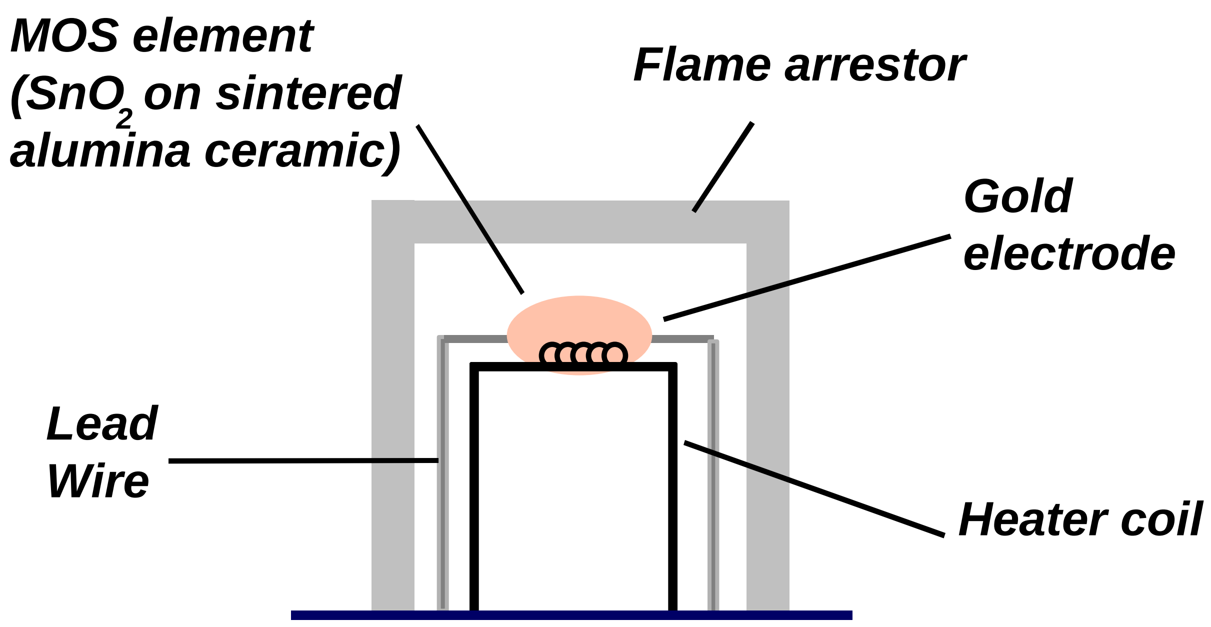
= Recognized (military) Chemical Warfare Agent

= Toxic Industrial Chemical (TIC)

MOS Detection Mechanism

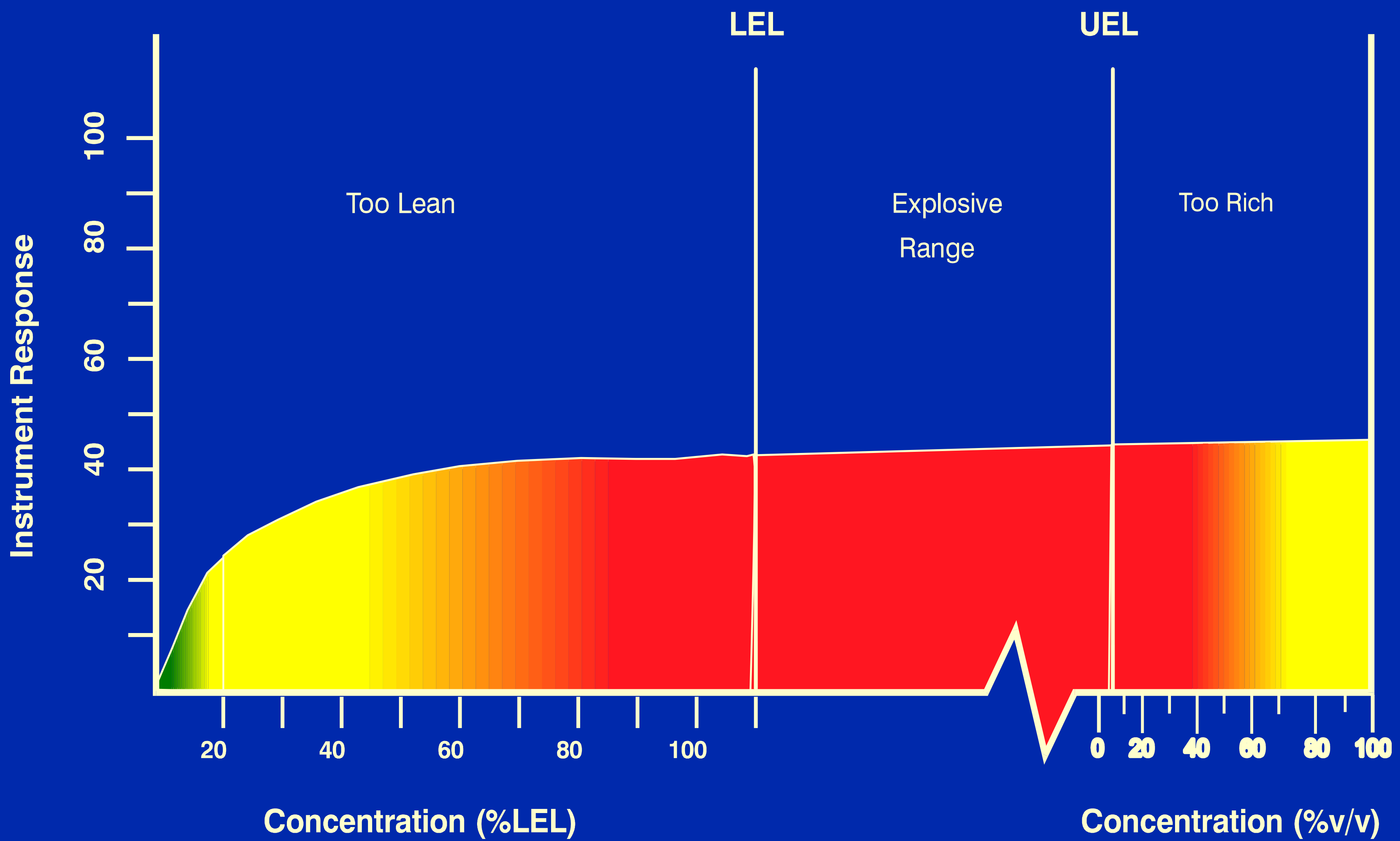
- ***Sensing element:***
  - ***Tin dioxide (SnO2) on sintered alumina ceramic***
  - ***In clean air electrical conductivity low***
  - ***Contact with reducing gases (such as CO or combustibles) increases conductivity***
  - ***Sensitivity to specific gases depends on temperature of sensing element***

Schematic of Metal Oxide Semiconductor (MOS) Sensor



GfG Instrumentation

Solid State Response Curve



Non-dispersive infrared (NDIR) sensors

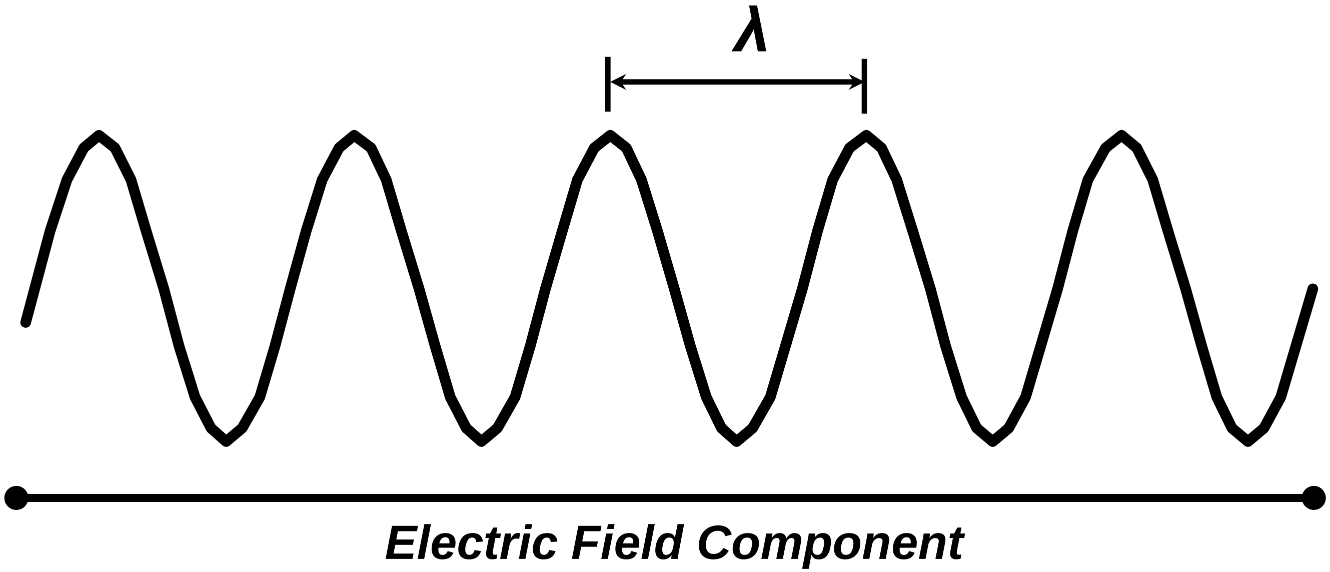
- *Many gases absorb infrared light at a unique wavelength (color)*
- *In NDIR sensors the amount of IR light absorbed is proportional to the amount of target gas present*

GfG Instrumentation

- *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)*

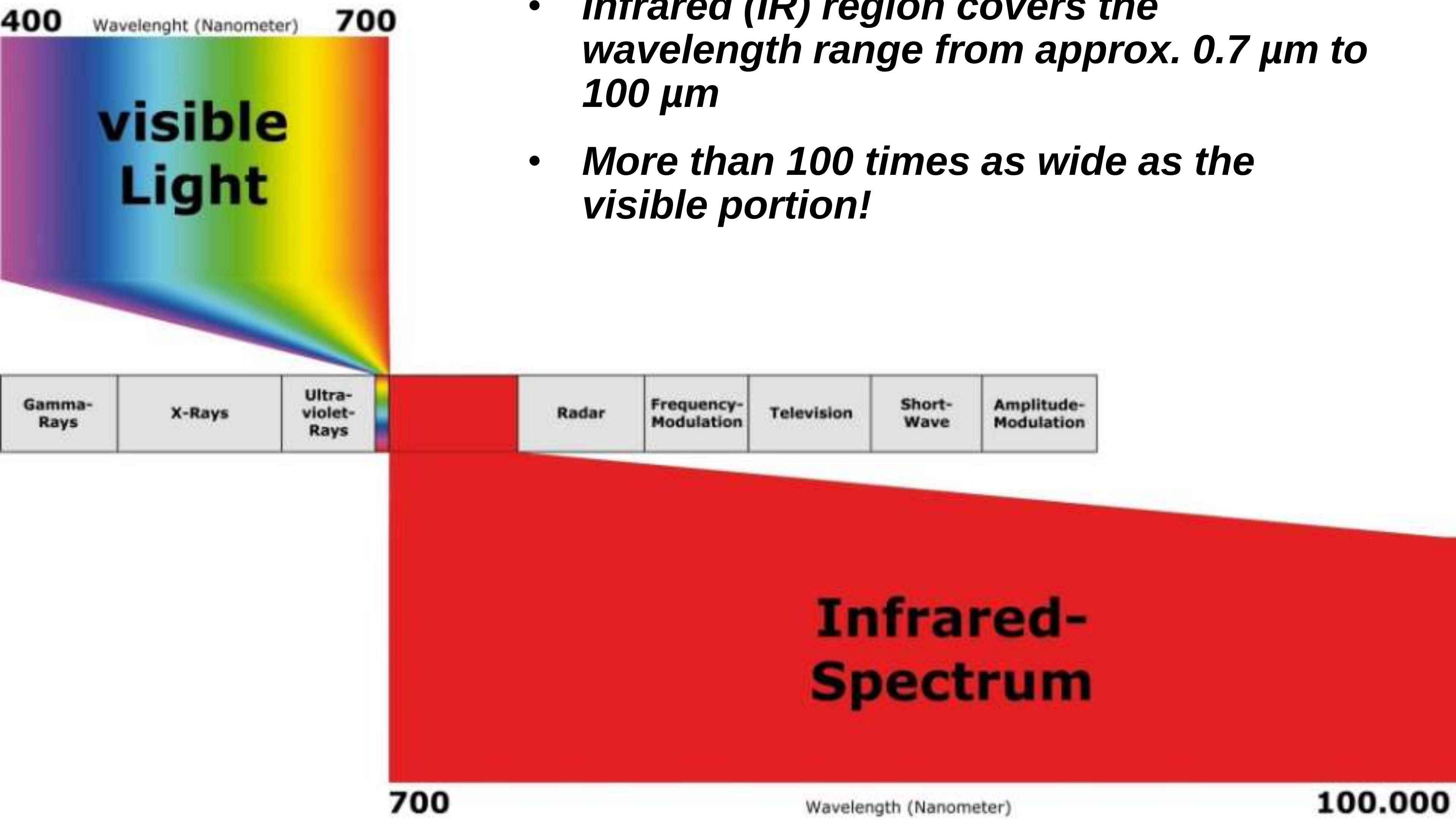
Properties of Light

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

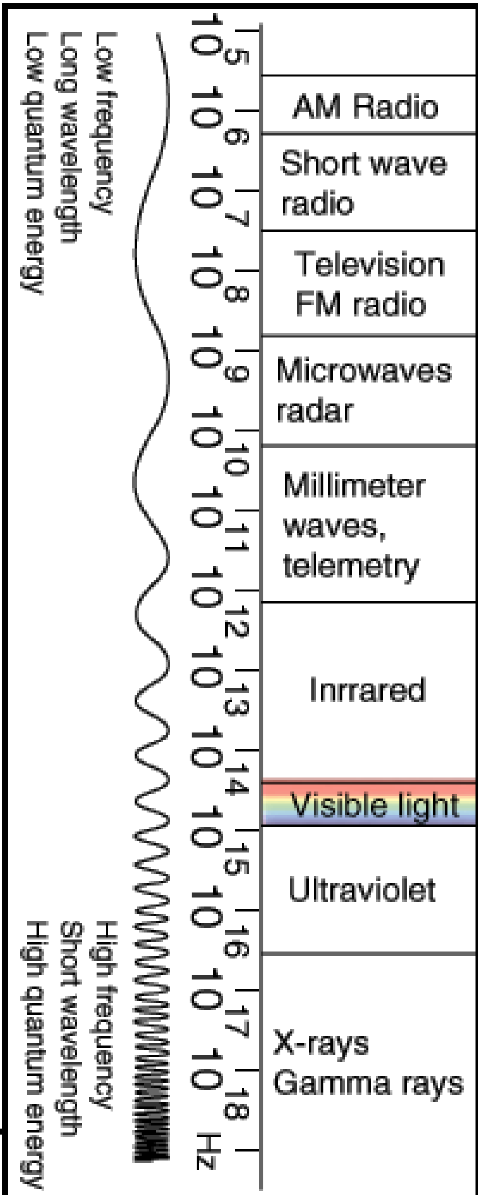


Electromagnetic radiation spectrum

- ***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



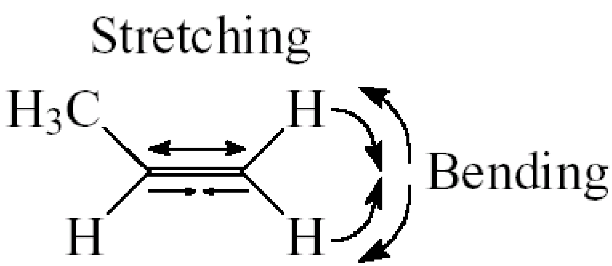
	Wavelength (m)	Frequency (Hz)	Energy (J)
Radio	> 1×10^{-1}	< 3×10^{9}	< 2×10^{-24}
Micro-wave	1×10^{-3} - 1×10^{-1}	3×10^{9} - 3×10^{11}	2×10^{-24}- 2×10^{-22}
Infrared	7×10^{-7} - 1×10^{-3}	3×10^{11} - 4×10^{14}	2×10^{-22} - 3×10^{-19}
Optical	4×10^{-7} - 7×10^{-7}	4×10^{14} - 7.5×10^{14}	3×10^{-19}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

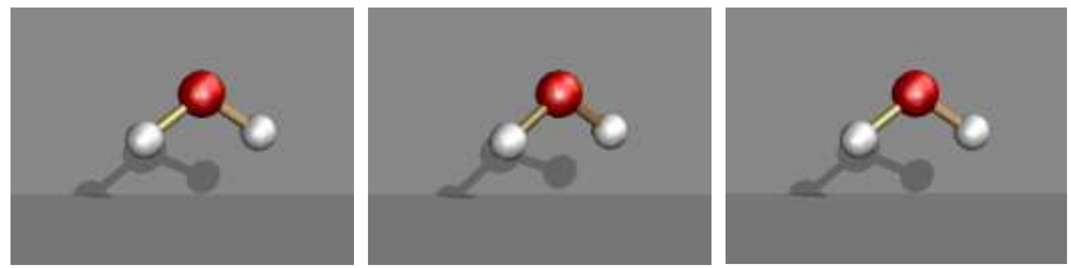
Infrared Detectors

- *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*

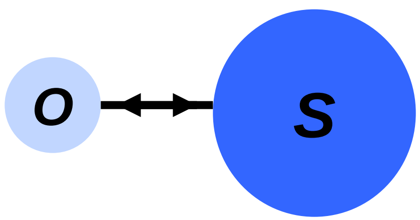
Energy Absorbed by "Bond Stretching" and "Bending" Vibration

- *Must have a COVALENT CHEMICAL BOND*





Symmetric Stretch *Asymmetric Stretch* *Bend*



Nonlinear Molecules

Linear molecules: SO

GfG Instrumentation

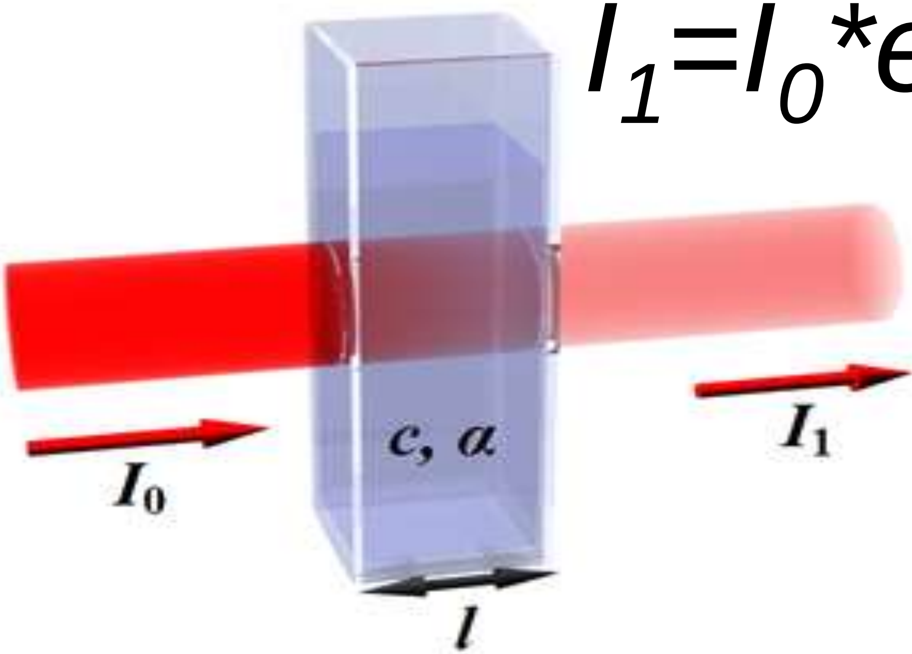
Absorbtion of light

- ***When a molecular bond vibrates at the same frequency as an IR wave is oscillating, the bond and the light are resonant***
- ***The bond is "excited" as the energy is transferred to the molecule, the light is said the be absorbed***
- ***IR frequencies are similar to vibrating bonds in molecules***

