



HA University

Gas Detection Theory and Sensor Technology

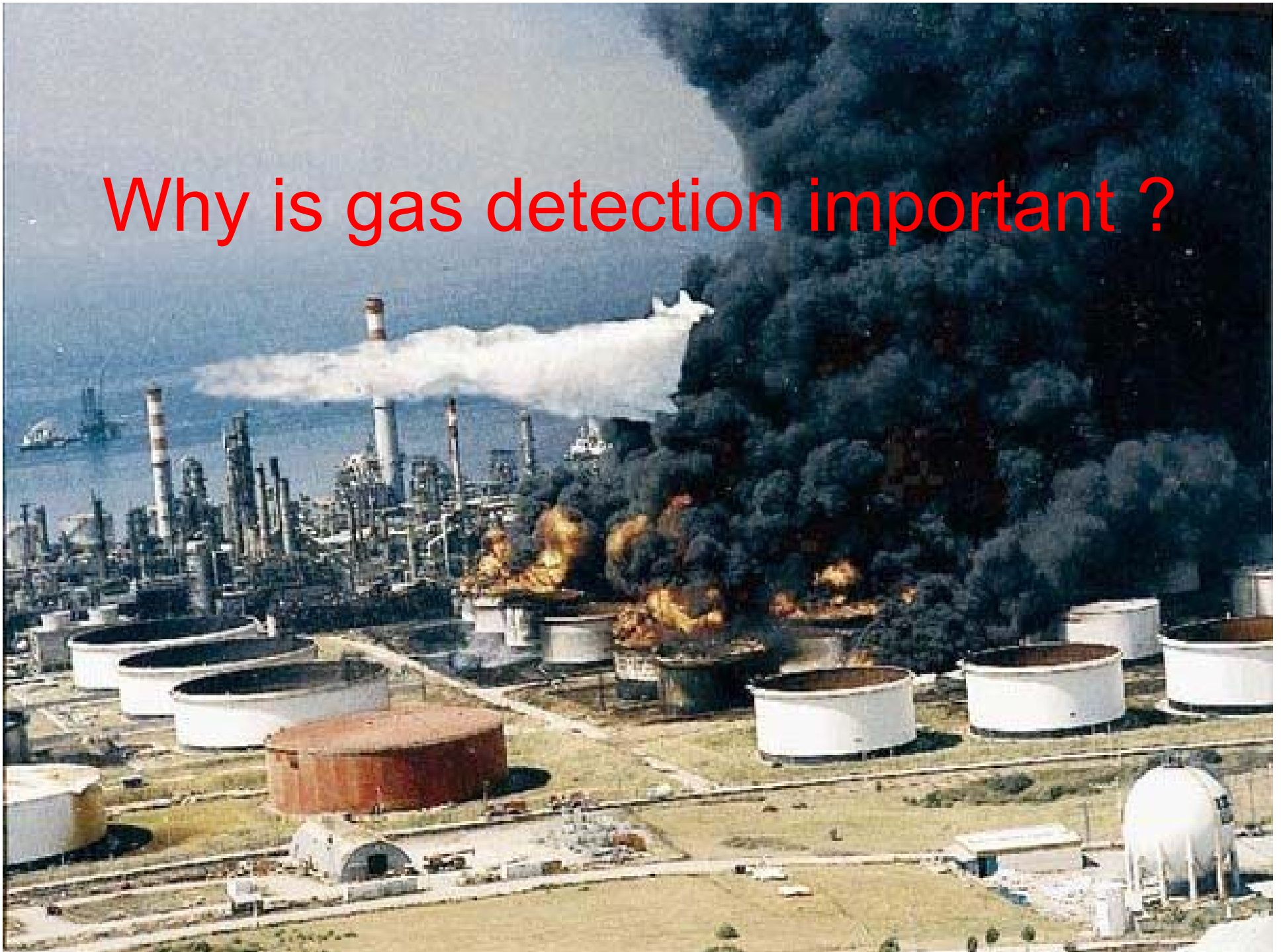
BW
Technologies
by Honeywell

Honeywell

S.P.A.C.E.R.

- Safety
 - Identify the Emergency exits
- Purpose
 - Provide product training of Honeywell Analytics/BW Technologies Gas Detection products
- Agenda
 - Discussed the core technologies surrounding Honeywell Analytics products
- Code of Conduct
 - Please turn off all Cell phones and computers (breaks will be provided through-out the secession when applicable)
- Expectations
 - Be on time
- Roles
 - Participate and ask questions

Why is gas detection important ?



Why is gas detection important ?

Honeywell

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.

Atmospheric conditions can change!

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Toxic fumes eyed in Oakville deaths of experienced duo

OAKVILLE -- Two veteran telecommunications workers died after being found unconscious in an underground Bell Canada vault yesterday morning.

The workers, employed by Wesbell Technologies, were found at the bottom of the five-metre-deep maintenance hole apparently working on cables in the Third Line and QEW area at around 10:25 a.m. Halton Sgt. Peter Payne said a co-worker found the men in the underground vault and realized they were in danger. He called emergency services. Once firefighters arrived, they had to put on air tanks to enter the vault. They found the two workers who "were overcome, likely by a deficiency in oxygen," Oakville deputy fire chief Bob Sumak said. Oakville firefighters used its rope rescue squad to rappel down the hole to reach the unconscious workers.

Firefighters and Halton EMS crews desperately tried to resuscitate the men. They were then sent to nearby Oakville Trafalgar Memorial Hospital where they were both pronounced dead. The victims, whose names weren't released, were experienced, Payne said.

One is a 33-year-old Brampton man with 15 years experience while his partner, a 52-year-old Binbrook man, has about 32 years in the field. What happened and why remains under investigation by Human Resources Development Canada Labour Program as telecommunications is governed by federal legislation.

TOXIC FUMES?

Part of the investigation will include air quality tests to determine if the two victims were overcome by toxic fumes or gases, and if there was any water in the workplace. "We understand. We feel for their families," said Jason Haffie, who was working at a nearby Oakville water treatment facility at the time of the on-the-job tragedy.

ENOUGH OXYGEN

He said he has experience working underground. "You take the precautions," he said, such as using gas meters and using fans to clear the air, or ensuring there is enough oxygen in the underground vault before entering. But whatever knocked out the two men, "they're too young to be dead," he said.

Wesbell was subcontracted by Expertech, which in turn was subcontracted by Bell Canada, to upgrade the fibre optic cables and network in the area, Expertech spokesman Philip Van Leeuwen said. The work crew was performing rod and roping, a technique of fishing cable through conduits between vaults, he said.

"This is a very sad and tragic outcome," Van Leeuwen said. He said it may take a day or two for investigators to determine what happened. Van Leeuwen said there is a full health and safety protocol in place for working underground, including a call-in routine and a buddy system. He said it doesn't appear to be "a case of people being rash or not equipped."

But he said the first priority at this point is to support the victims' families and the workers who were at the site. "This is a close family," Van Leeuwen said of the workers. He said he couldn't recall the last industrial incident where someone died, so "it really hits home how dangerous these jobs are."