- ***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*

GfG Instrumentation

Wavelength vs wavenumber (cm $^{-1}$)

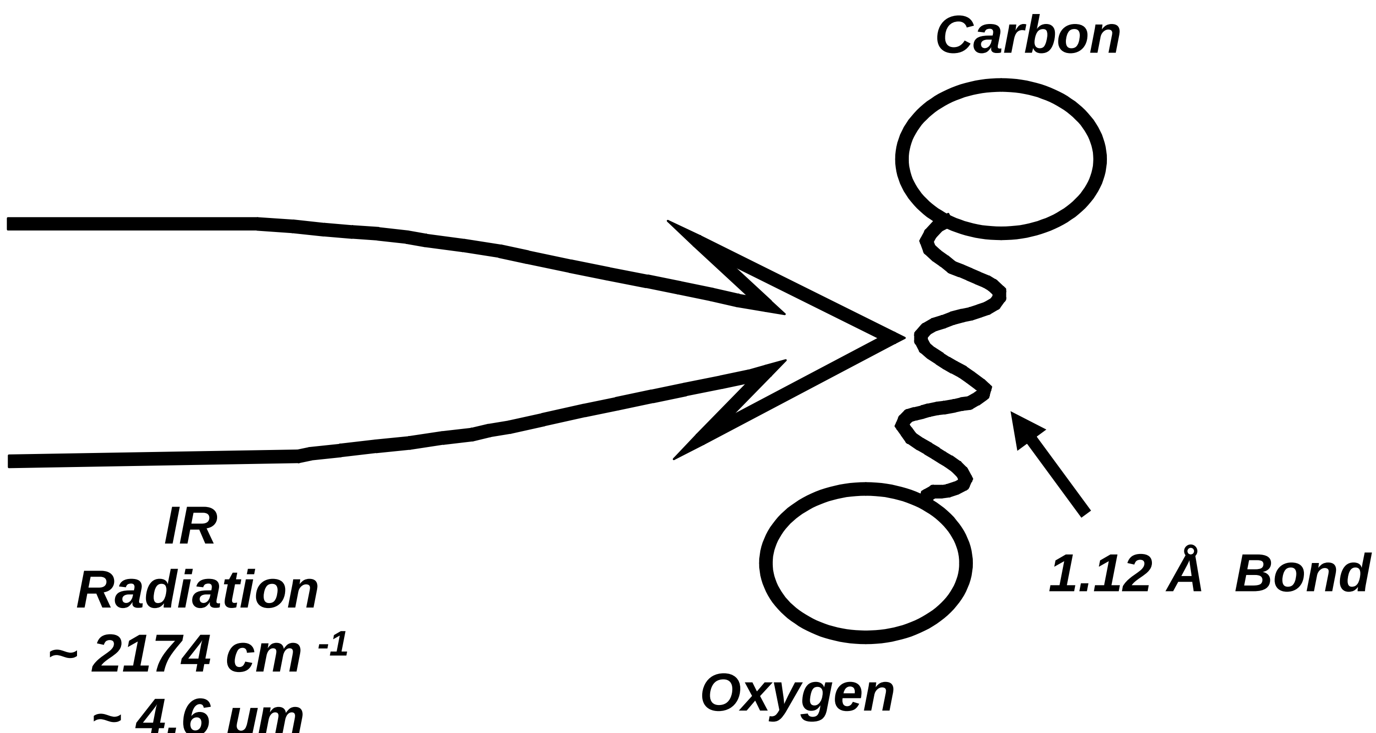
- ***Wavenumber is the number of waves per unit distance***
- ***Wavenumber is reciprocal of wavelength***
- ***In spectroscopy, wave number is usually expressed in reciprocal centimeters, as 100,000 cm^{-1} (100,000 per centimeter)***
- ***Example: The absorbance peak for CO is = 4.6 µm***

4.6 µm = .00046 cm

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

Wavenumber = 2174 cm $^{-1}$

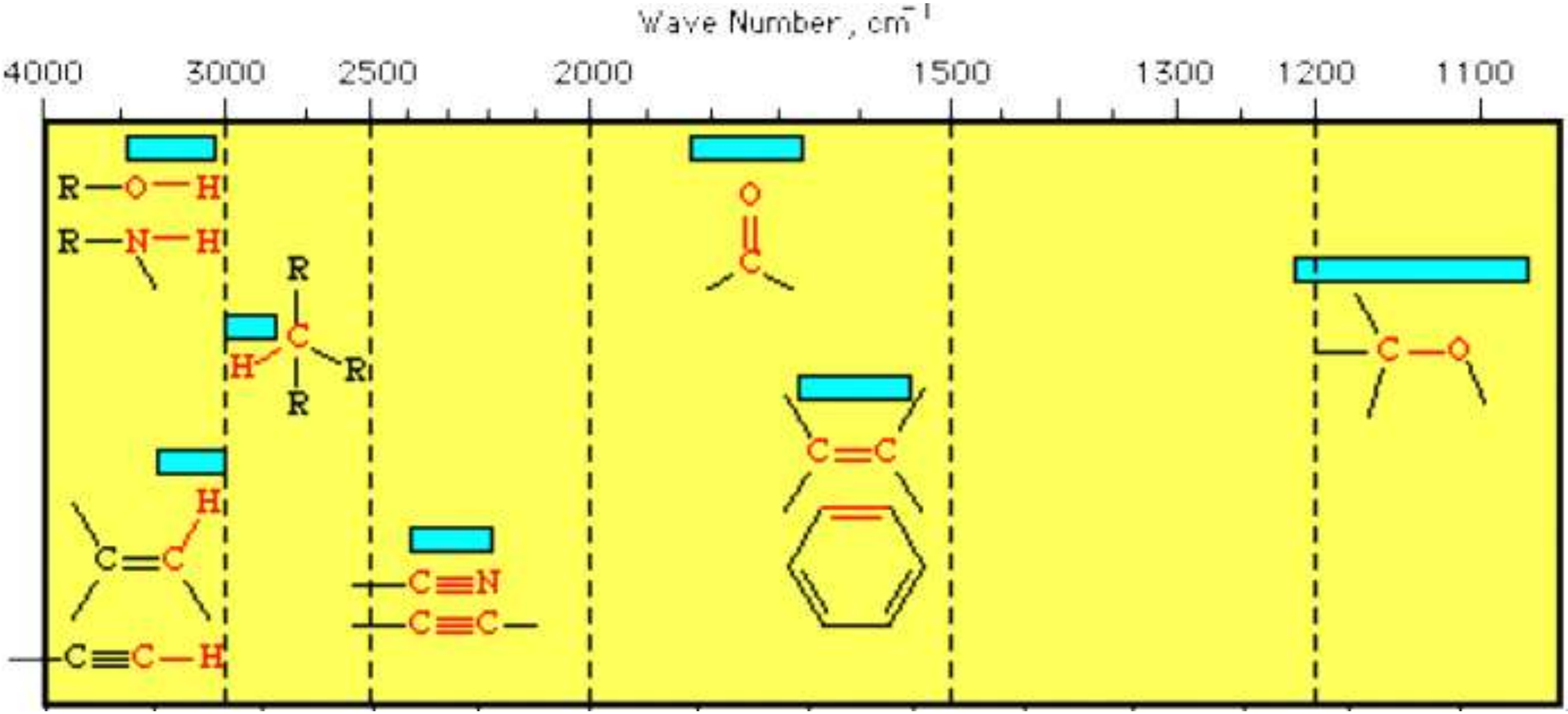
Infrared Absorption by CO



GfG Instrumentation

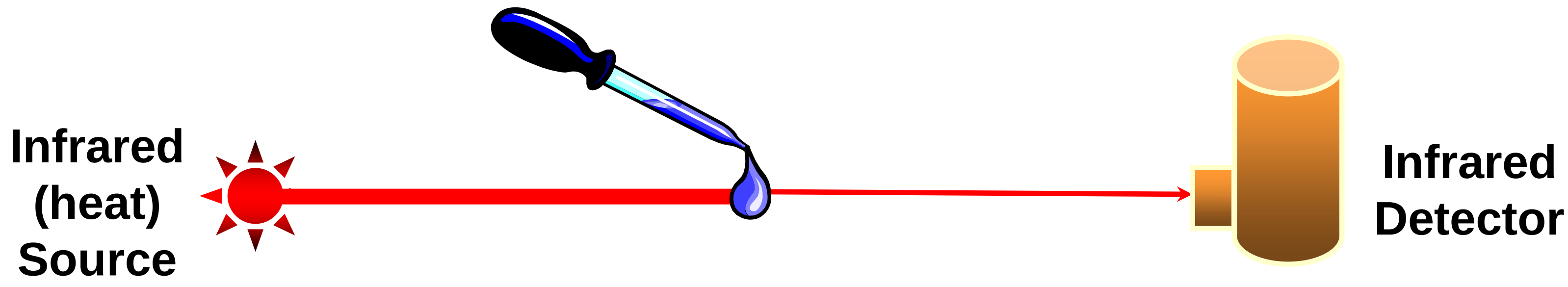
Infrared Spectroscopy

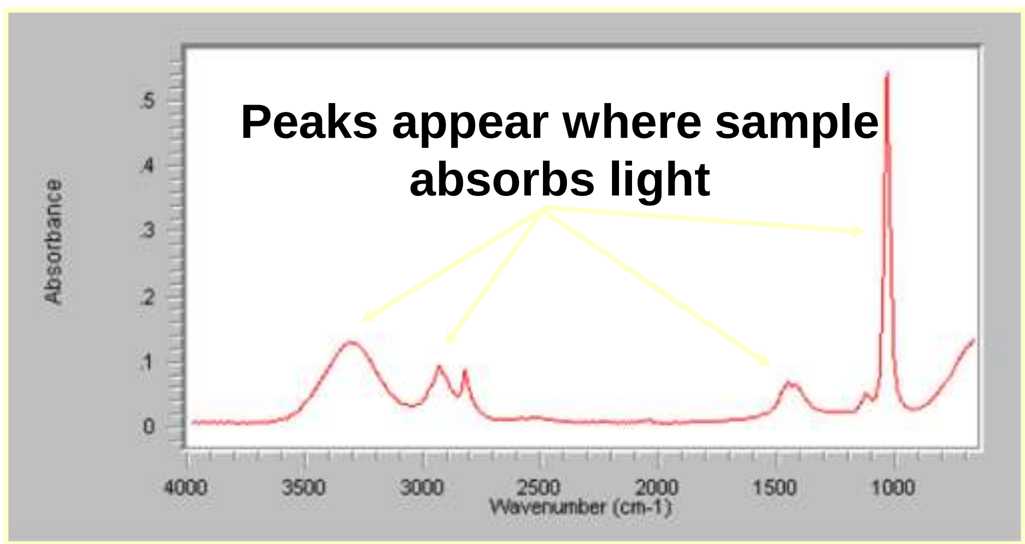
- ***Geometry of molecule and absorbance of light by specific bonds gives rise to a characteristic IR absorbance "fingerprint" of molecule***



Infrared Spectrum

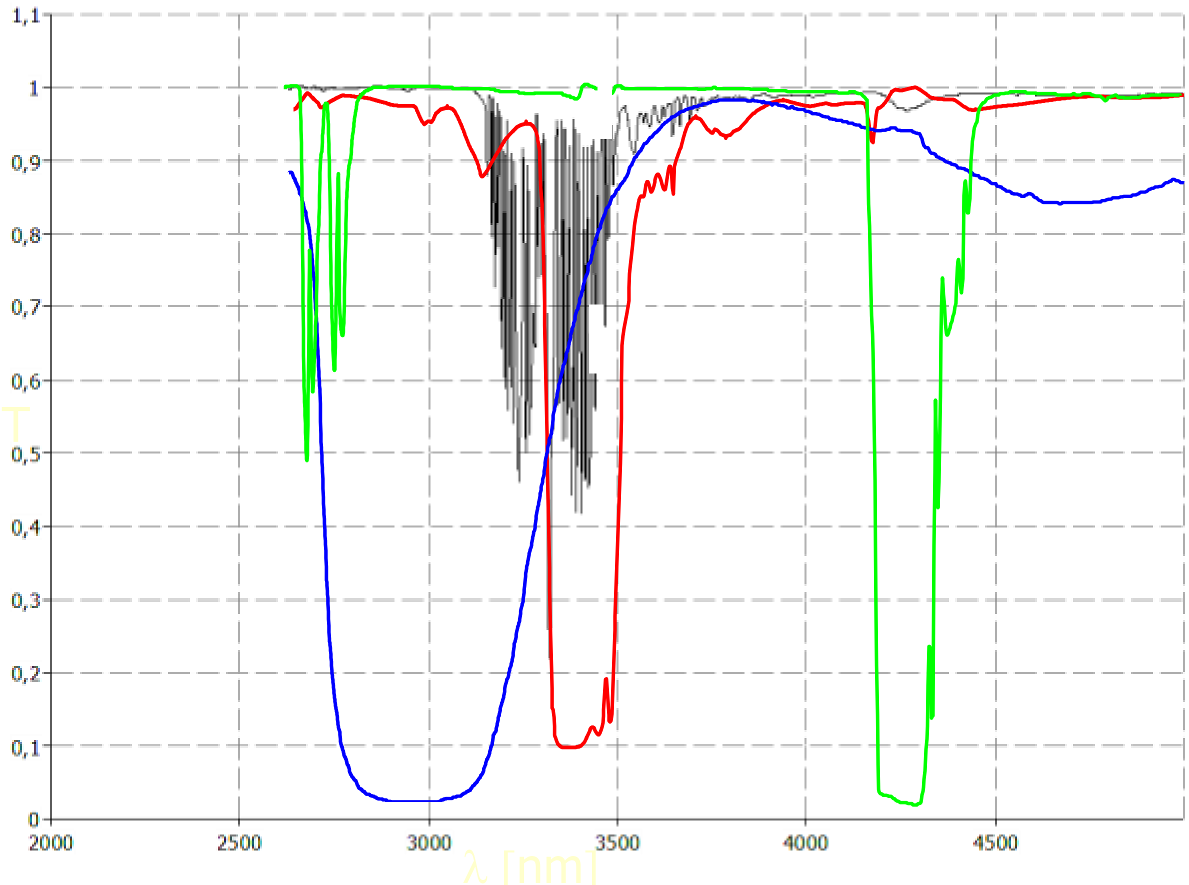
- *A spectrum is a graph of how much infrared light is absorbed by molecules at each wavenumber of infrared light*





GfG Instrumentation

Infrared absorption spectra for several gases



Gas absorption spectra

Methane CH_4

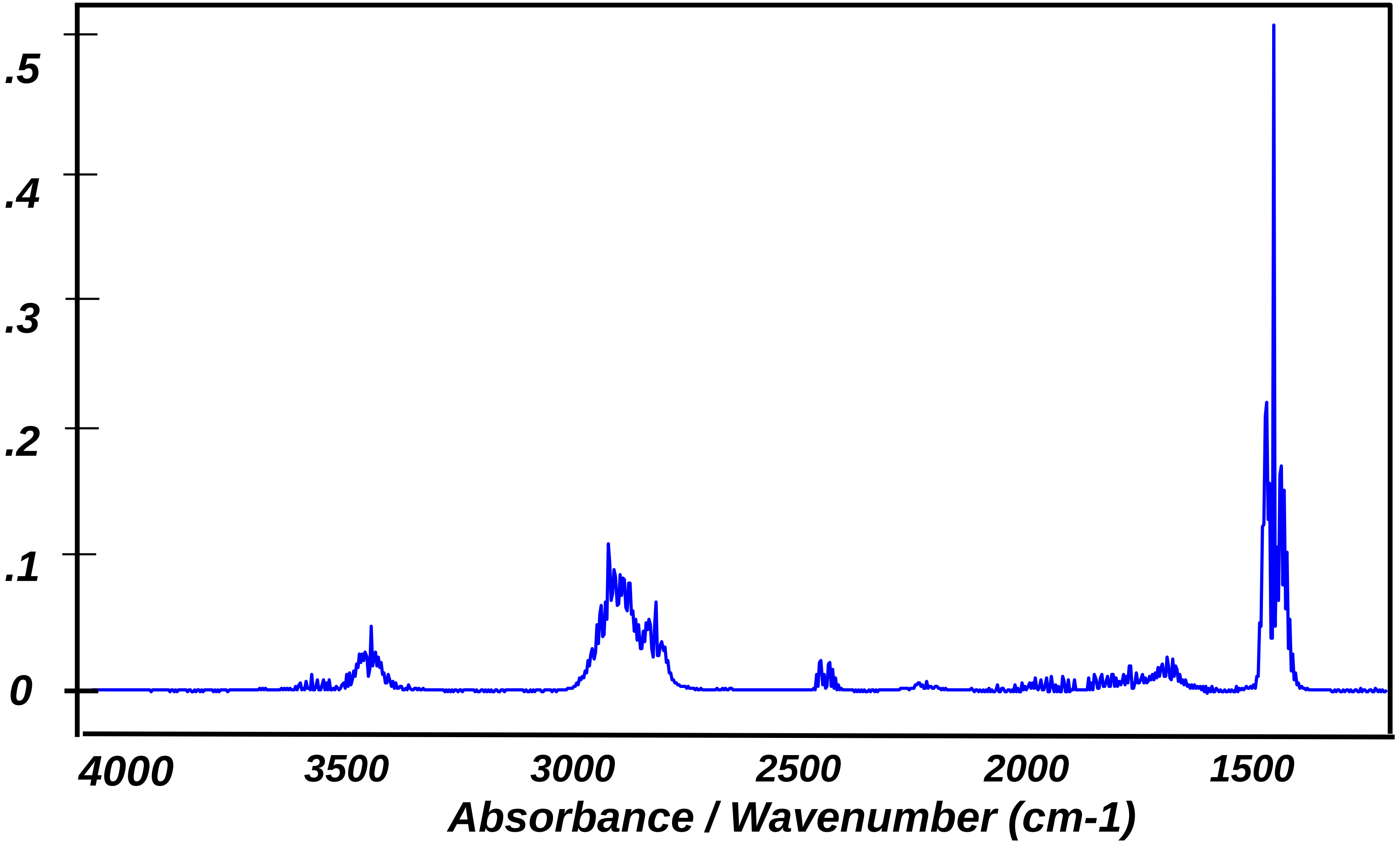
Propane C_3H_8

Water H_2O

Carbon dioxide CO_2

GfG Instrumentation

Methanol (CH_3OH) Absorbance Spectrum



GfG Instrumentation

Infrared Detectors

- ***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/*

Single wavelength NDIR sensors

- *Affected by:*
  - *Humidity*
  - *Temperature*
  - *Pressure*
  - *Aging of detector*
  - *Dust*
  - *Aging of IR-emitter*