Top 10 Deadliest Workplace Tragedies 2010 **Honeywell**

According to COSH, the following workplace tragedies made the top 10 list for 2010:

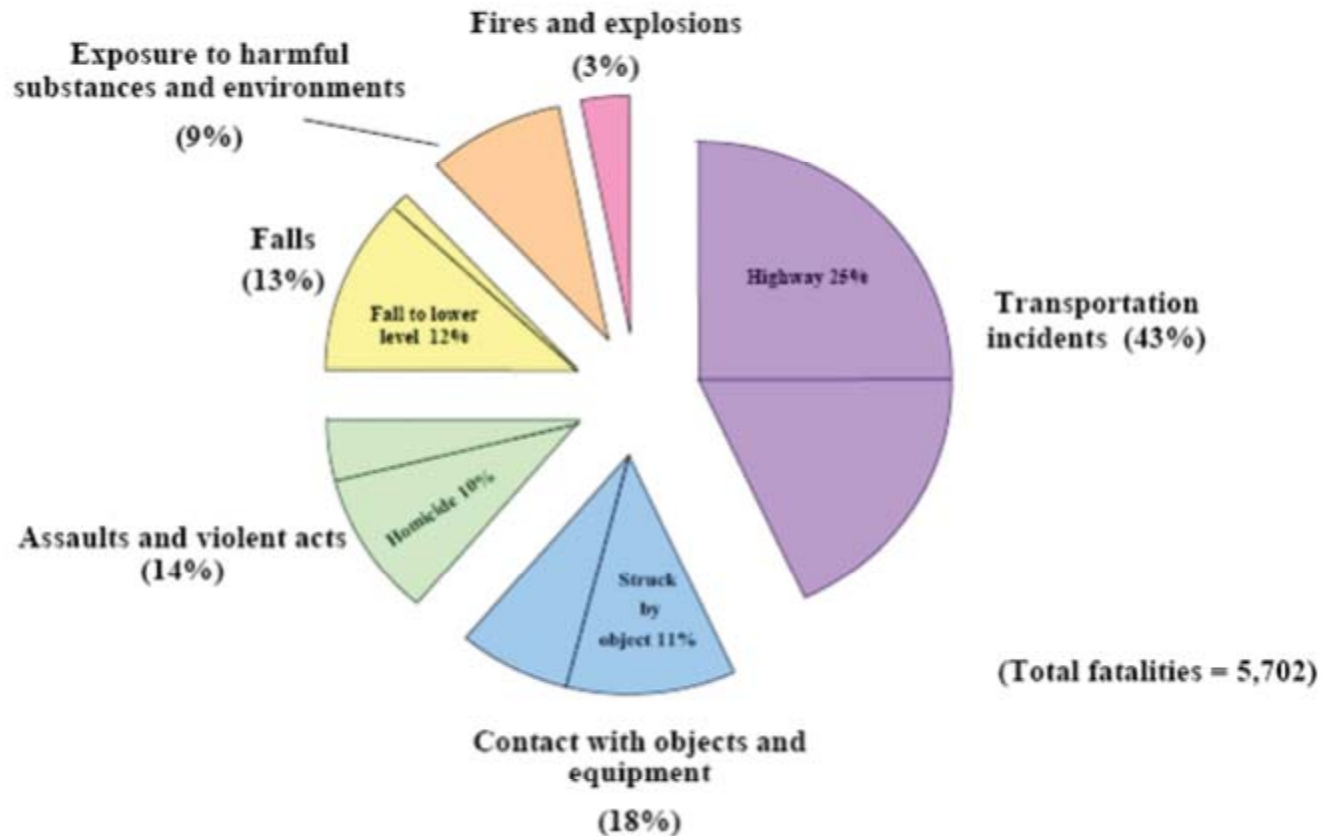
1. April 20, 2010 – Deepwater Horizon explosion. An explosion at the [Deepwater Horizon](#) offshore drilling rig in the Gulf of Mexico killed 11 workers, injured 17 others and resulted in the largest oil spill in the history of the petroleum industry. Media reports indicate that management knew key safety equipment had been compromised in earlier incidents, but chose to ignore the significance and continue operations.
2. April 5, 2010 – Upper Big Branch mine explosion, Montcoal, W.Va. An explosion at the [Upper Big Branch](#) mine in Raleigh County, W.Va., killed 29 workers. The accident represents the worst mining disaster in the U.S. since 1970. Public documents show that the mine’s owner, Massey Energy, has a long record of safety violations at the Upper Big Branch mine.
3. Feb. 7, 2010 – Kleen Energy Power Plant, Middletown, Conn. Contract workers at the [Kleen Energy](#) plant were performing a “gas blow,” a procedure that uses natural gas at very high pressure to clean pipes of debris. During the process, the gas encountered an ignition source resulting in a massive explosion, killing six workers and injuring 30 others. Following its in-depth investigation, the U.S. Chemical Safety Board (CSB) called natural gas blows “inherently unsafe practices” and called for the immediate ban on the procedure.
4. April 2, 2010 – Tesoro Refining & Marketing Company, Anacortes, Wash. A ruptured heat exchanger at the [Tesoro Refinery](#) caused an enormous explosion that rocked the plant and killed seven workers. A 6-month long investigation by Washington state OSHA personnel determined that the explosion could have been prevented if the company had carried out proper testing and maintenance of the equipment.
5. Dec. 9, 2010 – AL Solutions Plant, New Cumberland, W.Va. An explosion of undetermined origin killed two brothers working at the plant and injured a third worker. According to media accounts, the AL Solutions plant has earned a reputation as a “dangerous place to work” and the deaths of the two brothers represent the third and fourth deaths, respectively, at the plant in the last 15 years.

Top 10 Deadliest Workplace Tragedies 2010 **Honeywell**

6. March 2, 2010 – Northwest Insulation, Artesia, N.M. Four contractors were installing insulation on top of a new crude storage tank. Workers were welding when a fire ignited. Two workers were injured when they fell while a third remained on top of the tank and was fatally burned. A fourth worker was confirmed dead more than a week later. An OSHA investigation into the cause of the accident is ongoing.
7. May 5, 2010 – Amtec Corporation, Huntsville, Ala. Two workers were killed in a violent explosion at a plant that manufactures rocket fuel. Federal investigators later cited the plant's owners for six serious violations and willfully exposing workers to fire and explosive hazards without proper protection.
8. June 12, 2010 – Top Notch Cleaners, LLC, Valley, Ala. Two employees were buffing floors during the night at a mental health outpatient facility with machines that use propane gas. An employee of the outpatient facility discovered both men dead the next morning. Both the employee and the police who responded to the incident smelled gas when they entered the building where the men were working. Investigators believe carbon monoxide poisoning and inadequate ventilation contributed to the deaths.
9. July 22, 2010 – Horsehead Corp., Monaca, Pa. An explosion at the Horsehead zinc refinery, a facility with a long history of safety violations and OSHA citations, killed a pair of workers and injured two others. Although investigators have still not determined the cause of the blast, the company has a long history of safety violations.
10. July 23, 2010 – Northeast Energy Management Inc., Cheswick, Pa. Two workers engaged in arc welding were burned to death when the tank they were working on exploded, throwing their bodies approximately 60 feet away from the site of the ignition. The explosion and fire that killed the workers was the third involving Northeast Energy Management since September 2007, when one employee was severely burned in an explosion at a gas and oil well.

Why is gas detection important ?

The manner in which workplace fatalities occurred, 2005



More work-related fatalities resulted from transportation incidents than from any other event. Highway incidents alone accounted for nearly one out of every four fatal work injuries in 2005.

NOTE: Percentages may not add to totals because of rounding.
SOURCE: US Department of Labor, Bureau of Labor Statistics, Census of Fatal Occupational Injuries, 2005.

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



Meeting Basic CS Criteria

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



Permit Required Confined Spaces

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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

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Crawl Space Under a Building



Elevator Pit



- 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

Typical Confined Spaces

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

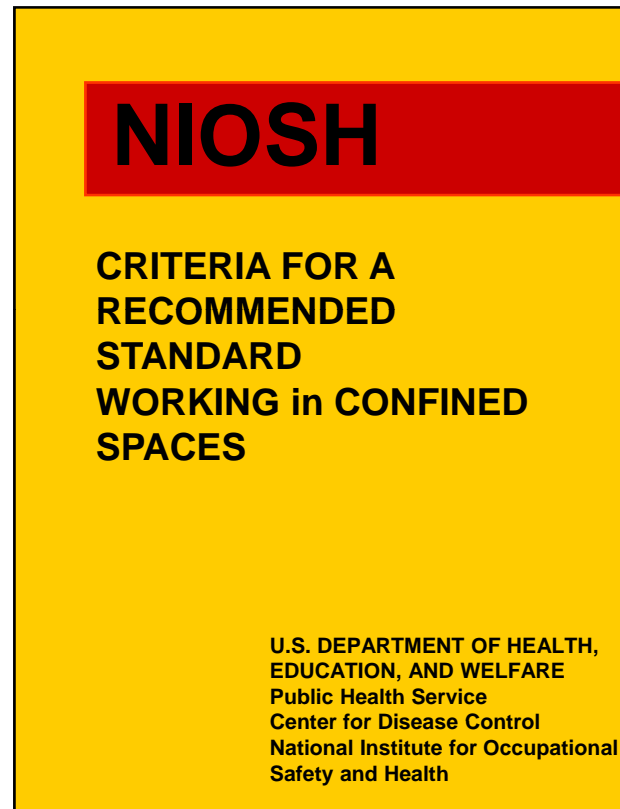


Some Confined Spaces are Open Topped

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

Confined Space Accidents

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



65% Fatalities due to Atmospheric Hazards

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Ref #	Accident Type	Events	Injuries	Deaths
1	Atmosphere 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

Confined Space Entry Requirements

- OSHA 29 CFR 1910.146 “Permit-Required Confined Spaces”



National Consensus Standards

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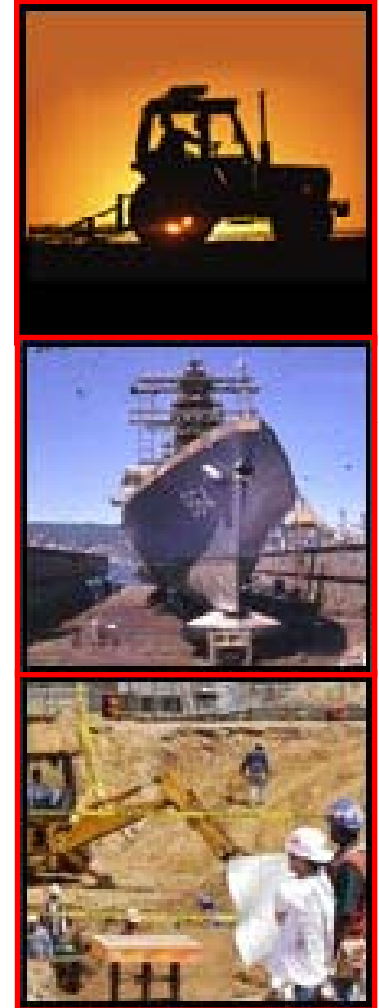
- The standards that are developed by NIOSH, ANSI, NFPA, and API are referred to as National Consensus Standards
- “National Consensus Standard” means any occupational safety and health standard that has substantial agreement on its adoption
- Unless referenced or incorporated into a governing standard,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



OSHA 29 CFR 1910.146

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- 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 (OSHA has created 29 CFR Part 1926, Confined Spaces in Construction; Proposed Rule)
 - Shipyards



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 Exceptions

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Initial construction of furnace – not covered



Subsequent repair of furnace – covered

- 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

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Employers Must:

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



1910.146 General Requirements

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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
- Ensure procedures and equipment necessary for rescue
- Protect entrants from external hazards
- Enforce established procedures

1910.146 General Requirements

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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

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Options for entry into Permit Required Confined Space (PRCS)

- Reclassification
- Alternate entry procedures
- Permit program



Reclassification as non PRCS

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

Reclassification as non PRCS

- Employer must certify that all hazards from space have been eliminated and provide that certification to all employees entering that space
- Reclassification is valid only as long as the hazard remains eliminated.

Temporary Reclassification
(From PRCS To Non-PRCS Certification)

Location of Confined Space: **Mixer in High Bay Area**

Date & time space is reclassified as a non-PRCS:
Date: **6/22/2005** Time: **4:05pm**

Certificate sections complying with this requirement may resemble the following:

Describe how hazards have been eliminated. Be detailed such as: lockout/tagout of electrical or mechanical hazards, isolation of gas lines, removal of engulfment hazards, etc.

Mixer has been locked out and no hazardous atmosphere present

I certify that all hazards have been eliminated.
Signature: **John Doe** Date: **6/22/2005** Time: **4:05pm**