Double wavelength NDIR sensors

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

Double wavelength NDIR sensors

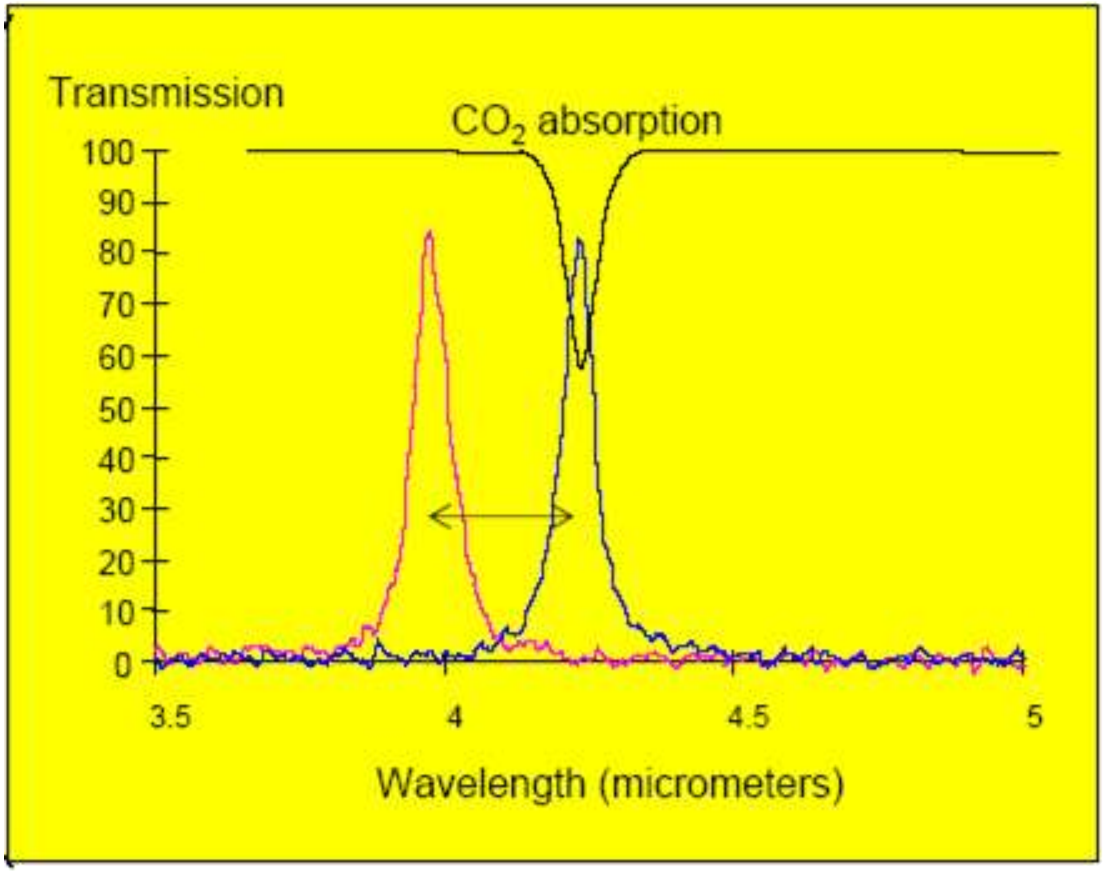
- ***Commonly used in many portable instruments***

GfG IR sensor (Note longer pathlength)

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

GfG Instrumentation

Double wavelength NDIR sensors

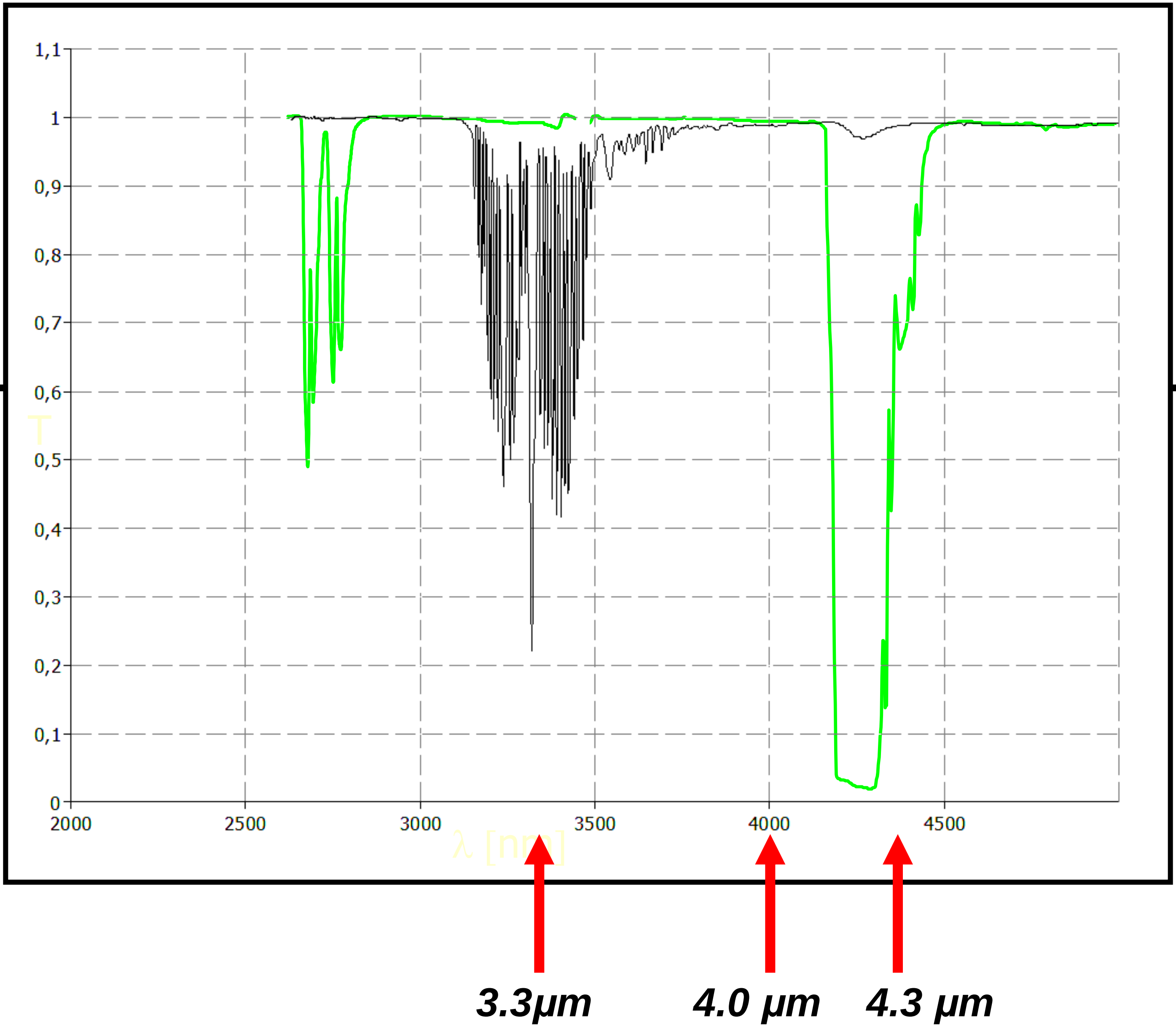


Measurement at CO_2 absorption wavelength and at a reference wavelength

GfG Instrumentation

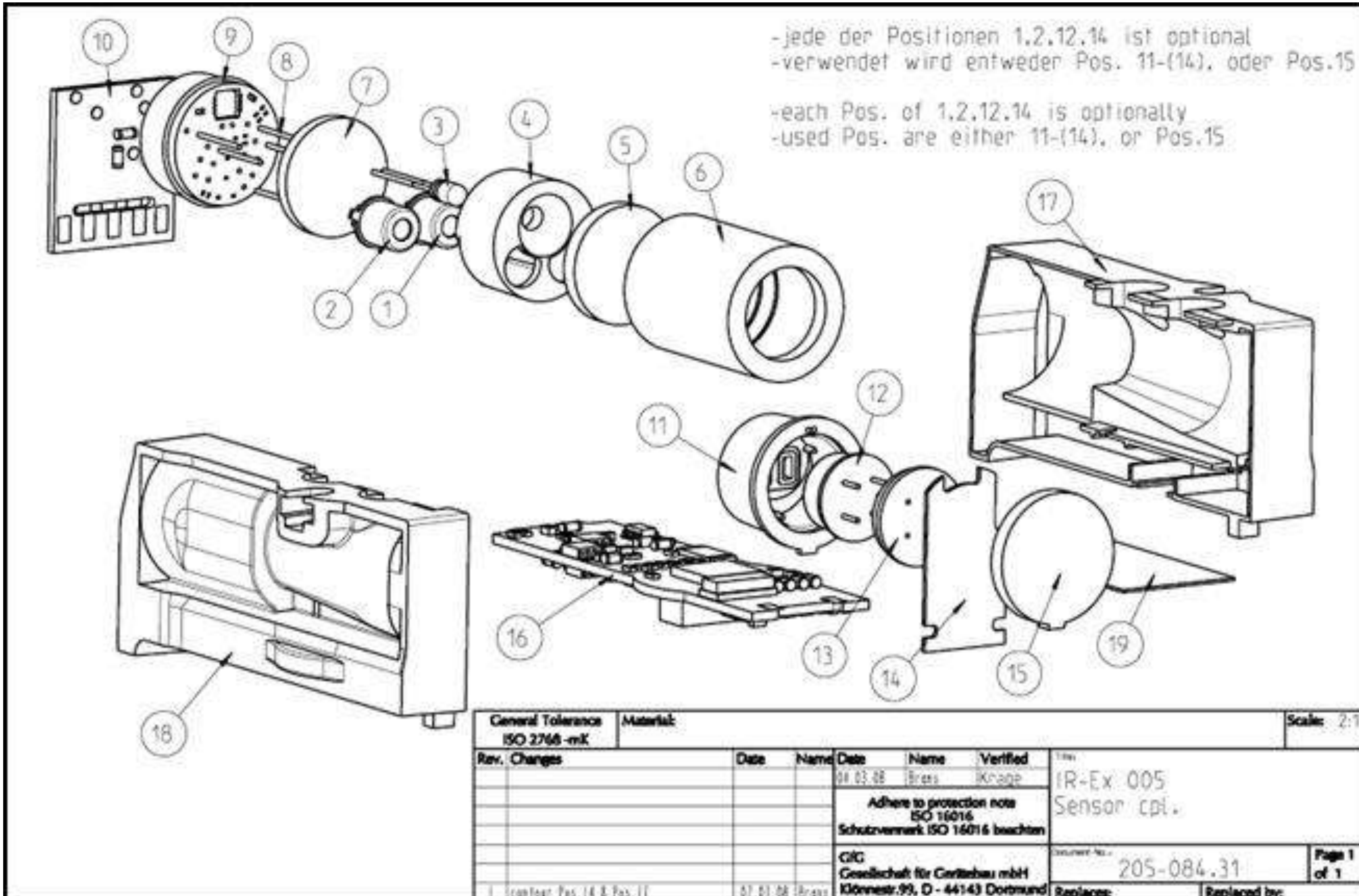
Three wavelength NDIR sensors

- ***Simultaneous measurement CO2 and combustible gas***
  - ***LEL: 3.3 µm***
  - ***CO2: 4.3µm***
  - ***Ref: 4.0µm***

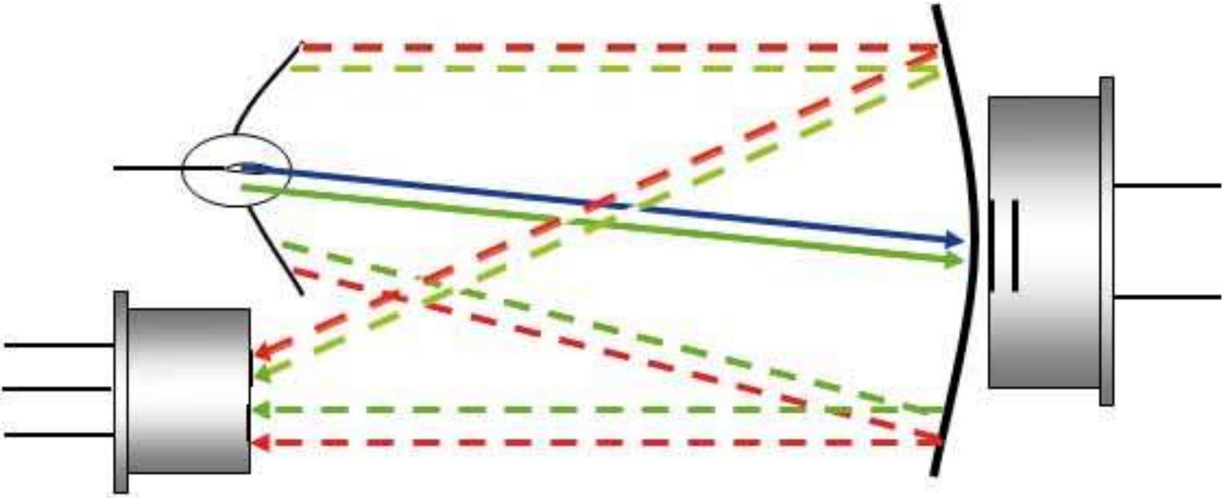


GfG Instrumentation

Three wavelength NDIR sensors

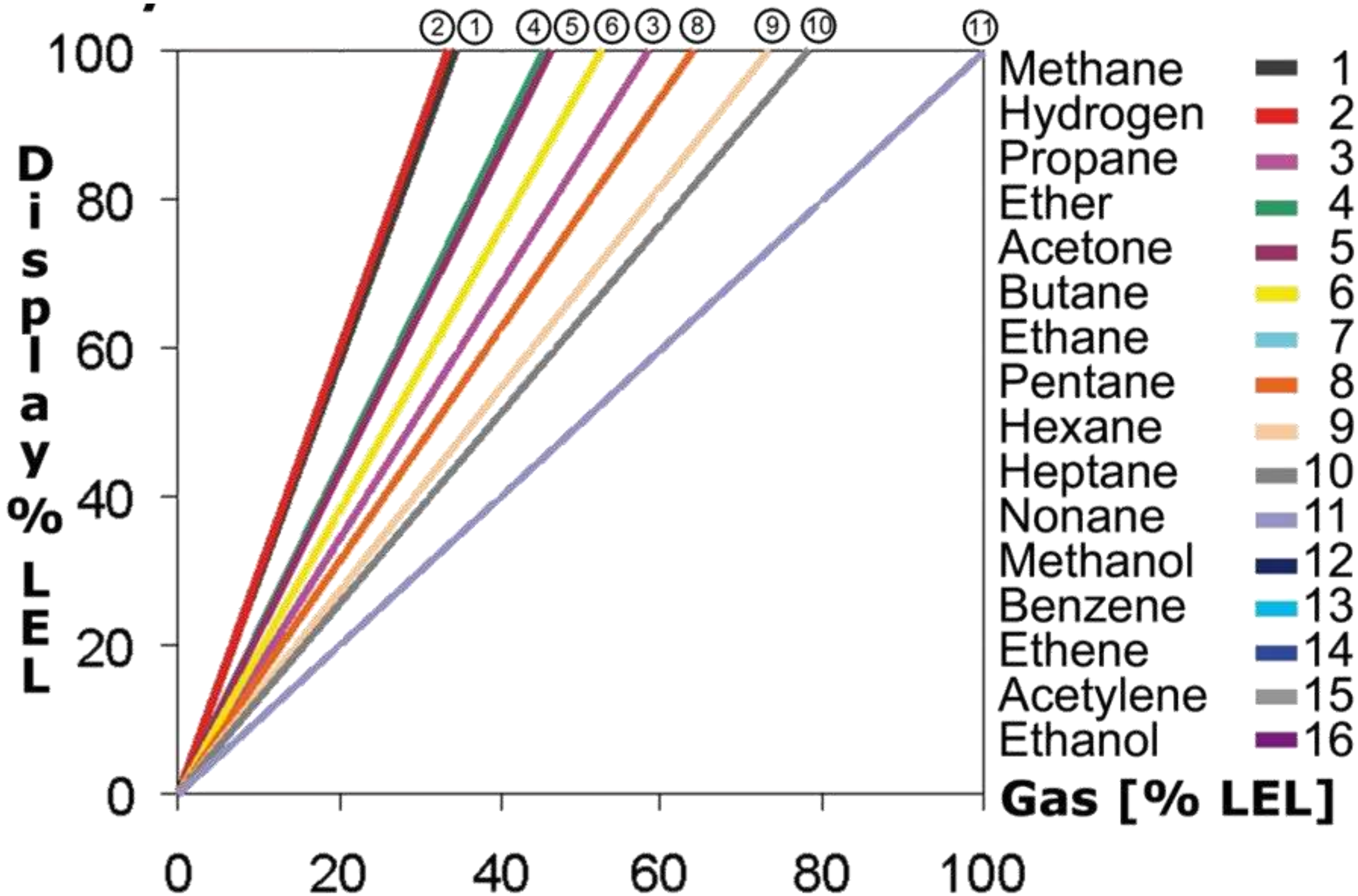


Light path through two wavelength NDIR sensor



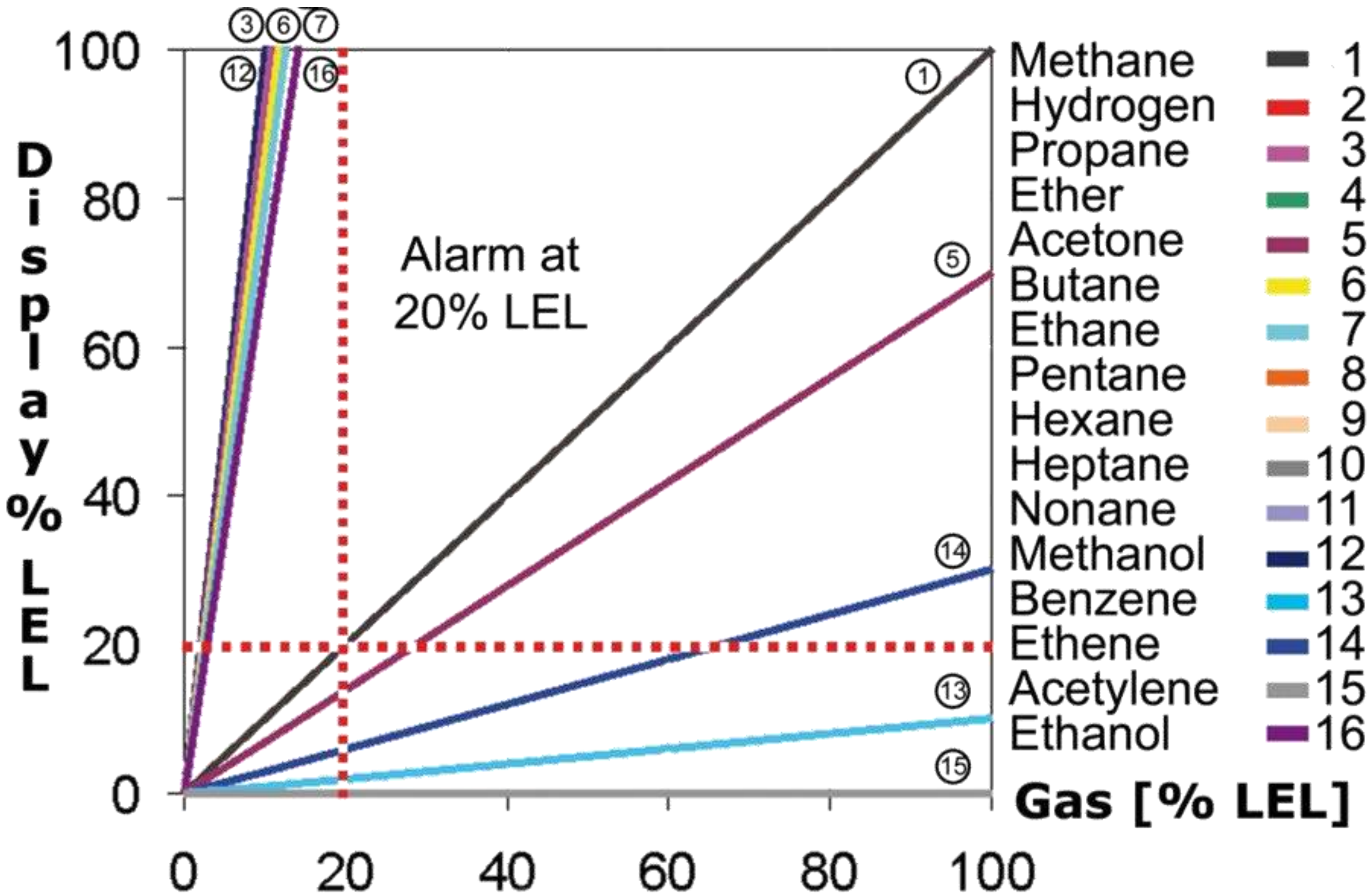
- *Affected by:*
  - *Humidity*
  - *Temperature*
  - *Pressure*
  - *Ageing of detector*
- *Not affected by:*
  - *Dust*
  - *Ageing of IR-emitter*