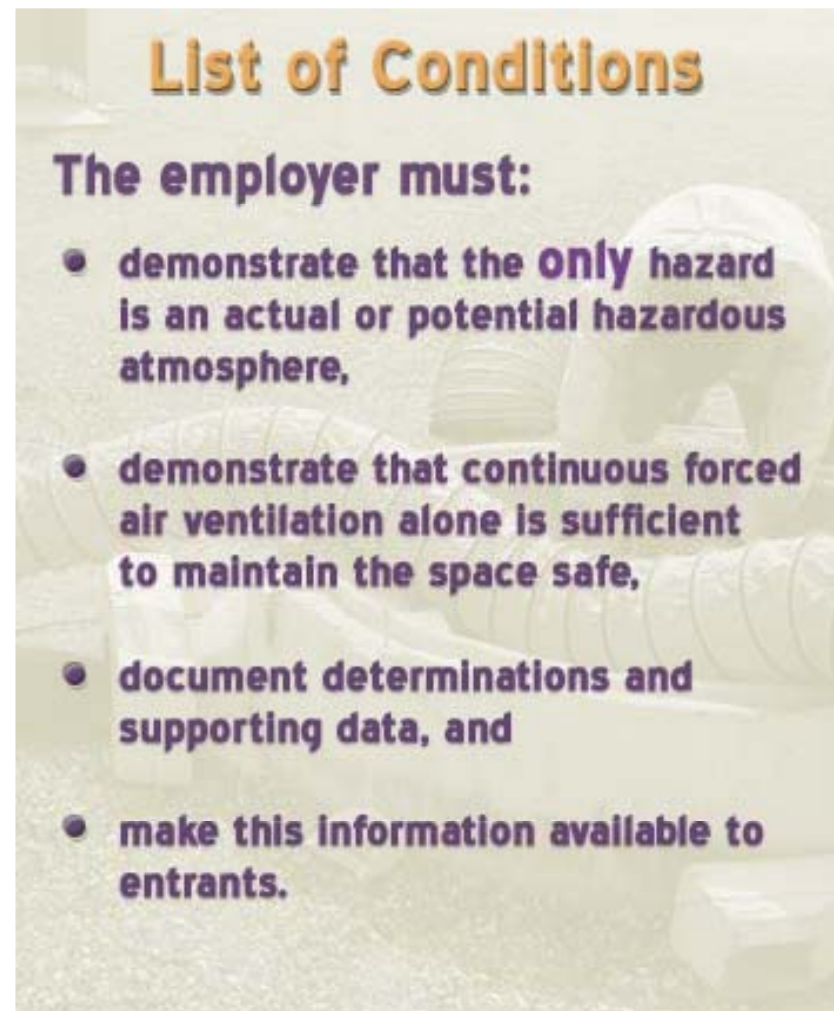
Elimination of hazardous conditions

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



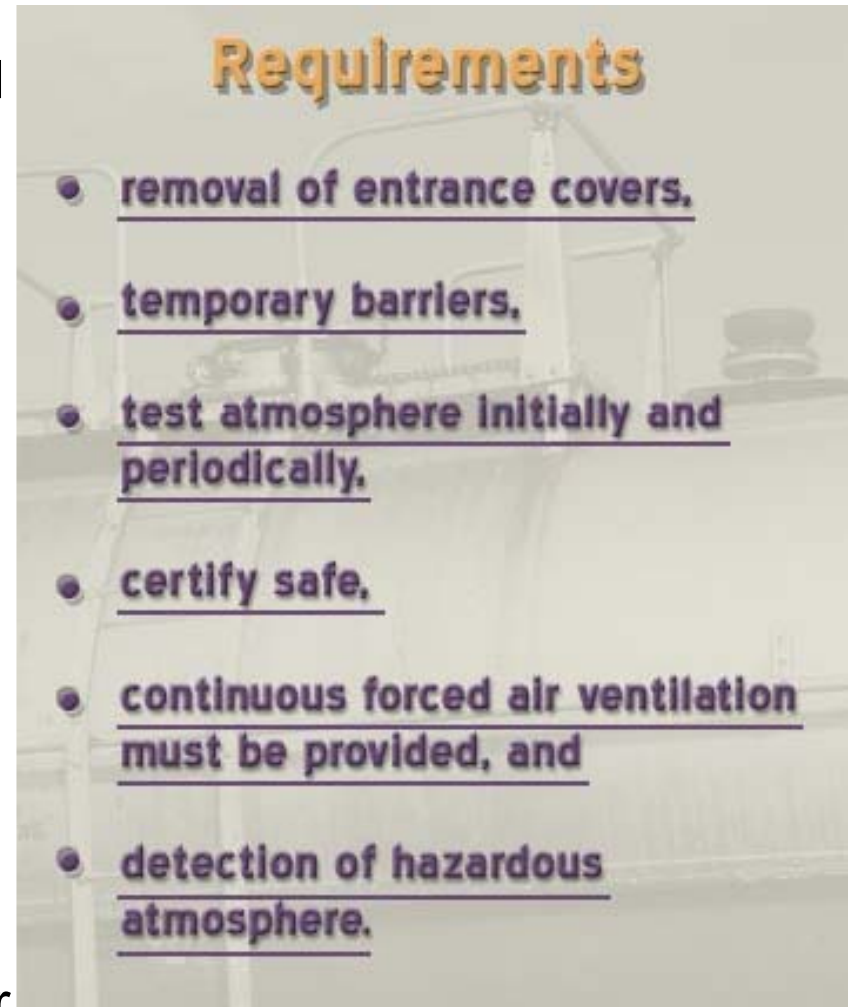
Alternate Entry Procedures

- 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



Alternate Entry Procedures

- Before an employee enters the space, the internal atmosphere shall be tested with a calibrated, direct-reading instrument, for oxygen content, for flammable gases and vapors, and for potential toxic air contaminants, in that order
- 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



Alternate Entry Procedures

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- 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



Alternate Entry Procedures

- 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



Alternate Entry Procedures

- Employer must certify 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	<u>20%</u>	20.9%	Yes <input checked="" type="checkbox"/>	No <input type="checkbox"/>
Percent LEL	<u>4%</u>	Less than 5% LEL	Yes <input checked="" type="checkbox"/>	No <input type="checkbox"/>
Carbon Monoxide	<u>10ppm</u>	Less than 25 ppm	Yes <input checked="" type="checkbox"/>	No <input type="checkbox"/>
Hydrogen sulfide	<u>3ppm</u>	Less than 5 ppm	Yes <input checked="" type="checkbox"/>	No <input type="checkbox"/>
Other: _____	_____	Less than 1/2 PEL	Yes <input type="checkbox"/>	No <input type="checkbox"/>

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

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		<i>Process Hall / SPC Mixer</i>			
PURPOSE OF ENTRY	<i>Clean Tank</i>	Date	<i>1-14-98</i>		
DEPARTMENT	<i>SWO@</i>	Time	<i>12:15</i>		
PERSON IN CHARGE OF WORK		<i>Jim Mayberry</i>			
AUTHORIZED ENTRANTS		TIME IN	TIME OUT		
<i>Jim Mayberry</i>		<i>1:45</i>	<i>3:20</i>		
<i>Jeff Berry</i>		<i>1:45</i>	<i>3:20</i>		
<i>Danny Green</i>		<i>1:45</i>	<i>3:20</i>		
<i>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.</i>					
SPECIAL REQUIREMENTS	YES	NO	Special Requirements (cont.)	YES	NO
Lockout/Tagout	<input checked="" type="checkbox"/>		Escape Harness Lifeline		<input checked="" type="checkbox"/>
Lines Broken-Capped or Blanked		<input checked="" type="checkbox"/>	Emergency Escape Unit		<input checked="" type="checkbox"/>
Purge-Flush and Vent		<input checked="" type="checkbox"/>	Fire Extinguisher	<input checked="" type="checkbox"/>	
Ventilation	<input checked="" type="checkbox"/>		Protective Clothing	<input checked="" type="checkbox"/>	
Secure Area	<input checked="" type="checkbox"/>		Hot Work		<input checked="" type="checkbox"/>
Communications Describe:	<i>N/A</i>	<input checked="" type="checkbox"/>	Respirator Type:	<i>Dust Mask</i>	<input checked="" type="checkbox"/>
ATMOSPHERIC TESTING <small>(Valid for one 8-hour turn only)</small>	P.E.L. <small>(Permissible Exposure Limit)</small>	Yes	No	Test Results	
% of Oxygen	below 19.5% or above 23%			<i>12.25</i>	
% of L.E.L.	Any % over 10		<input checked="" type="checkbox"/>	<i>19.0%</i>	
Carbon Monoxide	Above 35 ppm		<input checked="" type="checkbox"/>		
Name of Tester <i>Jim Mayberry</i> <small>Note: Continuous/periodic tests shall be established before beginning job.</small>					
INSTRUMENTS USED	NAME	TYPE	IDENT. NO.		
<i>Mini Gard III</i>		<i>air sampler</i>			
ATTENDENTS	SIGNATURE				
<i>Jeff Berry</i>	<i>Jeff Berry</i>				
<i>Danny Green</i>	<i>Danny Green</i>				
EMERGENCY RESPONSE NOTIFICATION NUMBERS:		SAFETY 1385/1382/1384			
AMBULANCE: <i>911</i>	FIRE: <i>911</i>	RESCUE: <i>911</i>			
ENTRY SUPERVISOR AUTHORIZATION <i>Jim Mayberry</i>		DATE <i>1-14-98</i>			

- 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

Emergency Response

- 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!