Catalytic pellistor combustible gas response curves



GfG Instrumentation

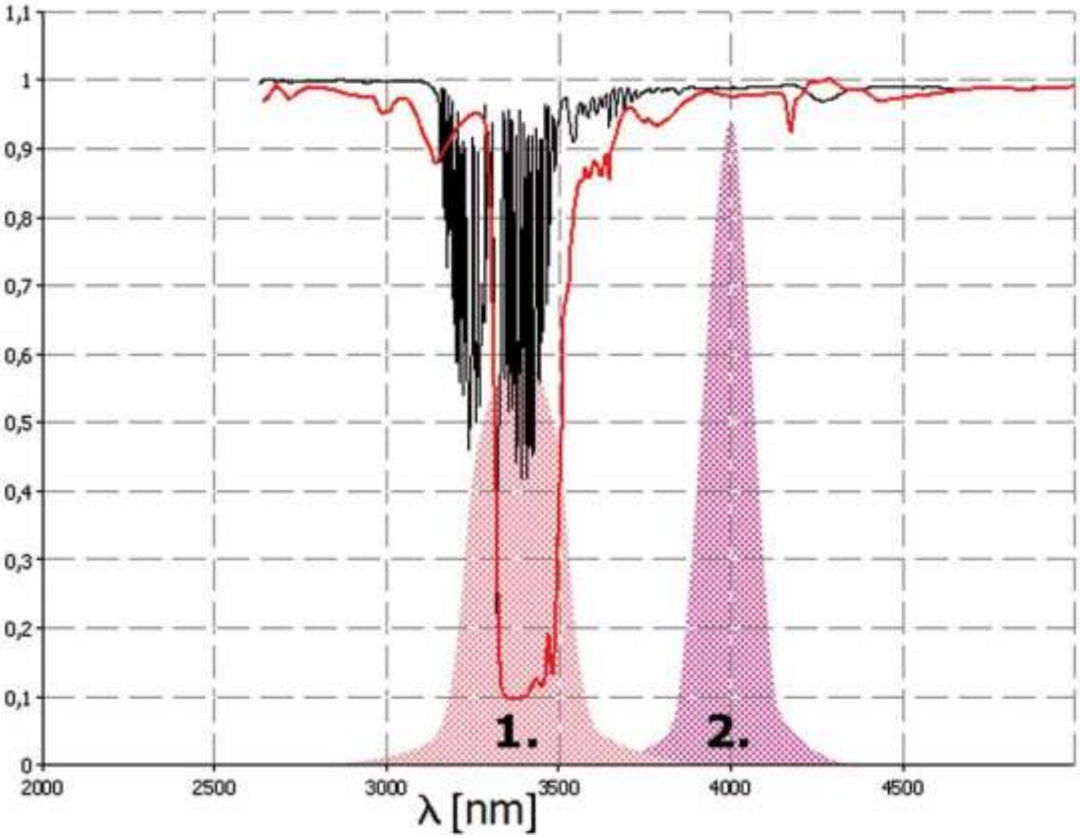
Two wavelength NDIR combustible gas response curves



GfG Instrumentation

Next on the horizon: Four wavelength NDIR combustible gas sensors

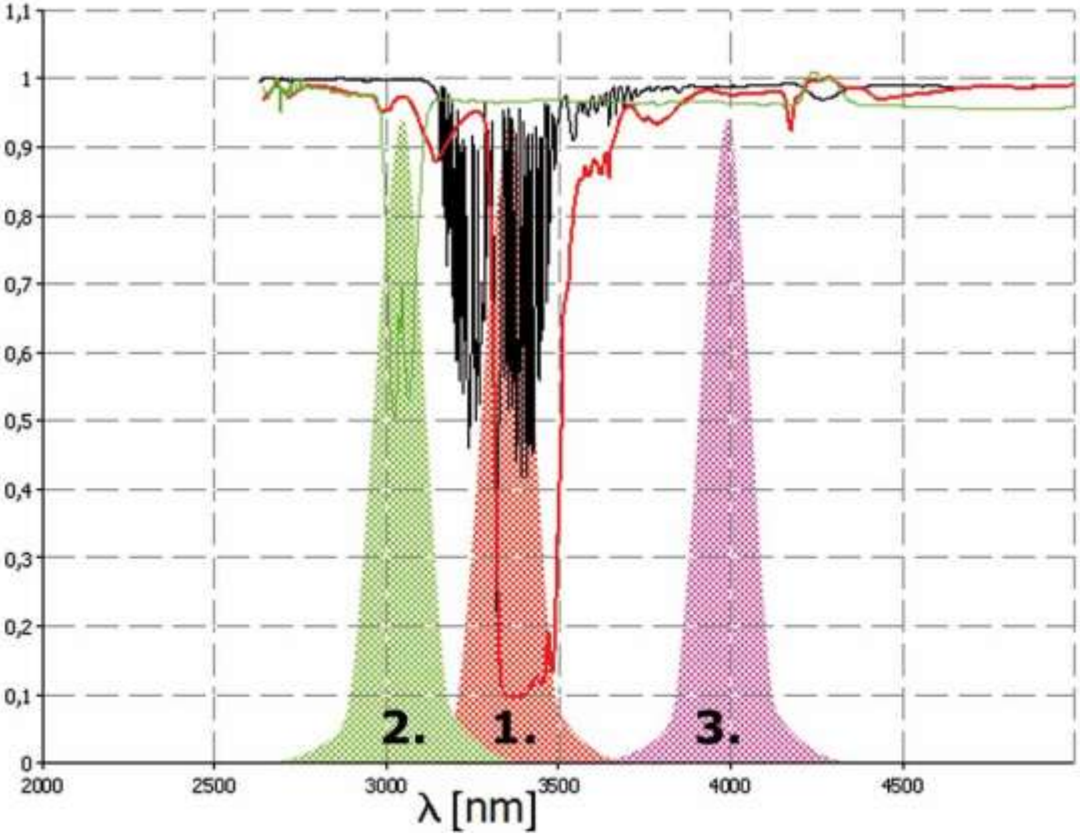
- *Measure at two wavelengths for combustible gas*
- *Measure at one reference wavelength*
- *Measure water vapor at another wavelength and deduct interfering effect from combustible gas reading*



2-wavelength Hydrocarbon-Detection

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

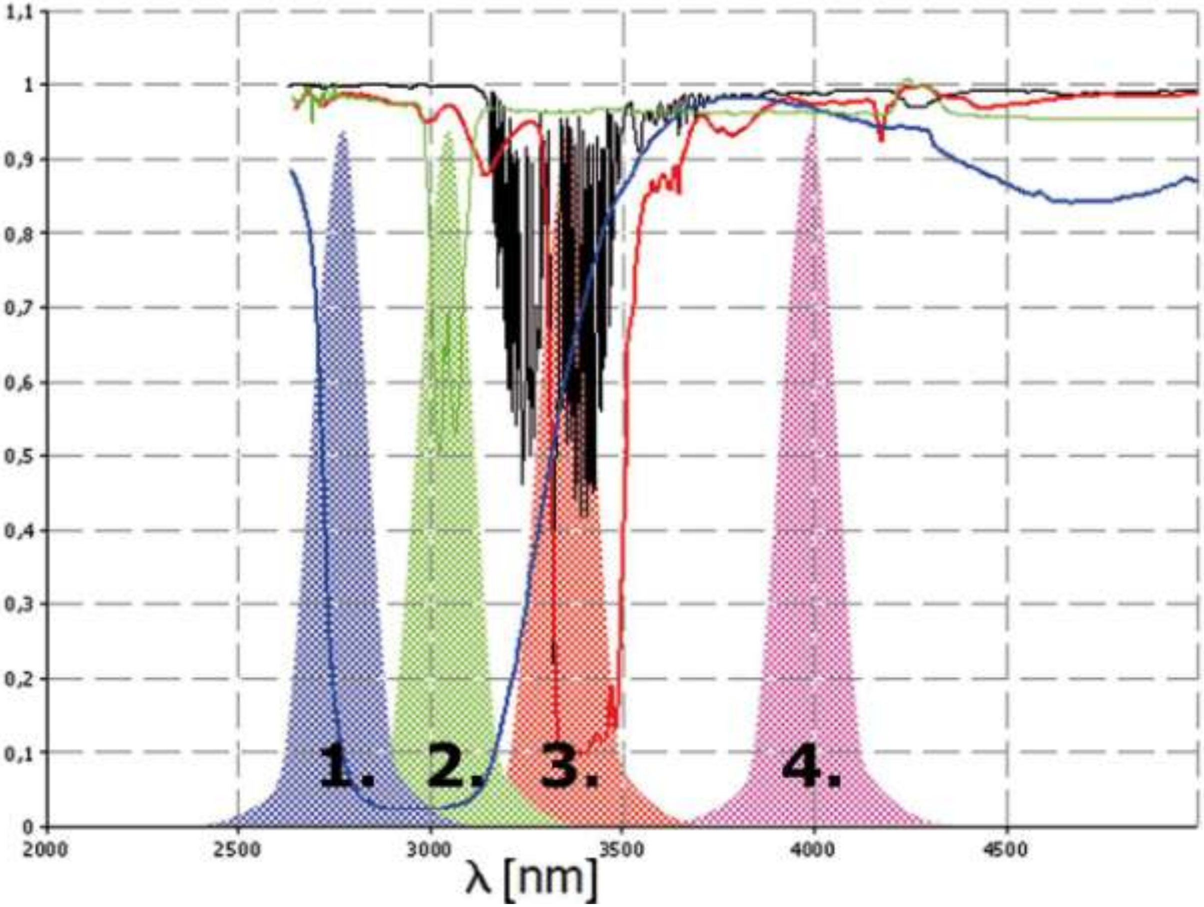
GfG Instrumentation



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

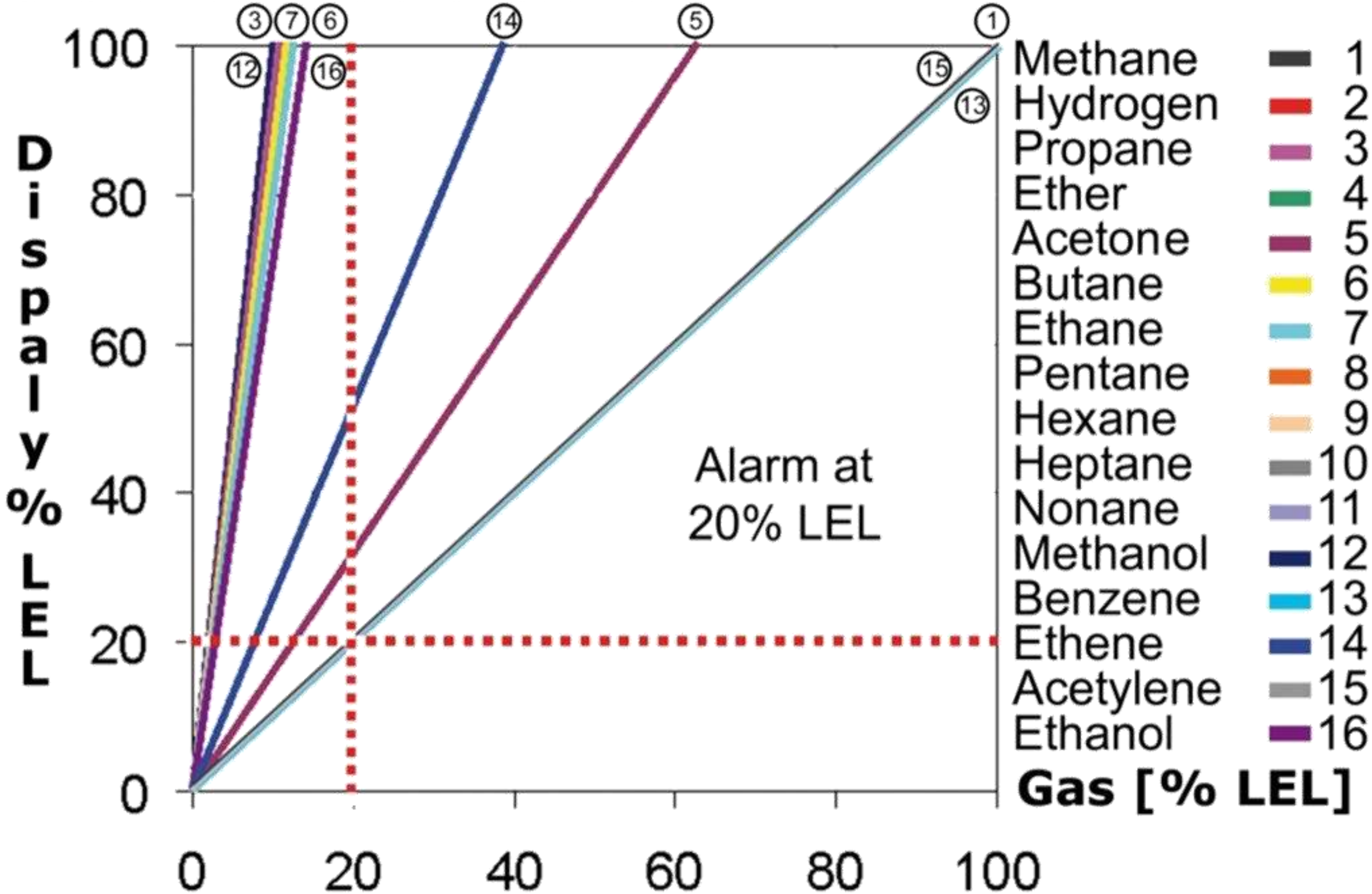
2. Acetylene C_2H_2 3,1 µm

3. Methane CH_4 } 3,3 µm
   Propane C_3H_8

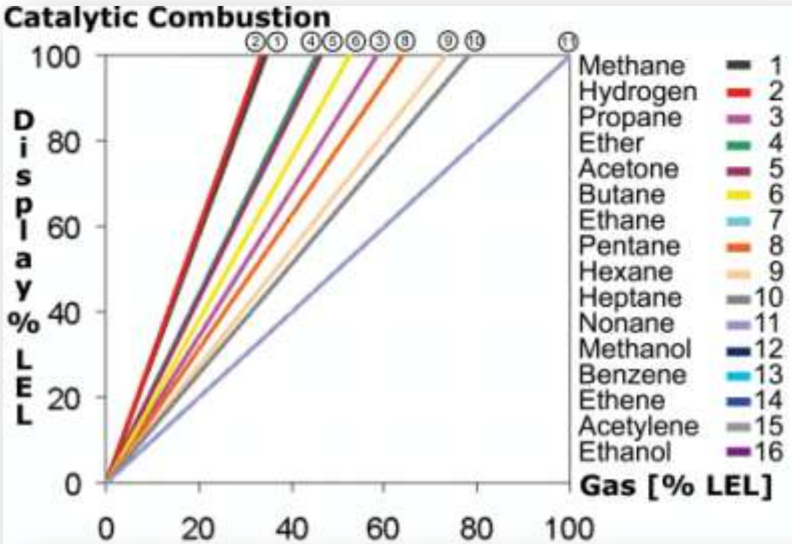
4. Reference 4,0 µm

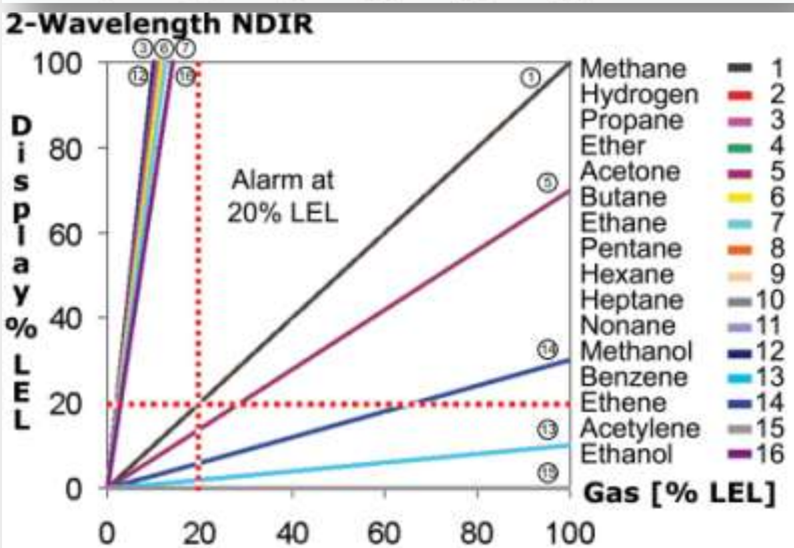
GfG Instrumentation

Four wavelength NDIR combustible gas response curves

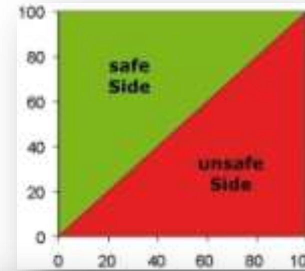


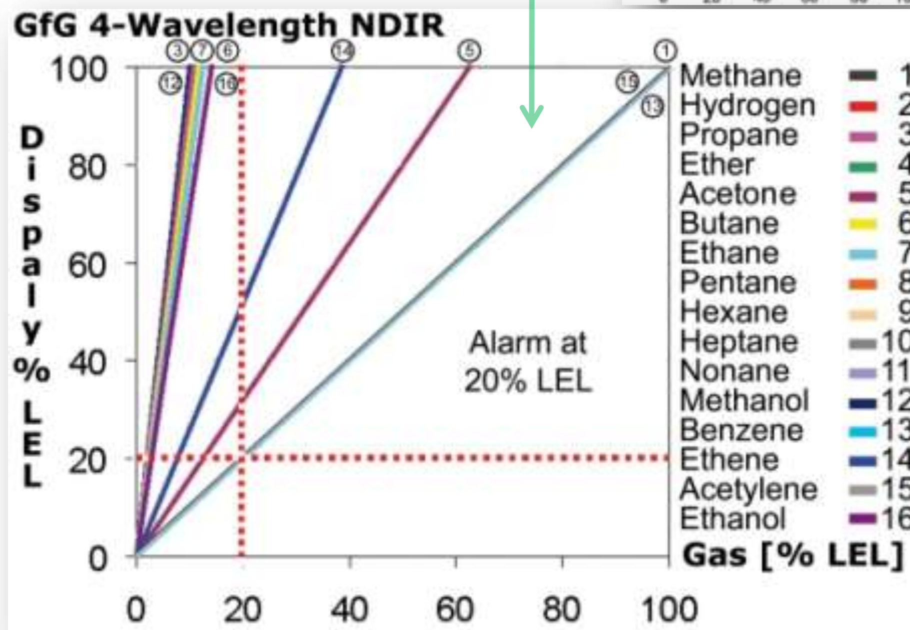
Side by side comparison





All gases on the safe side





GfG Instrumentation

IR-29 Closed Path Infrared Transmitters

- ***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***

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 or ModBus
- *45V DC:* 3 relays: 1-normally closed (NC), 2-normally open (NO)
  14 terminals

GfG Instrumentation

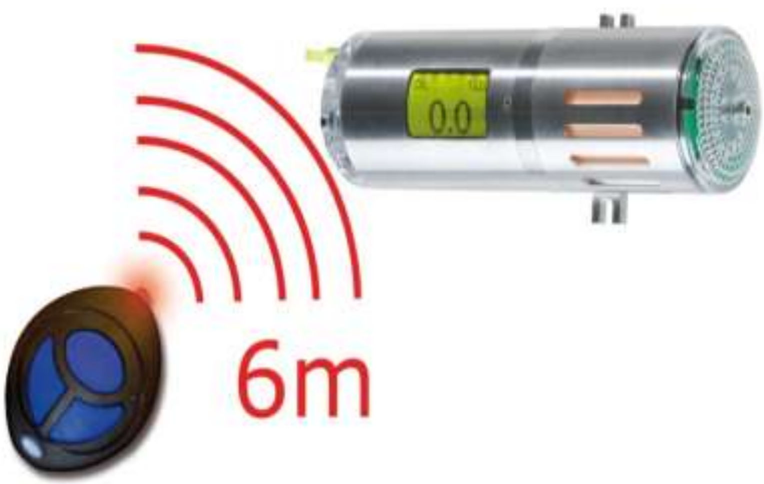
Accessory "gasfree calibration"

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

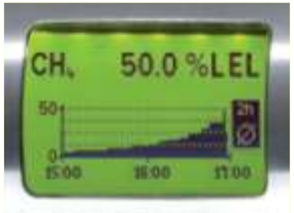
- *"One-man-calibration" at transmitter*
- *With hard-wired remote control RC2*
- *With wireless IR-remote control RC3*



GfG Instrumentation

IR-29 Closed Path Infrared Transmitters

- *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***

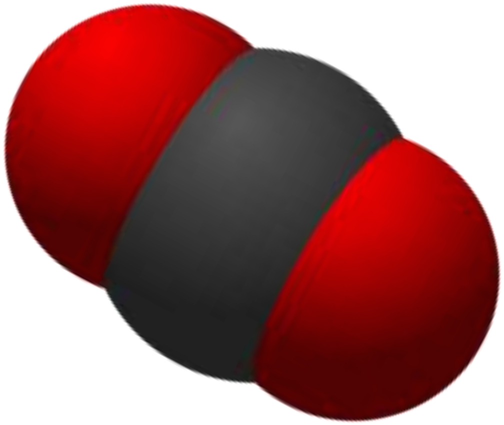
Non-dispersive infrared (NDIR) CO2 sensors

- ***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/***

GfG Instrumentation

Carbon dioxide

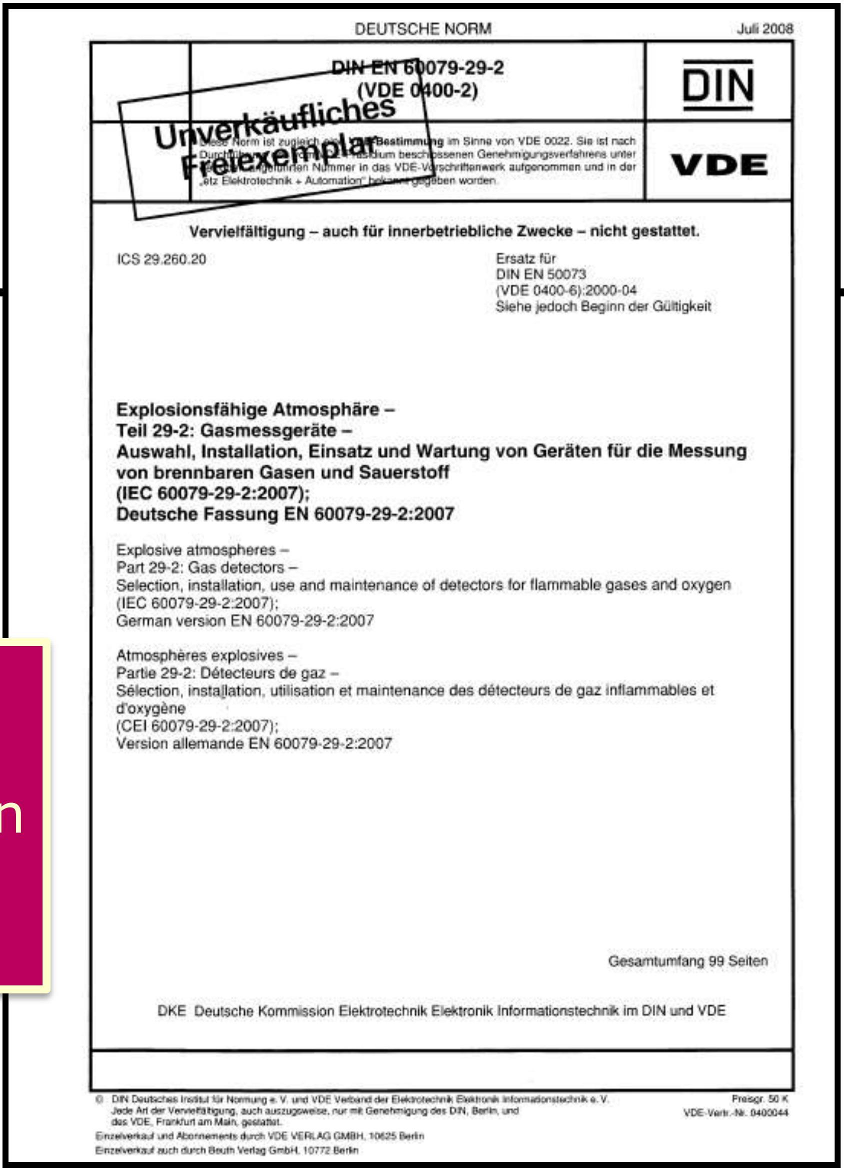
- ***Associated with:***
  - ***Confined space entry (produced by microbial decomposition)***
  - ***Wineries / breweries (byproduct of fermentation)***
  - ***Oil industry (injected into ground to decrease viscosity and aid extraction in old fields)***
  - ***Vessel inertion (used in form of dry ice as well as compressed gas)***
  - ***Greenhouses***
  - ***Mushroom farms***



German CS monitoring requirements

- ***Must* directly monitor all confined spaces for CO2**

Schlussfolgerung:
eine direkte Ermittlung von CO_2 ist dringend erforderlich und kann nicht über Sauerstoffgehalt gemessen werden



DEUTSCHE NORM   Juli 2008

DIN EN 60079-29-2
(VDE 0400-2)

DIN

VDE

Unverkäufliches Freiexemplar

Diese Norm ist zugleich eine **VDE-Bestimmung** im Sinne von VDE 0022. Sie ist nach Durchführung des vom VDE-Präsidium beschlossenen Genehmigungsverfahrens unter der oben angeführten Nummer in das VDE-Vorschriftenwerk aufgenommen und in der „etz Elektrotechnik + Automation" bekannt gegeben worden.

Vervielfältigung – auch für innerbetriebliche Zwecke – nicht gestattet.

ICS 29.260.20

Ersatz für
DIN EN 50073
(VDE 0400-6):2000-04
Siehe jedoch Beginn der Gültigkeit

Explosionsfähige Atmosphäre –
Teil 29-2: Gasmessgeräte –
Auswahl, Installation, Einsatz und Wartung von Geräten für die Messung von brennbaren Gasen und Sauerstoff
(IEC 60079-29-2:2007);
Deutsche Fassung EN 60079-29-2:2007

Explosive atmospheres –
Part 29-2: Gas detectors –
Selection, installation, use and maintenance of detectors for flammable gases and oxygen
(IEC 60079-29-2:2007);
German version EN 60079-29-2:2007

Atmosphères explosives –
Partie 29-2: Détecteurs de gaz –
Sélection, installation, utilisation et maintenance des détecteurs de gaz inflammables et d'oxygène
(CEI 60079-29-2:2007);
Version allemande EN 60079-29-2:2007

Gesamtumfang 99 Seiten

DKE Deutsche Kommission Elektrotechnik Elektronik Informationstechnik im DIN und VDE

Preisgr. 50 K
VDE-Vertr.-Nr. 0400044

Einzelverkauf und Abonnements durch VDE VERLAG GMBH, 10625 Berlin
Einzelverkauf auch durch Beuth Verlag GmbH, 10772 Berlin

GfG Instrumentation

107 Verletzte bei Gasunfall in Lackfabrik

Kohlendioxid nach Brand in Gewerbegebiet ausgetreten

Mönchengladbach. Bei einem Gasunfall in Mönchengladbach sind 107 Menschen verletzt worden, einige davon schwer. Etwa 150 Anwohner mussten am Samstag zeitweise ihre Wohnungen verlassen, 480 Rettungskräfte und Polizisten waren im Einsatz. Wegen eines Brandes in einem lackverarbeitenden Betrieb im Ortsteil Güdderath am Morgen war die Löschanlage ausgelöst worden, erklärte ein Polizeisprecher. Vermutlich wegen eines technischen Defekts trat das von der Anlage verwendete Kohlendioxid aus dem Gebäude aus. Normalerweise verschließen sich die Türen der Fabrik bei einem Brandfall automatisch.

Als der kleinere Brand schon unter Kontrolle war, sanken drei Feuerwehrleute zu Boden und verloren das Bewusstsein, so der Polizeisprecher. Sie mussten mit Sauerstoff beatmet werden. Kohlendioxid aus der Löschanlage hatte zu Atemnot geführt. Warum das normalerweise kontrolliert eingesetzte CO_2 in so hoher Konzentration auch außerhalb des Gebäudes auftrat, stand gestern noch nicht fest.

Da der Betrieb in einer Senke liegt, Windstille herrschte und Kohlendioxid schwerer als Luft ist, stieg die Konzentration des unsichtbaren Gases in dem Gewerbegebiet an. Motoren von Autos gingen aus, berichtete der Polizeisprecher. Als die Fahrer die Autos daraufhin verließen, wurde ihnen schwindlig, oder sie sanken gar zu Boden.

Die Bewohner von 50 Häusern mussten vorübergehend ihre Wohnungen verlassen, da die Feuerwehr erhöhte Konzentrationen von Kohlendioxid in den Kellern festgestellt hatte. Die Rettungskräfte lüfteten die Räume mit Hochleistungsgebläsen.

Die Polizei sperrte den Bereich den Vormittag über in einem Umkreis von zwei Kilometern ab und forderte die Bevölkerung auf, sich nicht im Freien aufzuhalten, Fenster und Türen zu schließen und höhere Stockwerke aufzusuchen. Mit zwei Hubschraubern zerstäubte die Polizei das Kohlendioxid. Die Ausfahrt Mönchengladbach-Güdderath der A61 musste vorübergehend gesperrt werden, auch die Regionalbahn von Köln nach Mönchengladbach konnte zwischenzeitlich nicht mehr fahren. Am Nachmittag wurde durch die Behörden dann Entwarnung gegeben. (ap)

Erneut Unfall mit CO_2-Löschanlage

Wuppertal. Aufgrund einer Fehlfunktion hat die Löschanlage in einer Wuppertaler Lackfabrik gestern 15 Tonnen Kohlendioxid freigesetzt. Fünf Menschen klagten danach über Schwindel. Die Polizei sperrte mehrere Straßen und forderte die Anwohner auf, Fenster und Türen geschlossen zu halten. Bereits am vergangenen Samstag hatte es in einem Lack-Lager in Mönchengladbach einen Zwischenfall mit einer CO_2-Löschanlage gegeben, 107 Personen wurden dabei verletzt. (ddp)

Freitag, 22. August 2008

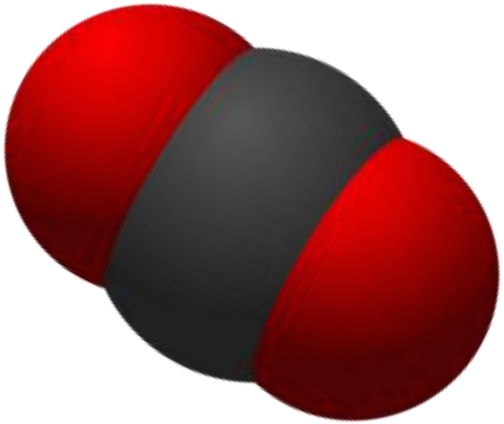
GfG Instrumentation

Carbon dioxide

- *Associated with:*
  - *Confined space entry (produced by microbial decomposition)*
  - *Wineries / breweries (byproduct of fermentation)*
  - *Oil industry (injected into ground to decrease viscosity and aid extraction in old fields)*
  - *Vessel inertion (dry ice)*
  - *Greenhouses*
  - *Mushroom farms*

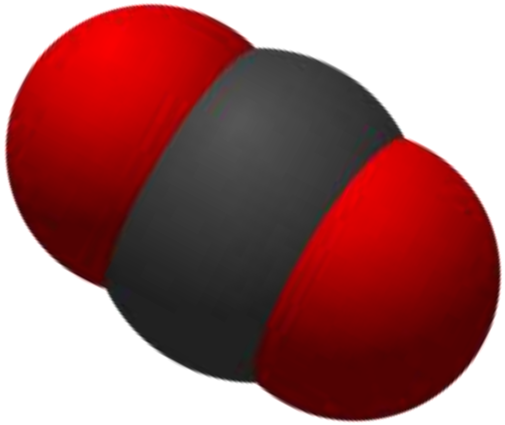
CO2 Properties

- ***Present as a natural component in fresh air (approximately 350 ppm)***
  - ***Colorless***
  - ***Odorless***
  - ***Tasteless***
  - ***Heavier than air (density of 1.5 times that of fresh air).***
  - ***When released into enclosed space it tends settle to bottom***
  - ***Because of tendency to settle, as CO2 produced it can reach higher and higher concentrations***



CO_2 exposure symptoms

- ***Besides displacing oxygen in fresh air, high concentrations may worsen symptoms related to oxygen deficiency, and interfere with successful resuscitation***
- ***Exposure Symptoms include***
    - ***Headaches***
    - ***Dizziness***
    - ***Shortness of breath***
    - ***Nausea***
    - ***Rapid or irregular pulse***
    - ***Depression of central nervous system***



GfG Instrumentation

CO2 is toxic contaminant with strictly defined exposure limits

- *Most widely recognized exposure limit is 8-hour TWA of 5,000 ppm, with a 15-minute STEL of either 15,000 ppm or 30,000 ppm.*

Standard / Country	8-hour Time Weighted Average	15-minute Short Term Exposure Limit
United Kingdom WEL	5,000 ppm	15,000 ppm
USA NIOSH REL	5,000 ppm	30,000 ppm
USA OSHA PEL	5,000 ppm	None Listed
ACGIH® TLV®	5,000 ppm	30,000 ppm

Even moderate indoor concentrations can produce symptoms

Concentration	Symptom
250 – 350 ppm	Normal background concentration in outdoor ambient air
350 – 1,000 ppm	Concentrations typical of occupied indoor spaces with good air exchange
1,000 – 2,000 ppm	Complaints of drowsiness and poor air
2,000 – 5,000 ppm	Headaches, sleepiness, and stagnant, stale, stuffy air. Poor concentration, loss of attention, increased heart rate and slight nausea may also be present
>5,000 ppm	Exposure may lead to serious oxygen deprivation resulting in permanent brain damage, coma and even death

GfG Instrumentation

- *Criteria to use when choosing an atmospheric monitor*

Choosing the Best Gas Detector

- ***"Best" gas detector doesn't come from any one manufacturer; it's the instrument that best fulfills the requirements for <u>your</u> monitoring program***

- ***Ways in which gas detectors are used can vary widely between different programs***

- ***The instrument that provides the best service and value for one program may not be the best choice for another***

GfG Instrumentation

Classification for Intrinsic Safety

- ***Intrinsically Safe devices prevent explosions in hazardous locations by employing electrical designs that eliminate the possibility of ignition***
  - ***Generally involves adding protective components in series with energy storage devices to reduce risk of ignition due to spark or increased surface temperature of components***
  - ***Design elements may also include flame arrestors or other components to locally contain an explosion in the event that there is ignition***
  - ***Combustible sensors contain an integral flame arrestor for this purpose***
  - ***Classification for Intrinsic Safety is based on performance of the instrument when tested in a specific flammable atmosphere***

UL / CSA Product Markings

- ***Typical North American Marking:***
  - ***c-CSA-us or c-UL-us Classified as to intrinsic safety for use in Class I, Division1 Groups A, B, C, and D, and Class II Groups E, F and G Hazardous Locations***
    - ***Class I: A location where there is a danger of explosion due to the presence of a flammable gas or vapor***
      - ***Under the North American system the hazardous gases are subdivided into Divisions. The IEC system divides it into Zones***
    - ***Class II: A location where there is a danger of explosion due to the presence of a flammable dust***

Class I Divisions vs. Zones

CEC/NEC Division Classification	IEC Zone Classification
Class I, Division 1: Ignitable concentrations can exist under normal operating conditions; may exist frequently because of repair, maintenance or leakage; or may exist due to breakdown of equipment in conjunction with an electrical failure	**Class I, Zone 0:** Where ignitable concentrations are present continuously or for long periods of time **Class I, Zone 1:** Where ignitable concentrations are likely to exist under normal operations; may exist frequently because of repair, maintenance or leakage; may exists due to breakdown of equipment in conjunction with an electrical failure; or adjacent to Class I, Zone 0 locations.
Class I, Division 2: Where volatile flammable liquids are stored, etc. in closed containers; where ignitable concentrations are normally prevented by positive pressure ventilation; or adjacent to Class I, Division 1 locations	**Class I, Zone 2:** Where ignitable concentrations are not likely to exist in normal operation or may exist for a short time only; where volatile flammable liquids are stored, etc. in closed containers; where ignitable concentrations are normally prevented by positive pressure ventilation; or adjacent to Class I, Zone 1 locations.

Classification for Intrinsic Safety

- *Hazardous Location Classifications*
    - *Class I, Division 1, Groups A, B, C, D*
    - *Class II, Groups E, F, G*
- *Groups A,B,C and D are explosive gases and vapors*
- *Groups E, F, and G are explosively combustible dusts*

GfG Instrumentation

UL / CSA / NEC Combustible Gas Classification Groups

- ***Class I, Division 1 Groups A, B, C, D***

Group	Gas or Vapour	LEL (%)	UEL (%)
A	Acetylene	2.5	80.0
B	Hydrogen	4.0	5.0
C	Diethyl ether	1.9	48.0
C	Ethylene	3.1	32.0
C	H2S	4.3	45.0
D	Ammonia	15.0	28.0
D	Butane	1.9	8.5
D	Gasoline	1.4	7.6
D	Methane	5.3	15
D	CO2	12.5	74.2
D	Propane	2.2	9.5

European Cenelec / ATEX Product Markings

Complies with European harmonized standards

Protection concept symbol – The main concept appears first in the code

EEx ed IIC T4 T_{amb} - 40° to + 50°C

For use in explosive atmospheres

Gas grouping

Temperature code

Ambient temperature range in service

European Combustible Gas Classification Groups

- Combustible gas categories divided into two groups:
  - Group I for mines susceptible to methane
  - Group II for explosive gases for locations other than mines; group II is divided into three sub groups:
    - IIA: Atmospheres containing propane or gases of an equivalent hazard
    - IIB: Atmospheres containing ethylene or gases of an equivalent hazard
    - IIC: Atmospheres containing hydrogen or gases of an equivalent hazard.