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

Atmospheric conditions can change!

- Work in confined spaces can produce dangerous atmospheric conditions
 - Welding
 - Painting
 - Degreasing
 - Scraping
 - Sandblasting
 - Mucking
 - Inerting



Monitor and Ventilate continuously

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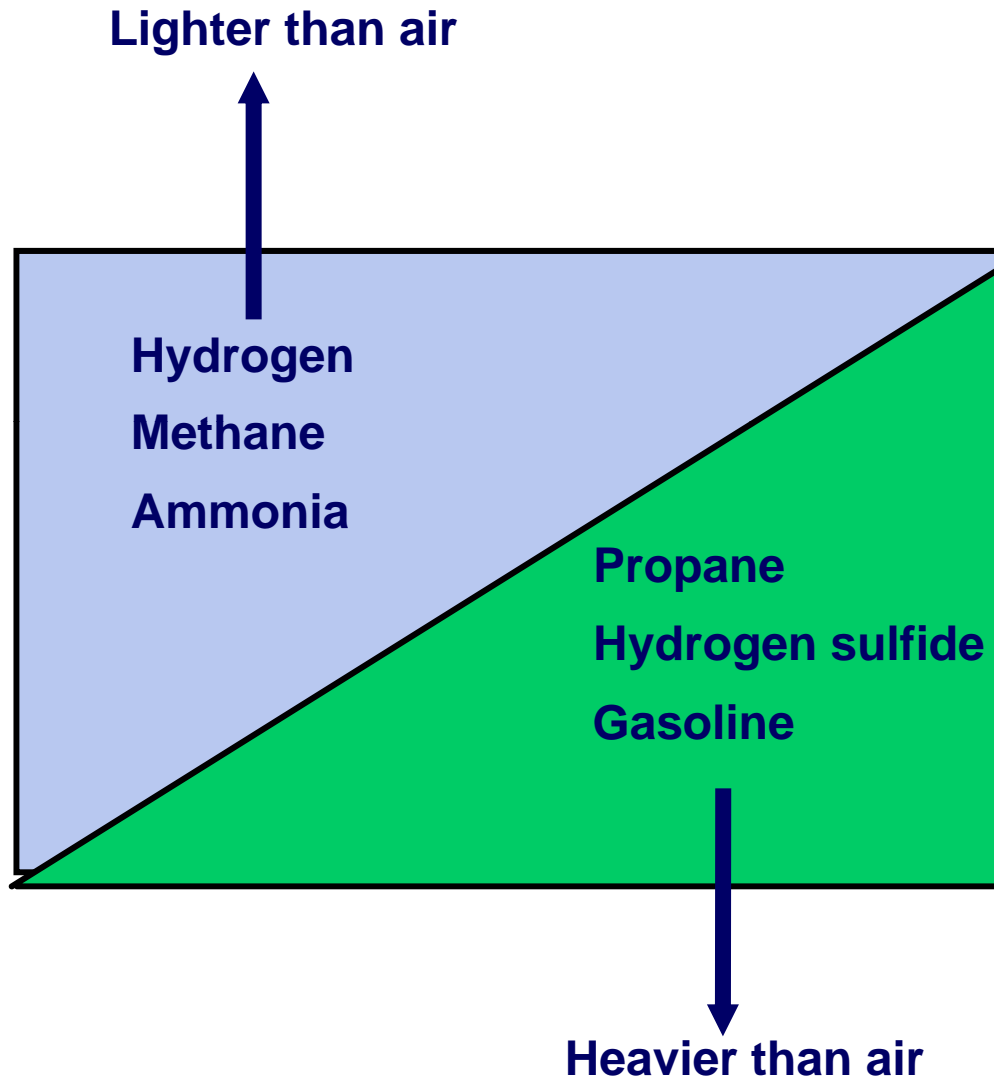
- Many accidents result from changes in the CS atmosphere which occur after the entry is initiated
- Monitoring determines the air is safe, ventilation keeps it that way
- The only way to pick up changes before they become life threatening is to monitor continuously!