GfG Instrumentation

Temperature Codes

- ***The auto-ignition temperature is the temperature, in ℃, at which a gas will ignite spontaneously without another source of ignition***
- ***Temperature code groupings correspond to the range of autoignition temperatures in which a particular gas belongs***

Substance	*Temperature Classification*	*AIT (°C)*
Methane	*T1*	*595*
Propane	*T1*	*470*
Ethylene	*T2*	*425*
Acetylene	*T2*	*305*
Hydrogen	*T1*	*560*

Temperature Codes

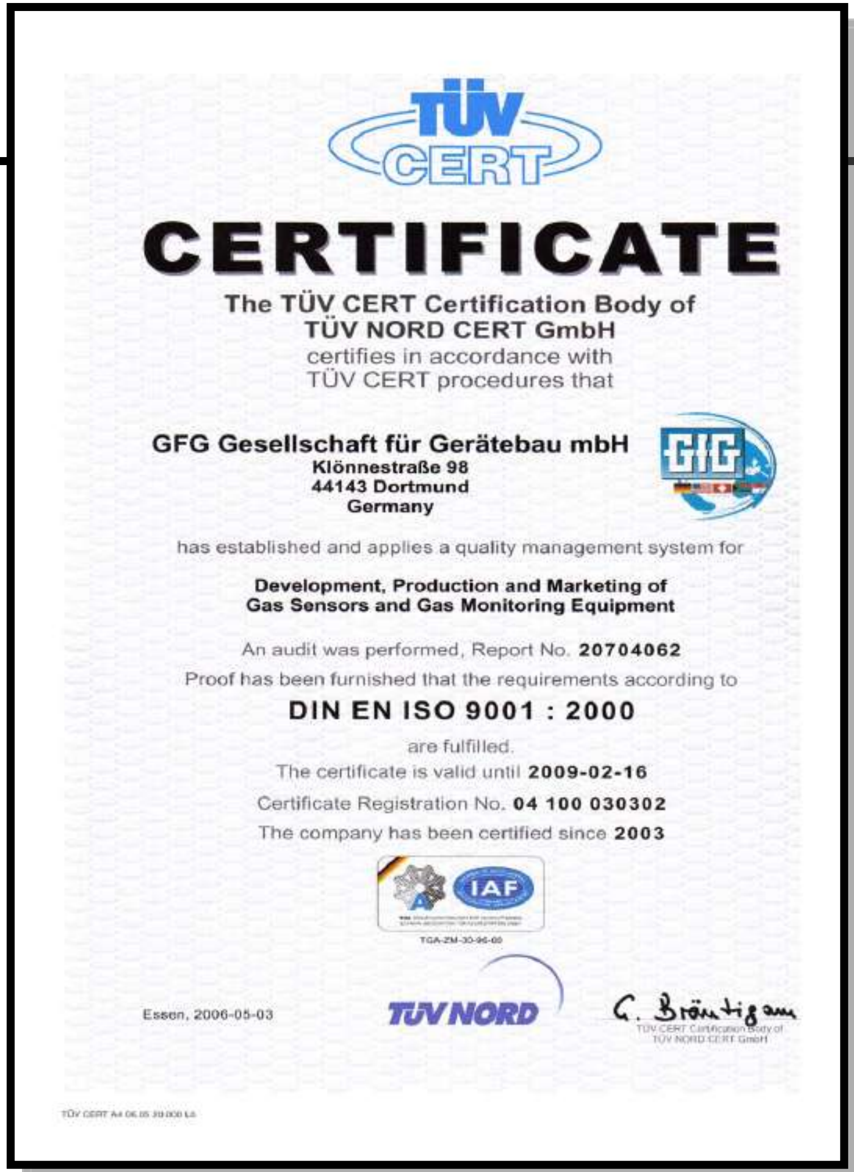
- *Temperature code groups can also be expressed as a range of temperatures*
- *Gases with low autoignition temperatures are the ones most easily ignited by increasing the temperature once the gas is present in LEL concentrations*
  - *As an example: A T3 rating means that the instrument is only Classified as IS for gases with autoignition temperatures greater than 200 °C.*
  - *The AIT for propane is 470 °C.*
  - *Using an instrument with a T3 rating to monitor for the presence of propane would be well within the scope of its IS Classification.*

Temperature Class	Autoignition Temperature Limit for Gases Measured (°C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

- *"CE" stands for the French "Conformité Européene"*
- *CE Marking on a product is the manufacturer's declaration that the product conforms with the relevant European health, safety and environmental "Product Directives"*
- *Product Directives contain the essential requirements, performance levels, and "Harmonized Standards" for technical specifications to which the products must conform*
- *CE Marking indicates to EEC governmental officials that the product may be legally placed on the market in their country*
- *CE Marking includes declaration that the product conforms with EMC Directive 89/336/EEC which governs product susceptibility to RFI / EMI interference*

ISO Registration

- *9001: 2000 Edition*
- *Old edition allowed mediocre quality, as long as product produced consistently*
- *New edition includes requirement for "continual product improvement"*



TÜV CERT

CERTIFICATE

The TÜV CERT Certification Body of
TÜV NORD CERT GmbH
certifies in accordance with
TÜV CERT procedures that

GFG Gesellschaft für Gerätebau mbH
Klönnestraße 98
44143 Dortmund
Germany

has established and applies a quality management system for

Development, Production and Marketing of
Gas Sensors and Gas Monitoring Equipment

An audit was performed, Report No. **20704062**

Proof has been furnished that the requirements according to

DIN EN ISO 9001 : 2000

are fulfilled.

The certificate is valid until **2009-02-16**

Certificate Registration No. **04 100 030302**

The company has been certified since **2003**

TGA-ZM-30-96-00

Essen, 2006-05-03

TÜV NORD

TÜV CERT Certification Body of TÜV NORD CERT GmbH

Ingress Protection

- ***Enclosure Rating Definitions for IEC (International Electrotechnical Commission)***
- ***The IEC enclosure rating always starts with the letters "IP" and ends in two numbers***
- ***The first number describes the degree of contact prevention and guarding against solid foreign objects***
- ***The second number describes the degree of water protection***

Ingress Protection

First No.	Degrees of Contact Prevention and Guarding Against Foreign Objects
0	No protection of personnel from direct contact with active or moving parts. No protection from access of a solid foreign object.
1	Protection of personnel from accidental large area direct contact with active or internal moving parts but no guard against intentional access to such parts. Protection from access of solid foreign object larger than 50mm in diameter.
2	Protection of personnel from finger contact with active or internal moving parts. Protection from access of solid foreign object larger than 12mm in diameter.
3	Protection of personnel from touching active or internal moving parts with tools, wires or similar foreign objects thicker than 2.5mm.. Protection from access of solid foreign matter larger than 2.5mm in diameter.
4	Protection of personnel from touching active or internal moving parts with tools, wires or similar foreign objects thicker than 1mm.
5	Total protection of personnel from touching voltage carrying or internal moving parts. Protection from harmful deposit of dust. Access of dust is not completely prevented.
6	Total protection of personnel from touching voltage carrying or internal moving parts. Protection from access of dust.

Ingress Protection

2nd No.	Protection	Details
0	*Not protected*	—
1	*Dripping water*	*Dripping water (vertically falling drops) shall have no harmful effect.*
2	*Dripping water when tilted to 15°*	*Vertically dripping water shall have no harmful effect when enclosure tilted at an angle up to 15° from normal position.*
3	*Spraying water*	*Water falling as spray at any angle up to 60° from the vertical shall have no harmful effect.*
4	*Splashing water*	*Water splashing against enclosure from any direction shall have no harmful effect.*
5	*Water jets*	*Water projected by a nozzle against enclosure from any direction shall have no harmful effects.*
6	*Powerful water jets*	*Water projected in powerful jets against the enclosure from any direction shall have no harmful effects.*
7	*Immersion up to 1m*	*Ingress of water in harmful quantity shall not be possible when immersed under defined conditions of pressure and time (up to 1 m of submersion).*
8	*Immersion beyond 1m*	*Suitable for continuous immersion in water under conditions specified by the manufacturer.*

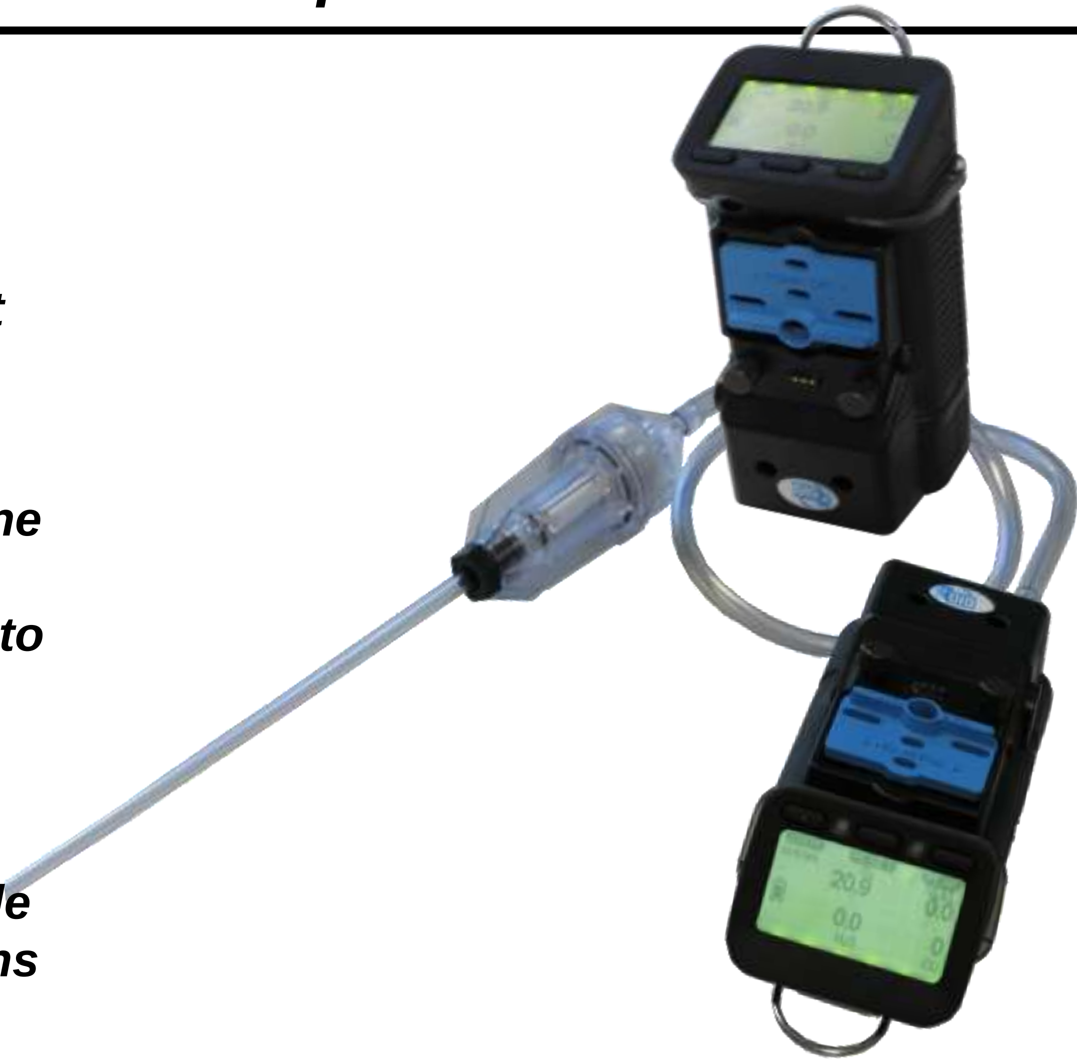
Sample-Draw vs. Diffusion

- ***Drawbacks of diffusion only designs:***
  - ***Instrument only able to monitor the atmosphere in the immediate vicinity of sensors***
  - ***Only way to obtain readings from remote location is to lower the instrument by rope or lanyard into the confined space***
  - ***Not possible to use monitor for "pick hole" sampling (requires additional hand aspirator sample draw kit or motorized pump)***

GfG Instrumentation

Sample-Draw vs. Diffusion

- ***Drawbacks of sample-draw only designs:***
  - ***Sample lag time: instrument cannot detect contaminants until they reach the sensors***
  - ***Potential for leakage in the system: critical to test system for leakage prior to use***
  - ***Potential for pump malfunction: some instruments only operable as long as pump functions***



Optimal design

- ***Instrument can be used in either diffusion or sample draw mod***
  - ***"Shuttered" pump designs allow instrument to be used in diffusion mode without having to remove the motorized pump***
- ***Motorized pump has its own power supply***
  - ***"Parasitic" type pumps are powered via the instrument battery, reducing operation time per charge***
- ***Motorized pump is diaphragm type design***
  - ***Improves pump flow rate and maximum remote sampling distance***

GfG Instrumentation

Hand-aspirated sample-draw kit

- ***Available for all models of diffusion type multi-gas instruments***
- ***Make sure to squeeze the bulb the required number of times for sample to reach the sensors***
- ***Continue to squeeze bulb until readings are stable***
- ***Make sure to test the system for leakage prior to use:***
  - ***Block end of the sample tubing or probe with finger***
  - ***Squeeze the aspirator bulb***
  - ***Bulb should stay deflated until blockage is removed***

GfG Instrumentation

Deciding Between Battery Types

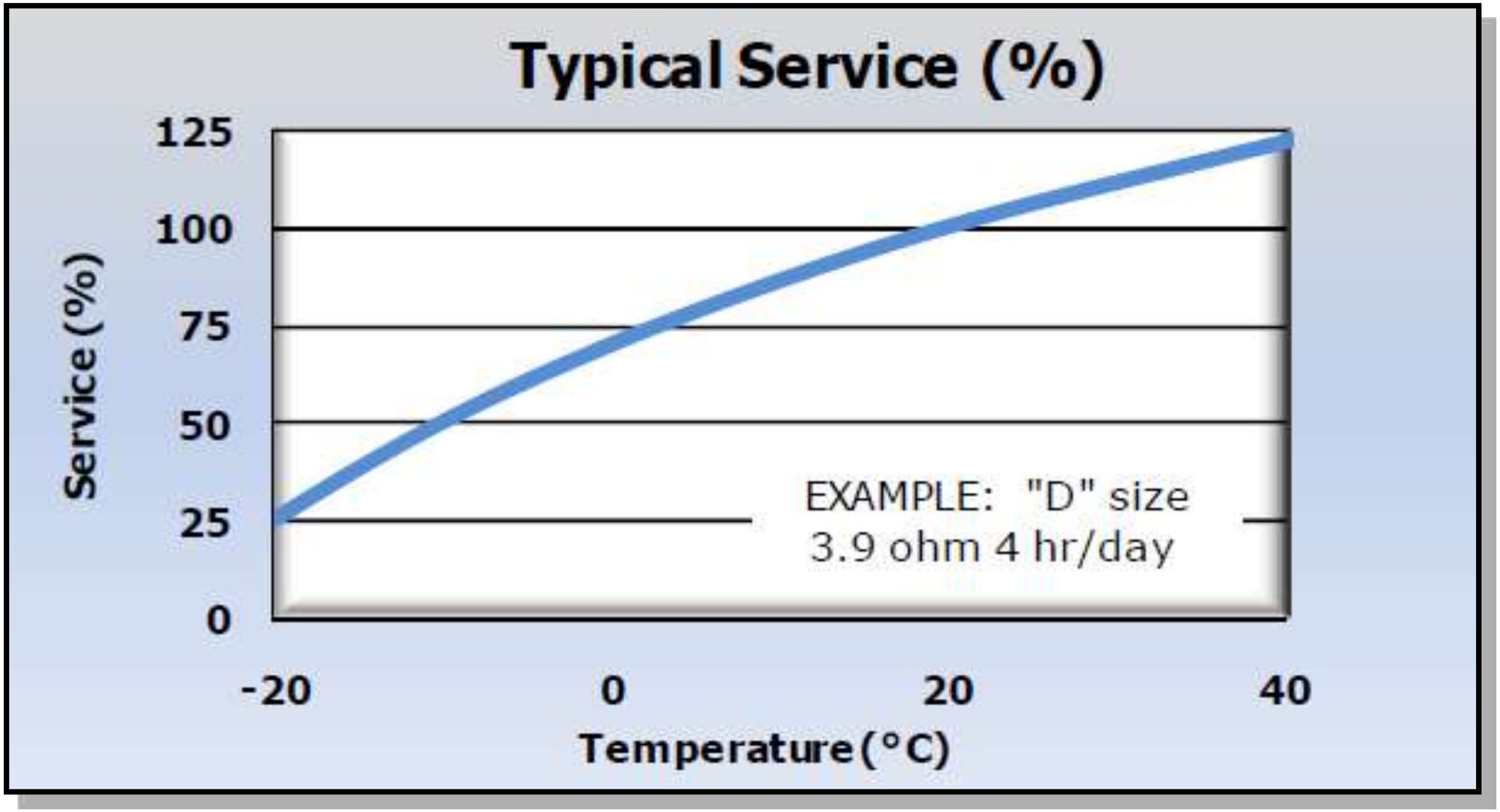
- ***Alkaline batteries or battery packs:***
  - ***Daily replacement of disposable batteries very expensive***
  - ***Environmentally unfriendly***
  - ***Convenient: Having ability to use "in a pinch" is strong design advantage***
- ***Rechargeable batteries or battery packs:***
  - ***Most cost effective approach***
  - ***Operation time per charge can be issue***
  - ***Recharging can be logistically complicated***
  - ***Time to recharge battery pack can be issue (especially if instrument used for long-duration or multiple shift jobs)***
- ***Optimal approach: Interchangeable alkaline or rechargeable battery packs***

Disposable (Alkaline) Batteries

- *Advantages*
  - *Excellent capacity per volume*
  - *Good cold temp performance*
  - *Easy access*
  - *No charging downtime*
- *Disadvantages*
  - *Cost*
  - *Environmentally unfriendly*

GfG Instrumentation

Temperature performance of typical alkaline battery

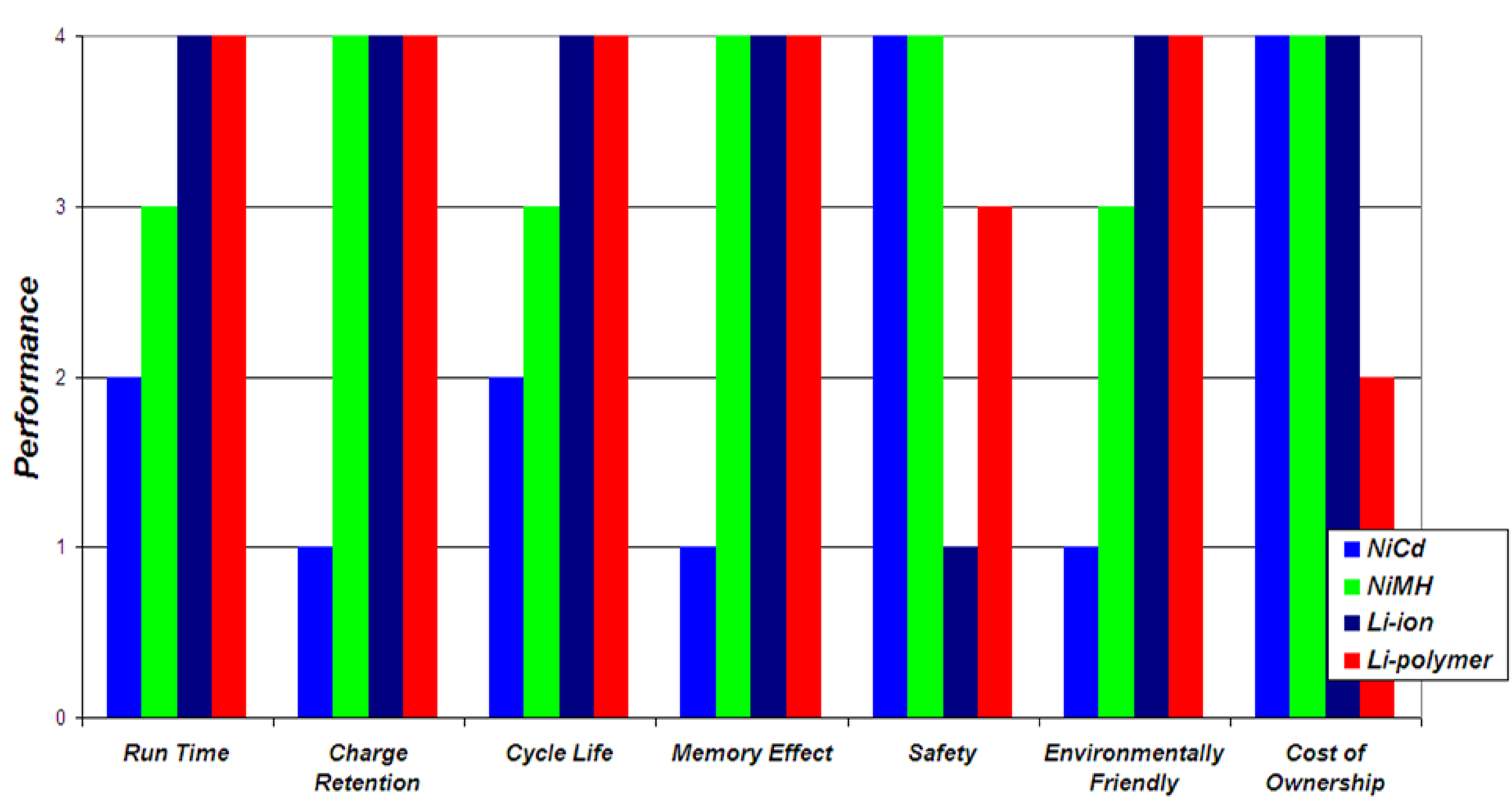


Example used is Energizer brandalkaline battery

Rechargeable Battery Types

- ***Rechargeable Batteries***
  - ***Lead-acid batteries***
  - ***Nickel Cadmium (NiCad) batteries***
  - ***Nickel-Metal Hydride (NiMH)***
  - ***Lithium-ion***
  - ***Lithium-polymer***