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

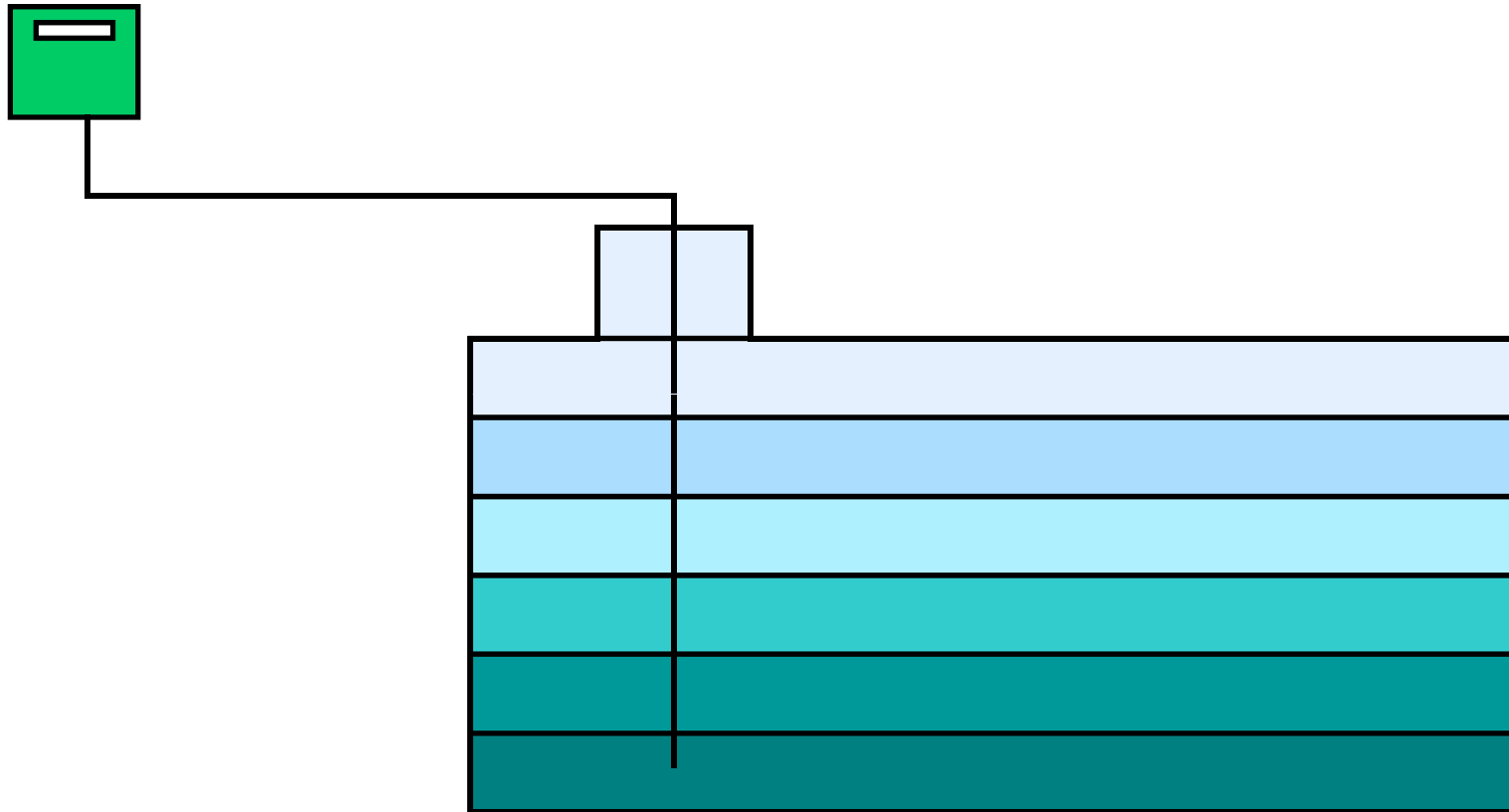
Vapor density

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

Stratification

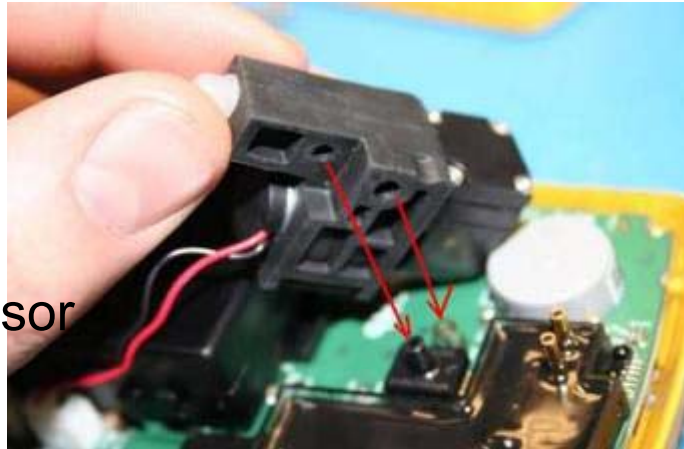


- Atmospheric hazards in confined spaces form layers
- Check all levels! Atmosphere tested (at least) a distance of approximately 4 feet (1.22 m) in the direction of travel and to each side

BW Pump options

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- The Sampler pack and M5 use Rotary Vane pumps
- The new MAX XT II uses a diaphragm pump
- The Sampler and M5 use changes in current draw to detect blocked Flow
- The MAX XT II uses a semiconductor pressure sensor



Guidelines for Remote Sampling

- It is essential to verify the integrity of the sampling train before use
- Always allow sufficient time for sample to reach sensors and then approximately 60 seconds for readings to stabilize

Instrument	Max Tubing Length	Sec/foot or pumps/foot
MAX XT II	20 m/75 feet	2 sec
Micro5	10 m/30 feet	2 sec
Sampler Pack	15 m/50 feet	2 sec
Manual Pump	How many times are you willing to squeeze?	1 squeeze/foot



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Hazard Measurement

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Miner's Canary



Japanese Waltzing Mouse



Flame Safety Lamp

Portable Products

Honeywell

World's Most Advanced Family of Gas Detection Products



GasAlertQuattro



Rig Rat



Impact Pro



GasAlertMicro5



GasAlert MaxXT II



Gas Alert MicroClip XT



GasAlert Extreme



MicroDock II

Gas Detection Acronyms

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- LEL Lower Explosive Limit (combustible gases)
- PPM Parts Per Million (toxic & VOC)
- %VOL Percent by volume (oxygen)
- VOC Volatile Organic Compounds (PID)
- PID Photo Ionization Detection (VOC)
- TWA Time Weighted Average (toxic gases)
- STEL Short Term Exposure Limit
- IP Ionization Potential & Ingress Protection
- IS rating Intrinsic Safety (UL, CSA)
- T90 Time sensor needs to reach 90% full response



What is a Gas?

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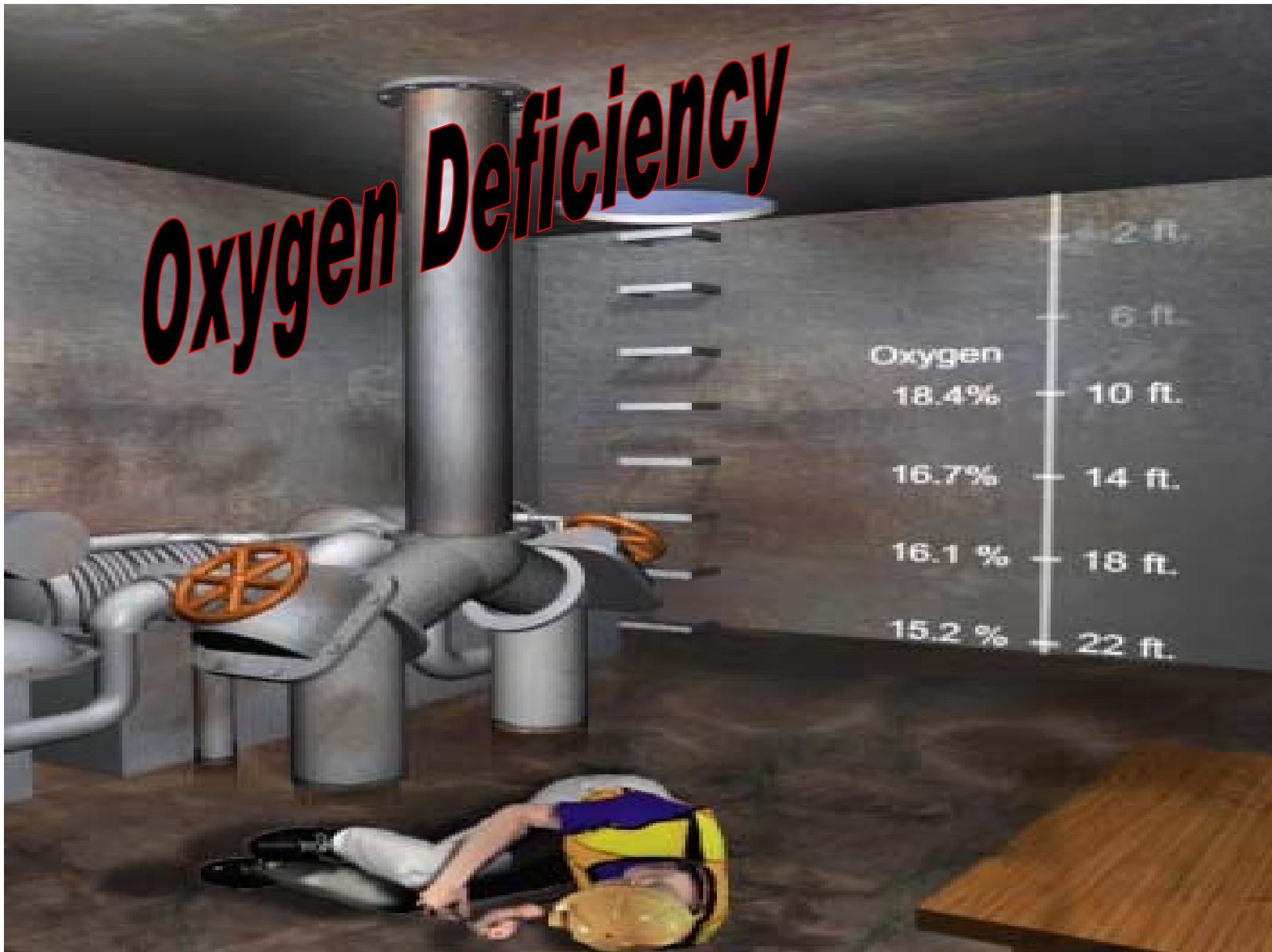
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3 basic types of atmospheric hazards