Rechargeable Battery Characteristics

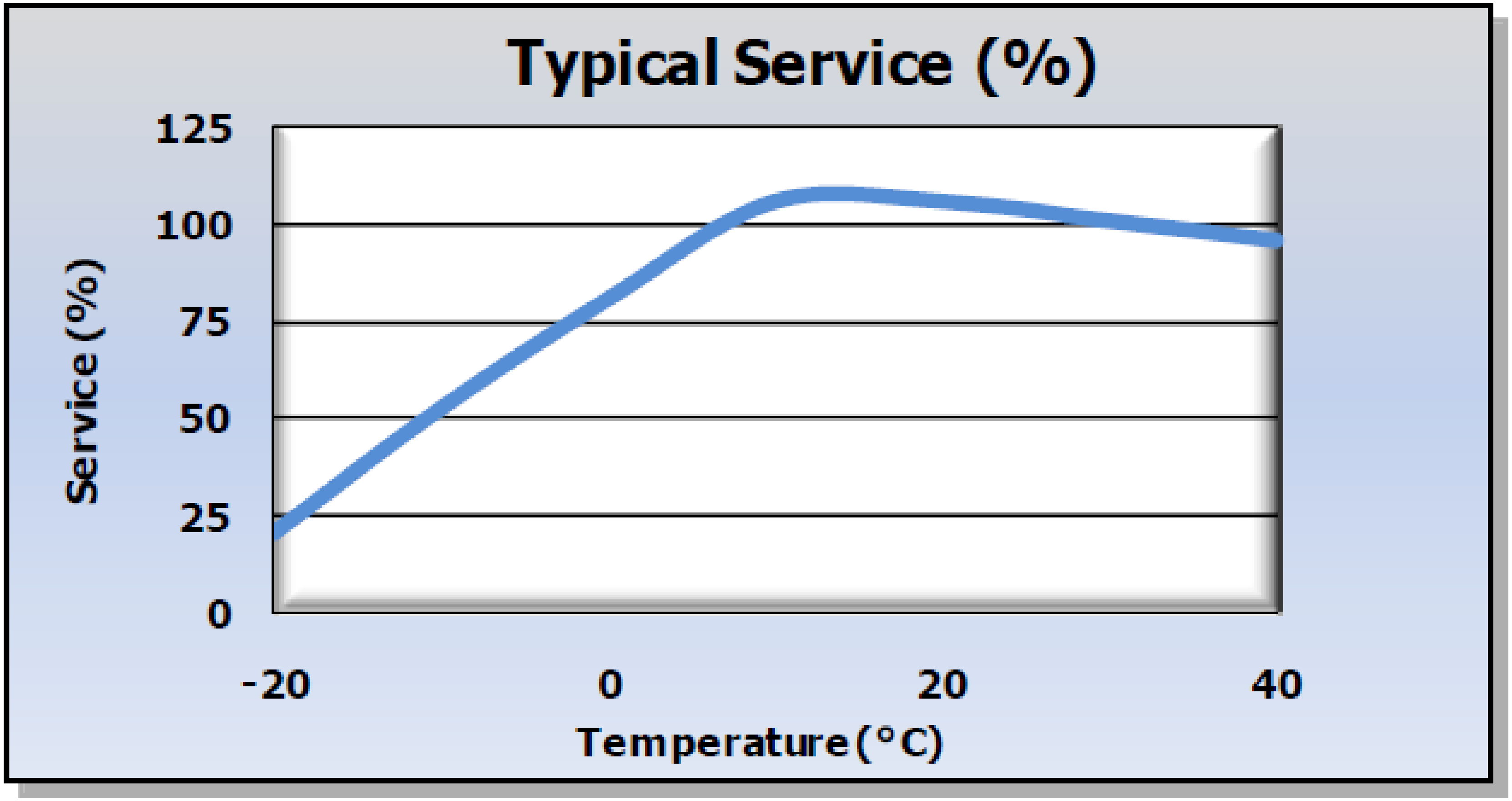


Nickel Metal Hydride (NiMH) rechargeable batteries

- *Advantages:*
  - ***Better TC rating than Li-ion***
  - ***Electrolyte is not flammable!***
  - ***Excellent energy density***
  - ***Good cold temp performance***
  - ***Excellent cycle life***
  - ***Low loss of capacity as function of overcharging***
  - ***Environmentally friendly***

GfG Instrumentation

Temperature performance of typical NiMH rechargeable battery

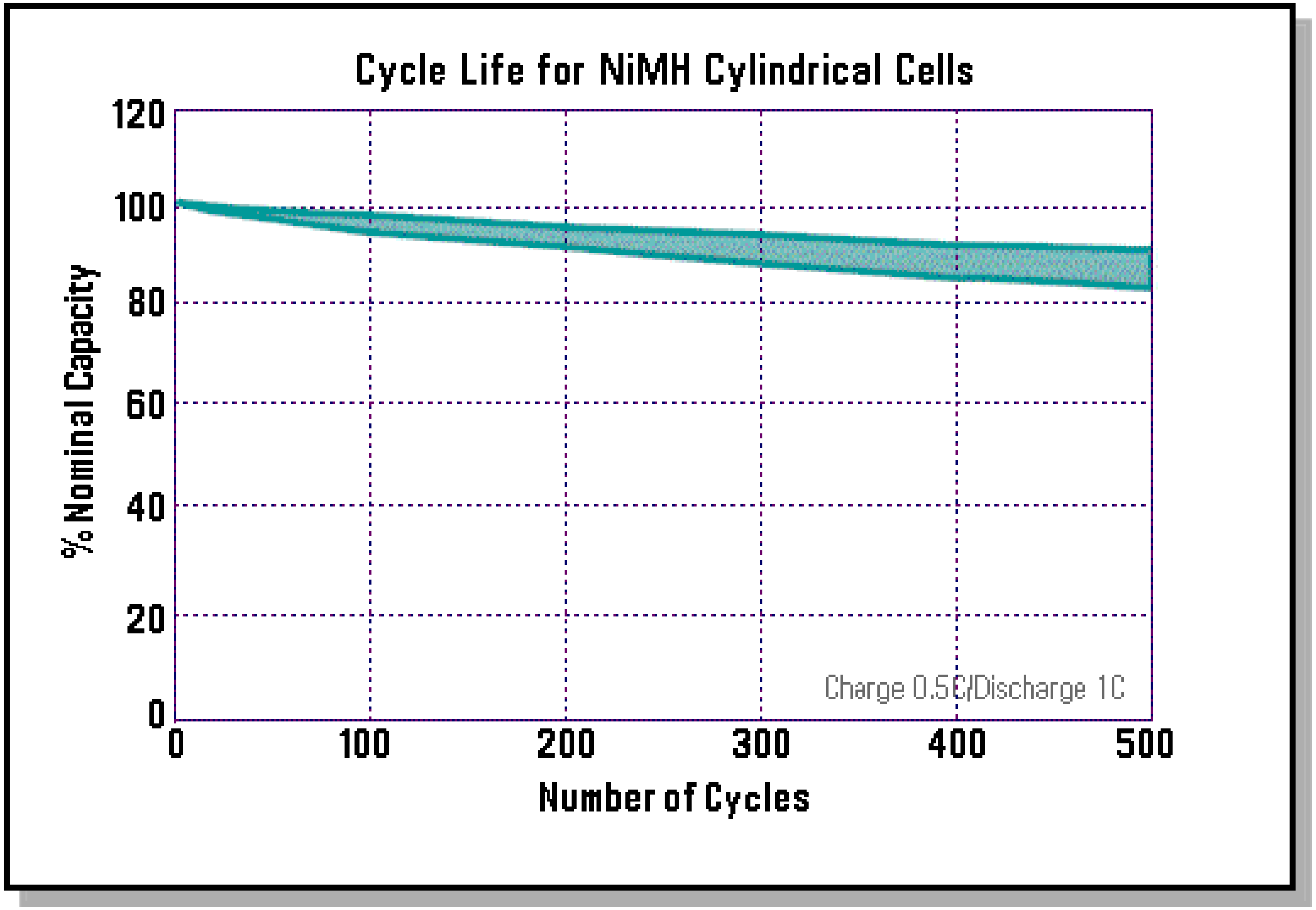


Example used is Energizer brand NiMH battery

GfG Instrumentation

NiMH Battery Performance

- ***NiMH batteries generally retain better than 80% of their original capacity even after 500 charging cycles***

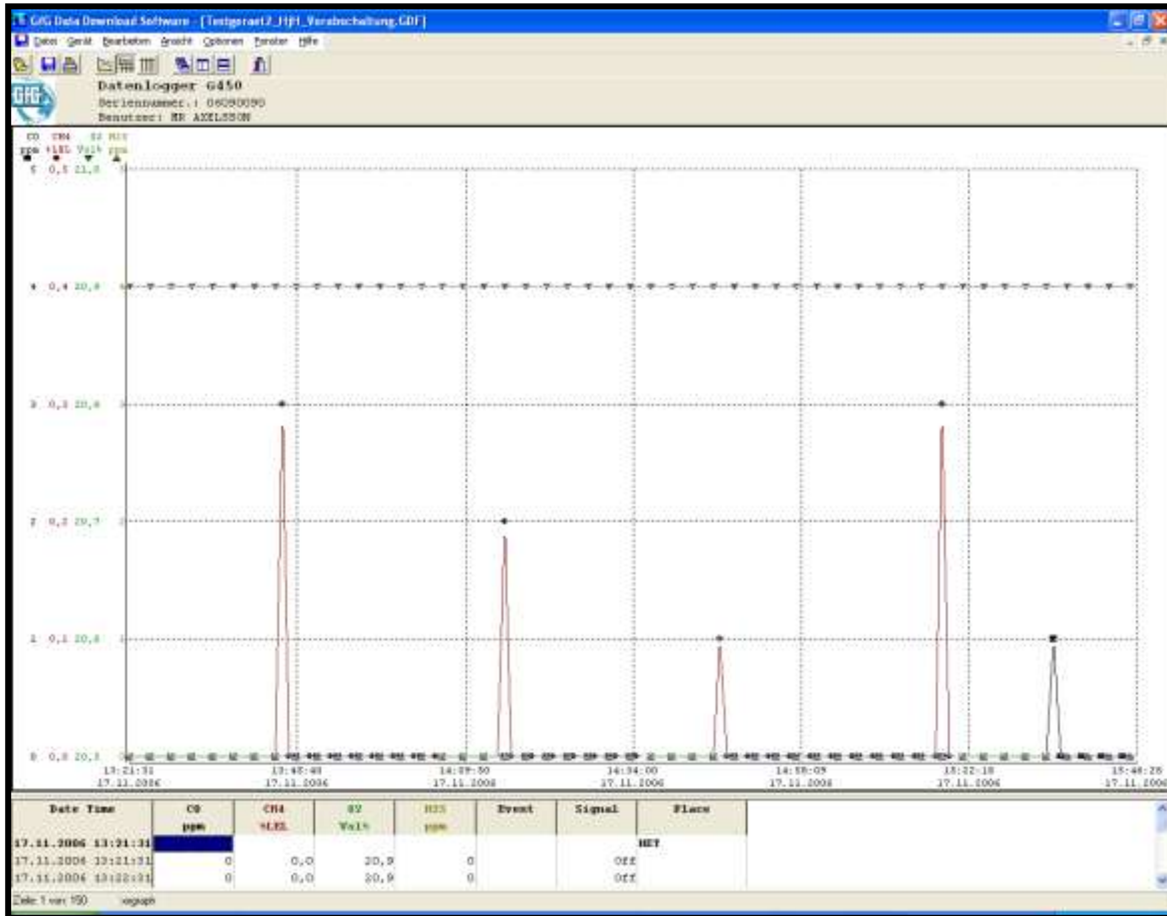


"Smart" Battery Chargers

- *Some rechargeable batteries (especially NiCd) can be damaged or lose capacity by overcharging*
- *Many users refer to this loss of capacity as "developing a memory"*
- *Allowing battery to completely discharge can also cause irreversible harm*
- *"Memory" effect really due to heating of the battery cells during prolonged overcharging*
- *Damaged battery pack may only provide a few minutes of power instead of normal hours of continuous operation*
- *"Smart" battery chargers minimize this type of damage*
  - *Initial phase of charging cycle "fast"*
  - *When charging complete convert to "trickle" charging mode*

Datalogging vs. Non-datalogging

- ***Datalogging AND Event Logging standard with G450 and G850 detectors***



GfG Instrumentation

Make sure you have the needed accessories !

- ***Charger?***
- ***Calibration gas and regulator?***
- ***Sample draw kit?***
- ***Datalogging kit?***
- ***Carrying case?***

Warranty

- ***Make sure to verify coverage <u>before</u> purchasing an instrument!***
- ***In the attached warranty:***
  - ***Limited lifetime warranty on complete instrument applies to components and assemblies that are not consumed or degraded in normal operation***
  - ***Sensors have separately identified warranty period: 3-year warranty on O2, LEL, CO, H2S and COSH sensors***
  - ***One-year warranty on rechargeable NiMH battery pack and filters***

GfG Instrumentation

1194 Oak Valley Drive, Suite 20 • Ann Arbor, MI 48108 • US/Canada: (800) 959-0329 • Fax: (734) 769-1888

Portable Gas Detection Warranty

GfG Instrumentation warrants our products to be free from defects in material and workmanship when used for their intended purpose, and agrees to remedy any such defect or to furnish a new part (at the option of GfG Instrumentation) in exchange for any part of any product that we manufacture that under normal use is found to be defective; provided that the product is returned, by the purchaser, to GfG's factory, intact, for our examination, with all transportation costs prepaid, and provided that such examination reveals, in our judgment, that it is defective.

This warranty does not extend to any products that have been subjected to misuse, neglect, accident, or unauthorized modifications; nor does it extend to products used contrary to the instructions furnished by us or to products that have been repaired or altered outside of our factory. No agent or reseller of GfG Instrumentation may alter the above statements.

THIS WARRANTY IS EXPRESSLY IN LIEU OF ANY AND ALL OTHER WARRANTIES AND REPRESENTATIONS, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO, THE WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE. GFG WILL NOT BE LIABLE FOR LOSS OR DAMAGE OF ANY KIND CONNECTED TO THE USE OF ITS PRODUCTS OR FAILURE OF ITS PRODUCTS TO FUNCTION OR OPERATE PROPERLY.

Instrument & Accessory Warranty Periods

Product(s)	Warranty Period
AGM C, CGM II, G333, G450, G460, G600, G750, G850, Micro III, Micro IV	Limited lifetime warranty to the original purchaser. (As long as the instrument is in service)
Battery packs and chargers, sampling pumps and other components, which by their design are consumed or depleted during normal operation, or which may require periodic replacement	One year from the date of purchase

Sensor Warranty Periods

Instrument(s)	Sensor Type	Warranty Period
AGM C, CGM II Purchased before January 1, 2007	O_2, LEL, CO, H_2S and DualTox	1 Year
AGM C, CGM II, G333, G600, G750, G850, Micro III	O_2, LEL, CO, H_2S, DualTox and COSH (CO & H_2S)	2 Years
	All Other Sensors	1 Year
G450 Purchased before November 1, 2006	O_2, LEL, CO, H_2S and COSH (CO & H_2S)	2 Years
G450, G460, Micro IV	O_2, LEL, CO, H_2S and COSH (CO & H_2S)	3 Years
	CO-H, Cl_2, ClO_2, C_2H_4O, H_2, HCN, NO_2, NO, PH_3, SO_2	2 Years
	NH_3, HF, HCl, O_3, SiH_4	1 Year
	$COCl_2$	6 Months
All Others	All	1 Year

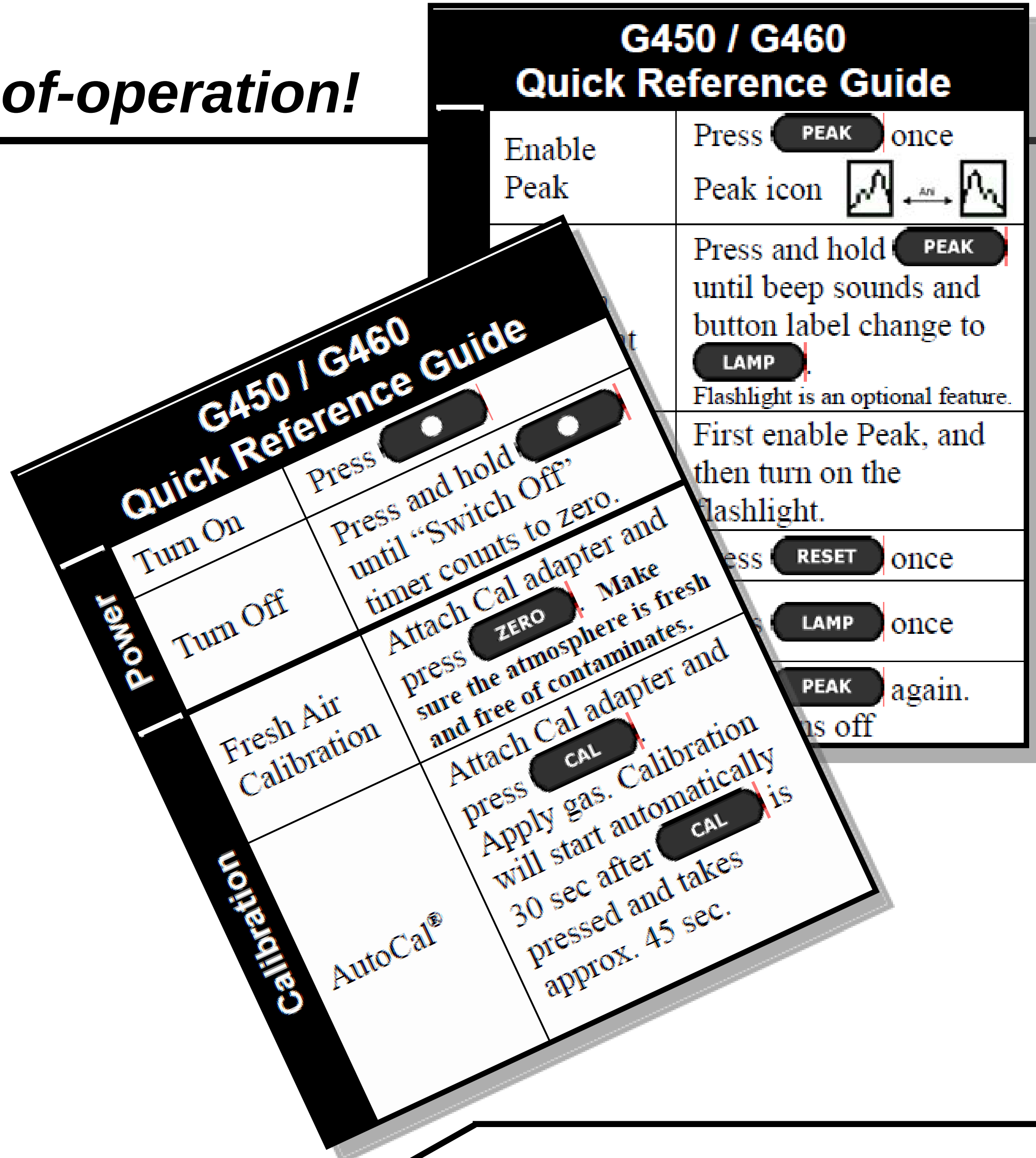
**** Damage to combustible gas sensors by acute or chronic exposure to known sensor poisons such as volatile lead (aviation gasoline additive), hydride gases such as phosphine, and volatile silicone gases emitted from silicone caulks/sealants, silicone rubber molded products, laboratory glassware greases, spray lubricants, heat transfer fluids, waxes & polishing compounds (neat or spray aerosols), mold release agents for plastics injection molding operations, waterproofing formulations, vinyl & leather preservatives, and hand lotions which may contain ingredients listed as cyclomethicone, dimethicone and polymethicone (at the discretion of GfG's Instrument Service department) void GfG Instrumentation's Standard Warranty as it applies to the replacement of combustible gas sensors.**

Revision 2008.4

GfG Instrumentation

Ease-of-operation!

- ***Basic instruments should be simple to operate***
- ***A good sign is when the manufacturer can summarize normal day-to-day procedures on a single "Quick Reference" card***



GfG Instrumentation

Alarm Setpoints and Take Action Criteria

- ***Alarm settings must be sufficiently conservative to allow self-rescue***
- ***Workers must have enough time to get to a position of safety before conditions become so hazardous that the ability to self-rescue is impaired!***

Alarm Setpoints

- ***Should be determined as function of :***
  - ***Potential hazards***
  - ***Nature of job being performed***
  - ***Environment being monitored***
  - ***Regulatory requirements***
  - ***Use "factory default" settings only if appropriate!***

Example of typical default setpoint

- ***OSHA 1910.146 specifies 10% LEL as the concentration at which the atmosphere is hazardous***
  - ***Most manufacturers use 10% LEL as the "default" alarm setting***
  - ***This is actually the maximum concentration to which the alarm may be permissibly set***
  - ***Watch out for jobs and environments which require a more conservative alarm setting***
  - ***If there is the slightest doubt use a more conservative setting!***

Alarm Settings Under "Alternate" Entry Procedures

- ***In the Preamble to 1910.146 "Permit Confined Spaces" the "safe for entry" level is 50% of the flammable or toxic substance that would otherwise constitute a hazardous atmosphere***
  - ***LEL = 5%***
  - ***Toxic gas = 1/2 PEL***

Alarm Setpoints

- ***Take action criteria should be subject to modification as function of job, circumstances, and/or other special conditions***
- ***Be alert to changes in the job or environment which may require changes in monitoring procedures!***

Regulatory Requirements

- ***OSHA 1910.146 "Permit-required confined spaces"***
- ***OSHA CPL 2.100 "Application of the Permit-Required Confined Spaces (PRCS) Standards, 29 CFR 1910.146"***
- ***1915 Subpart b "Confined and Enclosed Spaces and Other Dangerous Atmospheres in Shipyard Employment"***

Requirements for use of Confined Space Gas Detectors

- ***Use of gas detectors in hazard assessment***
- ***Use of gas detectors in non-permit spaces***
- ***Use of gas detectors in permit spaces which have been reclassified as non-permit spaces***
- ***Use of gas detectors in permit-required confined spaces (per 1910.146)***

- *“Pick-hole” sampling*
- *Pre-ventilation*
- *Sampling during initial (purge) ventilation*
- *Final pre-entry*
- *Monitor continuously while entry underway!*

Sample at all vertical levels!

- ***Atmosphere tested (at least) a distance of approximately 4 feet (1.22 m) in the direction of travel and to each side***

1910.146 Appendix E: “Sewer System Entry”

- *Major points:*
  - *Sewer workers' usual work environment is a permit space*
  - *Because isolation not complete, always potential for atmosphere to become suddenly and unpredictably lethal*
  - *Testing instrument should be carried by the entrant while in the sewer to warn of any deterioration*
  - *Atmospheric monitoring equipment must calibrated according to the manufacturer's instructions*

GfG Instrumentation

Broad range vs. substance specific sensors in sewer entry per Appendix E

- *Broad range best suited for initial use where actual or potential contaminants have not been identified*
- *However, such sensors only indicate that a hazardous threshold of a class of chemicals has been exceeded.*
- *Therefore, substance-specific best suited for use where actual and potential contaminants have been identified.*
- *However, sewers may change unpredictably, and substance-specific devices may not detect new potentially lethal hazards*

GfG Instrumentation

Broad Range vs. Substance Specific Sensors in Sewer Entry

- *OSHA emphasizes it's up to the employer to decide, based on knowledge and experience, what the best type of testing instrument may be for any specific entry operation.*

- ***Verify accuracy on a regular basis is to guard against any unexpected loss of sensitivity***
- ***Document!***

GfG Instrumentation

Mandatory to use a "calibrated" instrument maintained according to "manufacturer requirements"

- *1910.146(c)(5)(ii)(C):*
  - *Before an employee enters the space, the internal atmosphere shall be tested, with a calibrated direct-reading instrument*
  - *What does OSHA accept as a "calibrated" direct reading instrument?*
    - *A testing instrument maintained and calibrated in accordance with the manufacturer's recommendations*
    - *The best way for an employer to verify calibration is through documentation*

GfG Instrumentation

Why do instruments need to be tested and / or calibrated?

- *The response of gas detecting sensors can change over the life of the sensor*
- *The changes may be sudden, or can be gradual*
- *Substances or conditions present in the atmosphere can have an adverse effect on the sensors*
- *Different types of sensors have different constraints and conditions which can lead to loss of sensitivity or failure*
- *Important to know how sensors detect gas to understand conditions that can lead to inaccurate readings*

Make sure the instrument has been calibrated!

- ***Follow manufacturer recommendations***
- ***"Zero" instrument in fresh air prior to use***
- ***Verify Accuracy Daily!***
- ***Functional "bump" test sufficient***
- ***Adjust "span" only if necessary***

GfG Instrumentation

Loss of sensitivity can be due to:

- *Aging or desiccation of the sensors,*
- *Mechanical damage due to dropping or immersion*
- *Exposure to sensor poisons present in the atmosphere being monitored*
- *Loss of sensitivity due to other causes*

GfG Instrumentation

- ***OSHA 1910.146 requires use of a "calibrated" instrument***
- ***This means (per OSHA CPL 2.100) that the instrument must be maintained and calibrated according to manufacturer guidelines***

Manufacturer Guidelines

- ***OSHA holds instrument users accountable to maintain, calibrate and operate their instruments according to manufacturer guidelines***

UL / CSA Product Markings

- ***Typical North American Marking:***
  - ***c-CSA-us or c-UL-us Classified as to intrinsic safety for use in Class I, Division1 Groups A, B, C, and D, and Class II Groups E, F and G Hazardous Locations***
    - ***Class I: A location where there is a danger of explosion due to the presence of a flammable gas or vapor***
    - ***Class II: A location where there is a danger of explosion due to the presence of a flammable dust***

GfG Instrumentation

Calibration Frequency

- ***The safest course of action is to expose the sensors to known concentration test gas before each day's use!***
- ***This test is very simple and takes only a few seconds to accomplish***

GfG Instrumentation

Functional “Bump” Test vs. Calibration

- ***Functional “bump” test only provides verification of sensor performance***
- ***Calibration includes adjustment***
- ***Only necessary to adjust sensor sensitivity if readings are off***
- ***Most manufacturers recommend adjustment if readings are off by more than 10% of expected values***

GfG Instrumentation

Industrial Safety Equipment Association (ISEA) Guidelines

- ***Provides procedure for lengthening the interval between calibration checks***
  - ***During period of initial use of at least 10 days in the intended atmosphere, check the response daily to be sure there is nothing in the atmosphere which is poisoning the sensor(s).***
  - ***Period of initial use must be of sufficient duration to ensure that the sensors are exposed to all conditions which might have an adverse effect on the sensors.***

GfG Instrumentation

Industrial Safety Equipment Association (ISEA) Guidelines

- ***If these tests demonstrate that it is not necessary to make adjustments, the time between checks may be lengthened***
- ***This interval should not be lengthened beyond thirty days***
- ***History of the instrument should be tracked or logged***

GfG Instrumentation

Industrial Safety Equipment Association (ISEA) guidelines

- *Any conditions, incidents, or exposure to contaminants which might have an adverse effect on the sensors should trigger immediate re-verification before further use*
- *Any changes in the work being done, or environment in which the instrument is being used should trigger re-verification by means of daily checking that it is safe to lengthen the interval between calibration checks*

GfG Instrumentation

Conditions which should trigger immediate re-verification of calibration

- ***If there is any doubt at any time as to the accuracy of the sensors, verify the calibration of the sensors by exposing them to known concentration test gas before further use!***

Don’t be afraid of calibration!

- ***Modern designs make calibration easy and automatic***
- ***Keep the Calibration Materials With the Instrument!***
  - ***All-In-One Calibration Mixtures Make Functional Testing Easy!***

GfG Instrumentation

Is the concentration of gas used to calibrate instruments dangerous?

Not at all!

Consider the concentration if you leaked an entire cylinder of CO cal gas into the interior space of a typical passenger van

Approximate interior volume of Honda Odyssey EX-L = 300 cubic feet

Typical cal gas cylinder holds 34 liters = 1.2 cubic feet @ 50 ppm CO

1.2 cubic feet = 0.4% of the volume of the entire vehicle

50 ppm X .004 = concentration in vehicle = 0.2 ppm CO

GfG Instrumentation

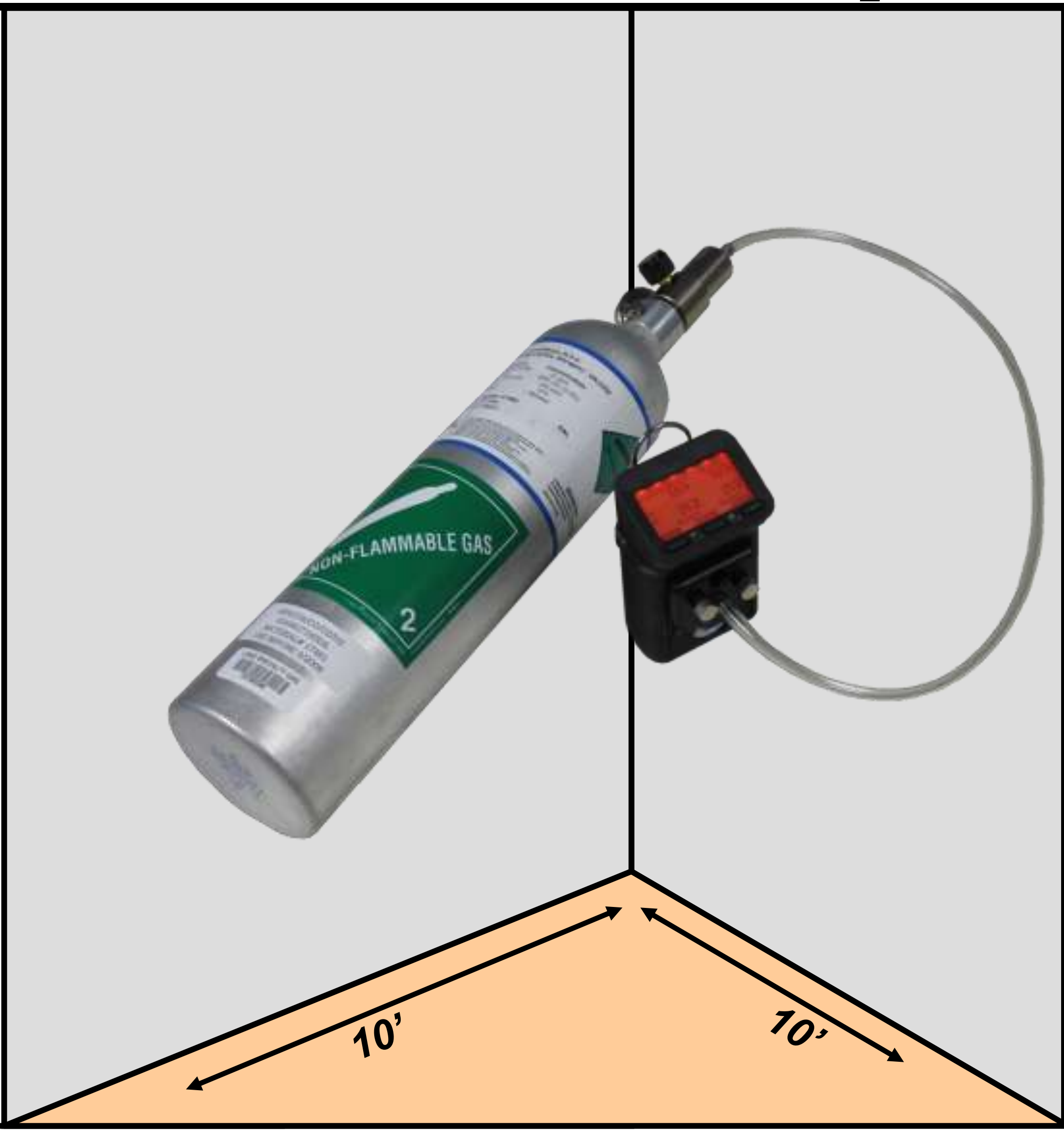
What about a cylinder that contains 25 ppm H_2S?

34 liters = 1.2 cubic feet @ 25 ppm H_2S

10 X 10 X 10 room = 1,000 cubic feet

1.2 cubic feet = 0.12% of the volume of the entire room

25 ppm X .0012 = concentration in room = 0.03 ppm H_2S



What about a cylinder that contains 25 ppm H2S?

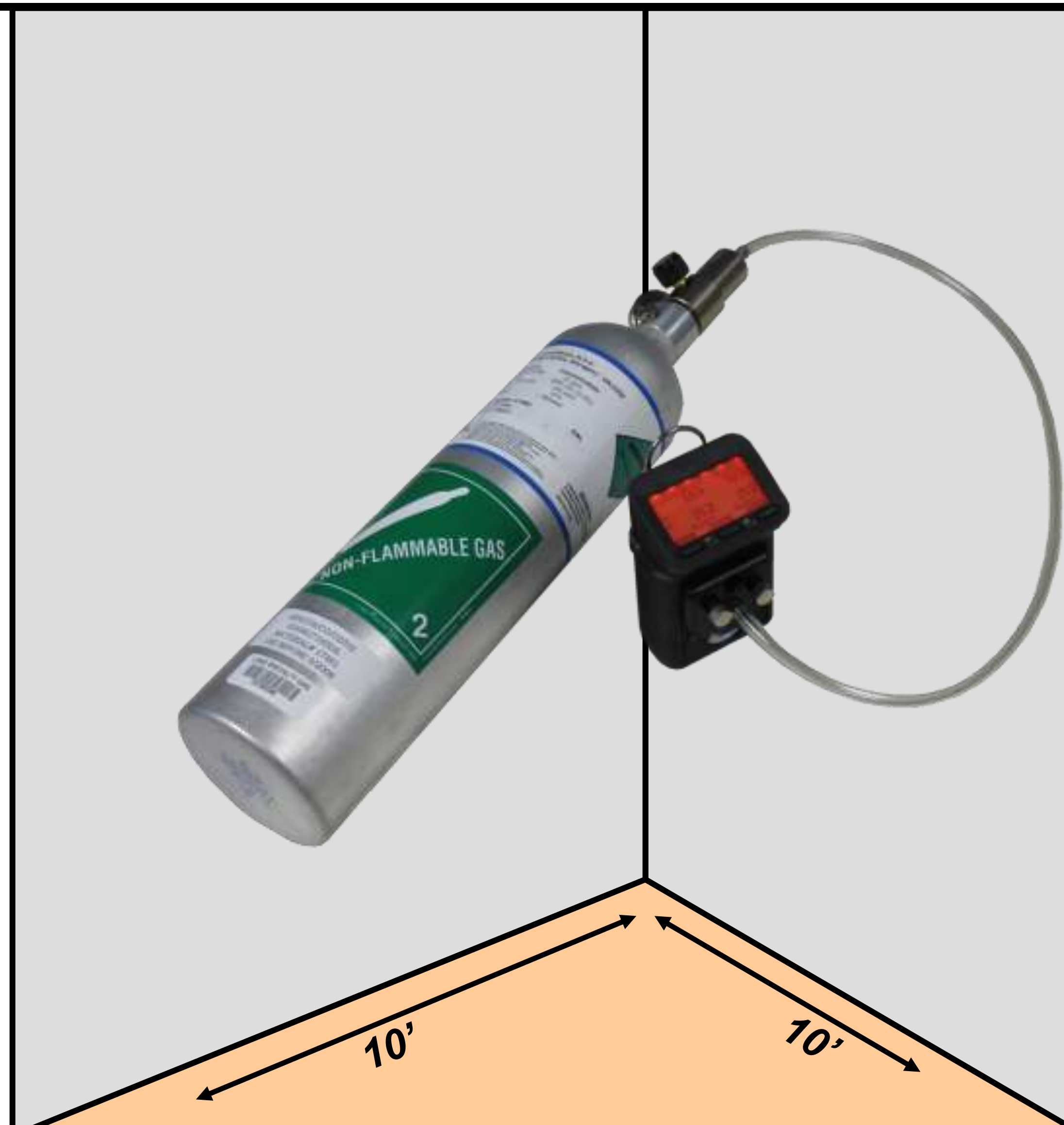
34 liters @ 25 ppm H_2S

3m X 3m X 3m room = 27 cubic meters

27 cubic meters = 27,000 liters

34 liters = 0.13% of the volume of the entire room

25 ppm X .0013 = concentration in room = 0.0325 ppm H_2S



Record Keeping

- ***Documentation is critical!***
- ***Without good records you cannot defend or explain your procedures***
- ***If you don't have the records to prove it was being done right -- it wasn't!***

DS400
Instrument Service Report

Date/Time	Identification	Details	Test	Sensor	Test	Zero	Gas
2009-06-01	Instrument	G450 S/N07122146 version 3.24	CAL	H2S	20PPM	PASS	PASS
08:59	Dock	DS400 S/N09053144 version 2.14	CAL	CO	200PPM	PASS	PASS
	User	LARS BOETTERN	CAL	O2	19VOL		N/A
			CAL	LEL	50LEL	PASS	PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-01	Instrument	G450 S/N09054845 version 3.24	Bump	H2S	20PPM		PASS
09:08	Dock	DS400 S/N09053144 version 2.14	Bump	CO	200PPM		PASS
	User		Bump	O2	19VOL		PASS
			Bump	LEL	50LEL		PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-01	Instrument	G450 S/N09054845 version 3.24	CAL	H2S	20PPM	PASS	PASS
09:12	Dock	DS400 S/N09053144 version 2.14	CAL	CO	200PPM	PASS	FAIL
	User		CAL	O2	19VOL		N/A
			CAL	LEL	50LEL	PASS	PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-02	Instrument	G450 S/N00000002 version 3.24	CAL	H2S	20PPM	PASS	PASS
08:52	Dock	DS400 S/N09053144 version 2.14	CAL	CO	200PPM	PASS	PASS
	User		CAL	O2	19VOL		N/A
			CAL	LEL	50LEL	PASS	PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-02	Instrument	G450 S/N09054860 version 3.24	Bump	H2S	20PPM		PASS
08:54	Dock	DS400 S/N09053144 version 2.14	Bump	CO	200PPM		PASS
	User		Bump	O2	19VOL		PASS
			Bump	LEL	50LEL		PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-02	Instrument	G450 S/N07122146 version 3.24	CAL	H2S	20PPM	PASS	PASS
09:04	Dock	DS400 S/N09053144 version 2.14	CAL	CO	200PPM	PASS	PASS
	User	LARS BOETTERN	CAL	O2	19VOL		N/A
			CAL	LEL	50LEL	PASS	PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-02	Instrument	G450 S/N08062689 version 3.23	CAL	H2S	20PPM	PASS	PASS
09:17	Dock	DS400 S/N09053144 version 2.14	CAL	CO	200PPM	PASS	PASS
	User		CAL	O2	19VOL		N/A
			CAL	LEL	50LEL	PASS	PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-02	Instrument	G450 S/N08062689 version 3.23	Bump	H2S	20PPM		PASS
09:25	Dock	DS400 S/N09053144 version 2.14	Bump	CO	200PPM		FAIL
	User		Bump	O2	19VOL		PASS
			Bump	LEL	50LEL		PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS
2009-06-02	Instrument	G450 S/N08062689 version 3.23	CAL	H2S	20PPM	PASS	PASS
09:29	Dock	DS400 S/N09053144 version 2.14	CAL	CO	200PPM	PASS	PASS
	User		CAL	O2	19VOL		N/A
			CAL	LEL	50LEL	PASS	PASS
				Audible	Alarm		PASS
				Visual	Alarm		PASS

Page 1 of 2

Atmospheric hazards are frequently invisible to human senses

- ***You don't know whether it's safe until it's been tested!***

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Questions?

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