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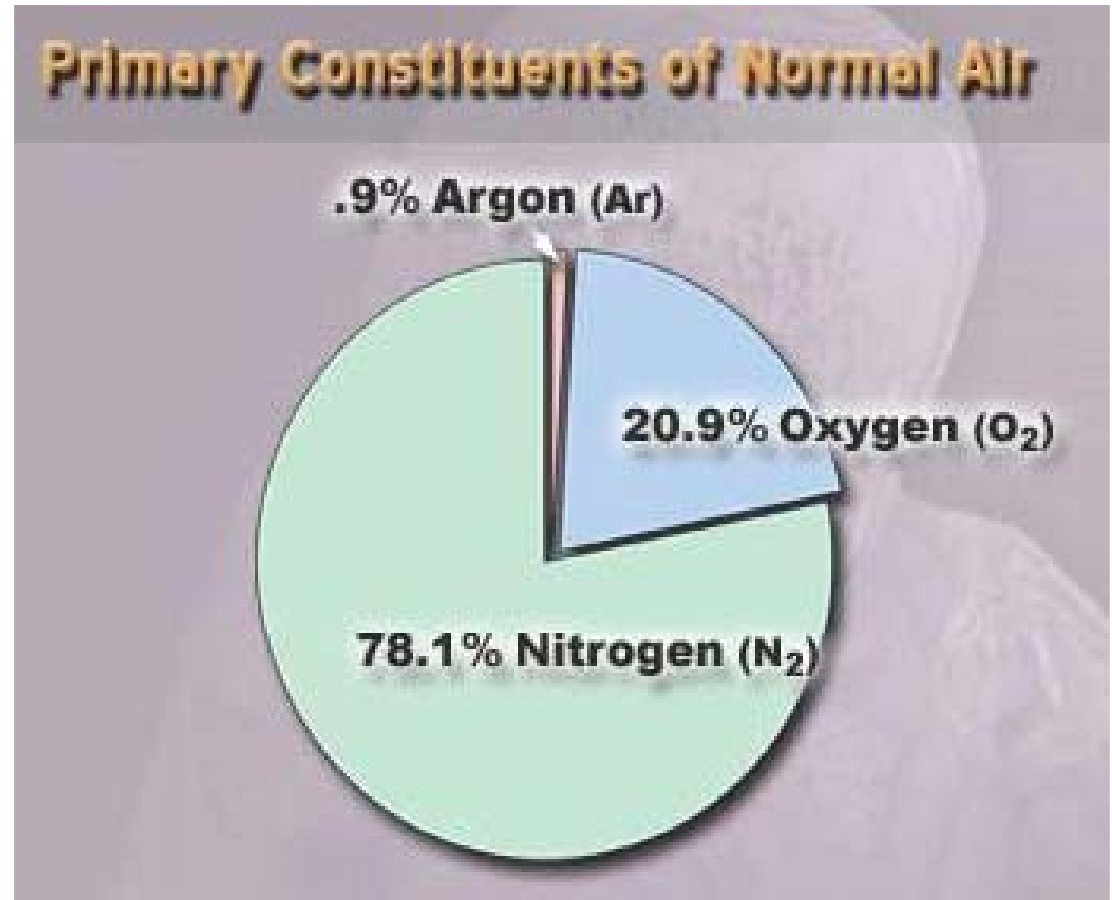
- Oxygen (deficiency and enrichment)
- Flammable gases and vapors
- Toxic contaminants

Oxygen Deficiency



Composition of fresh air

- 78.1 % Nitrogen
- 20.9 % Oxygen
- 0.9 % Argon
- 0.1 % All other gases
 - Water vapor
 - CO₂
 - Other trace gases



Oxygen Deficiency

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.

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

O₂ vs. % Vol at Varying Altitudes

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Height		Atmos. Pressure	PO ₂		Con
ft	M	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% O₂ at sea level = 18 kPa



Oxygen Deficiency

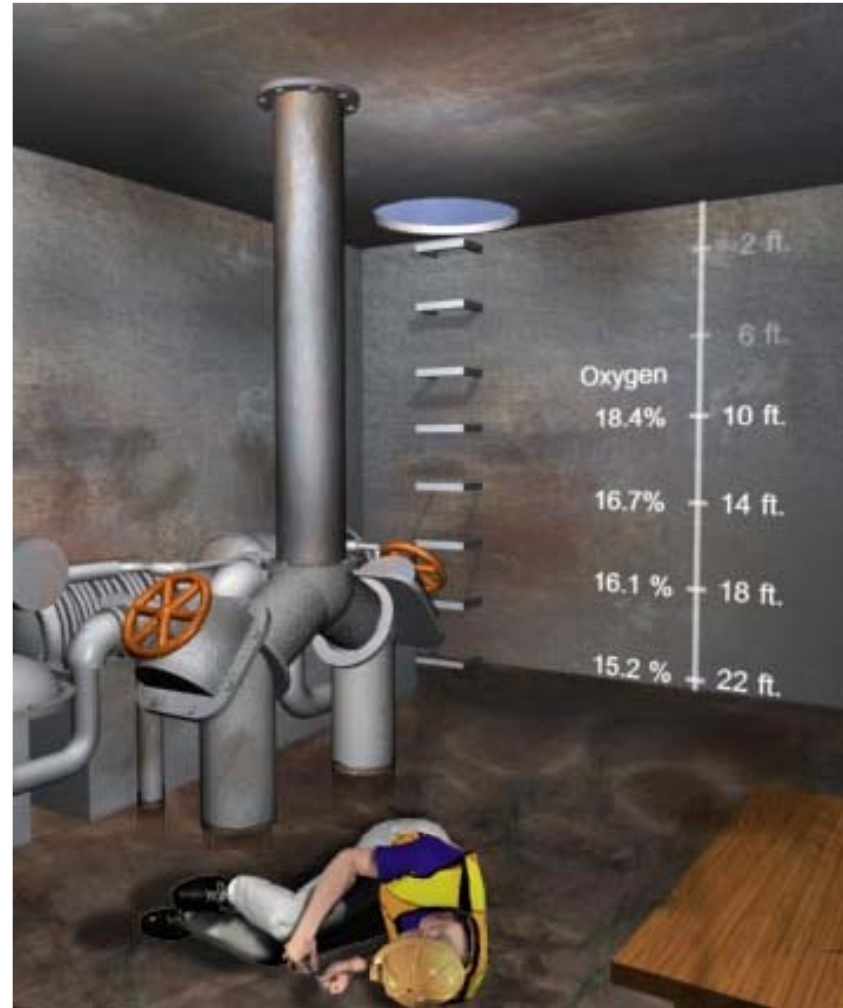
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- Occurrence associated with:
 - Confined spaces
 - Unventilated cellars
 - Sewers
 - Wells
 - Mines
 - Ship holds
 - Tanks
 - Enclosures containing inert atmospheres

Causes of Oxygen Deficiency

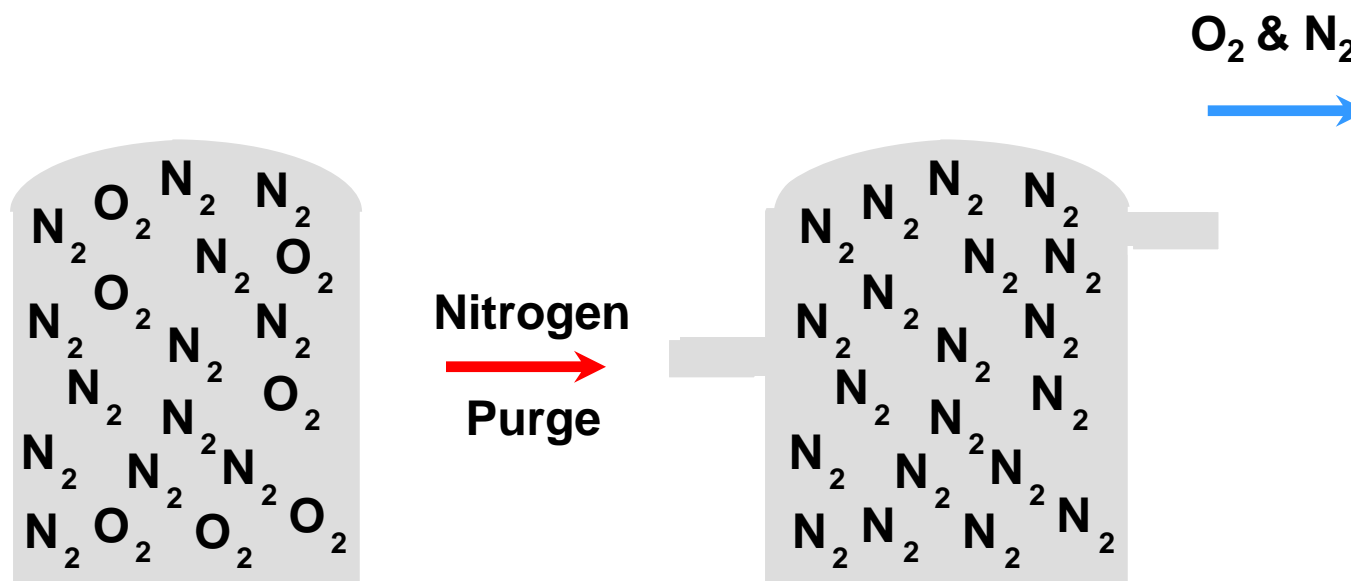
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- Displacement
- Microbial action
- Oxidation
- Combustion
- Absorption



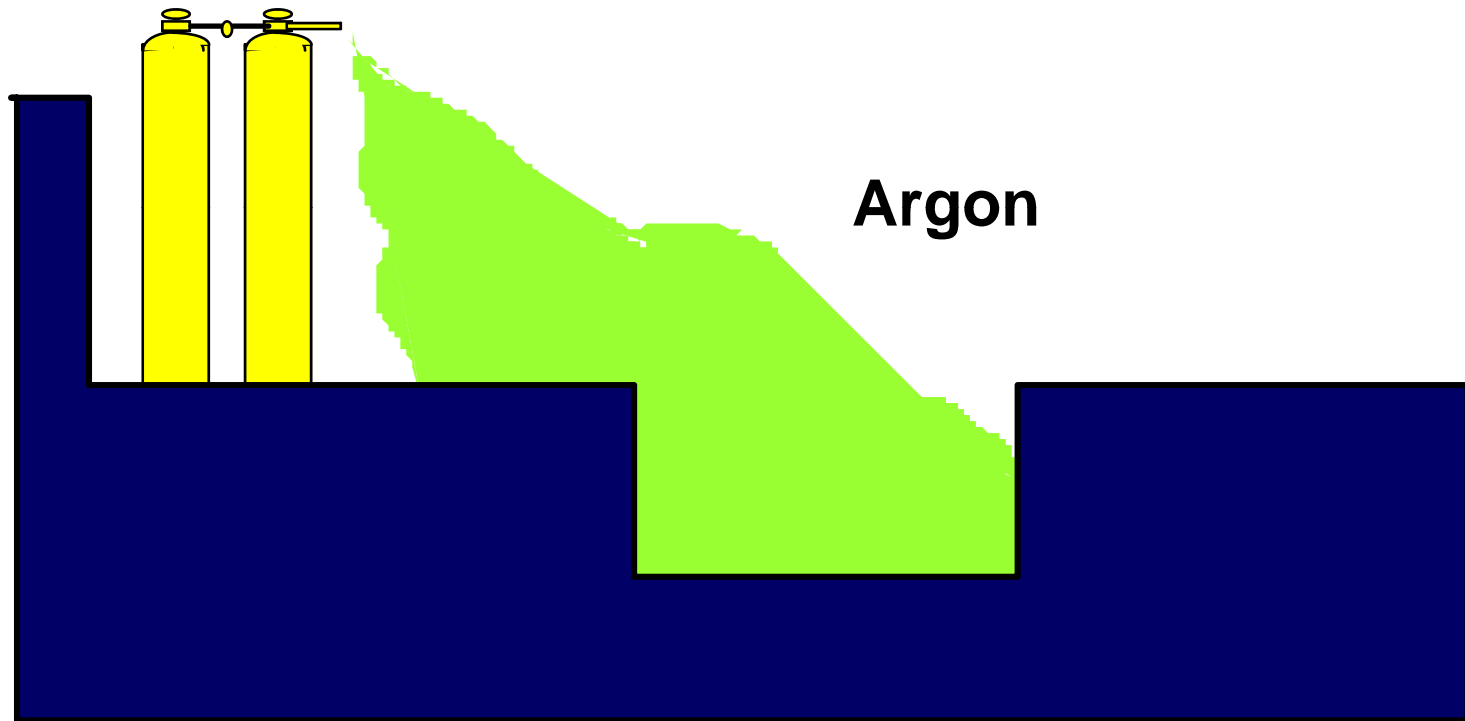
Oxygen Displacement

Enclosed Vessel



Oxygen displacement

Open topped confined space



Calculating Displacement

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- It is possible to calculate the approximate concentration of a displacing gas based upon the oxygen concentration using the following formula:

$$5.0(20.9 - \text{"O2 Reading"}) = \% \text{volume of displacing gas}$$

- Example: How much helium is present when in a displacing environment when the oxygen is reading 16.9%?

$$5.0(20.9 - 16.9) = 4$$

$$5 \times (4) = \underline{20.0\% \text{ helium}}$$

* This is an approximation

Symptoms of Oxygen Deficiency

Honeywell

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

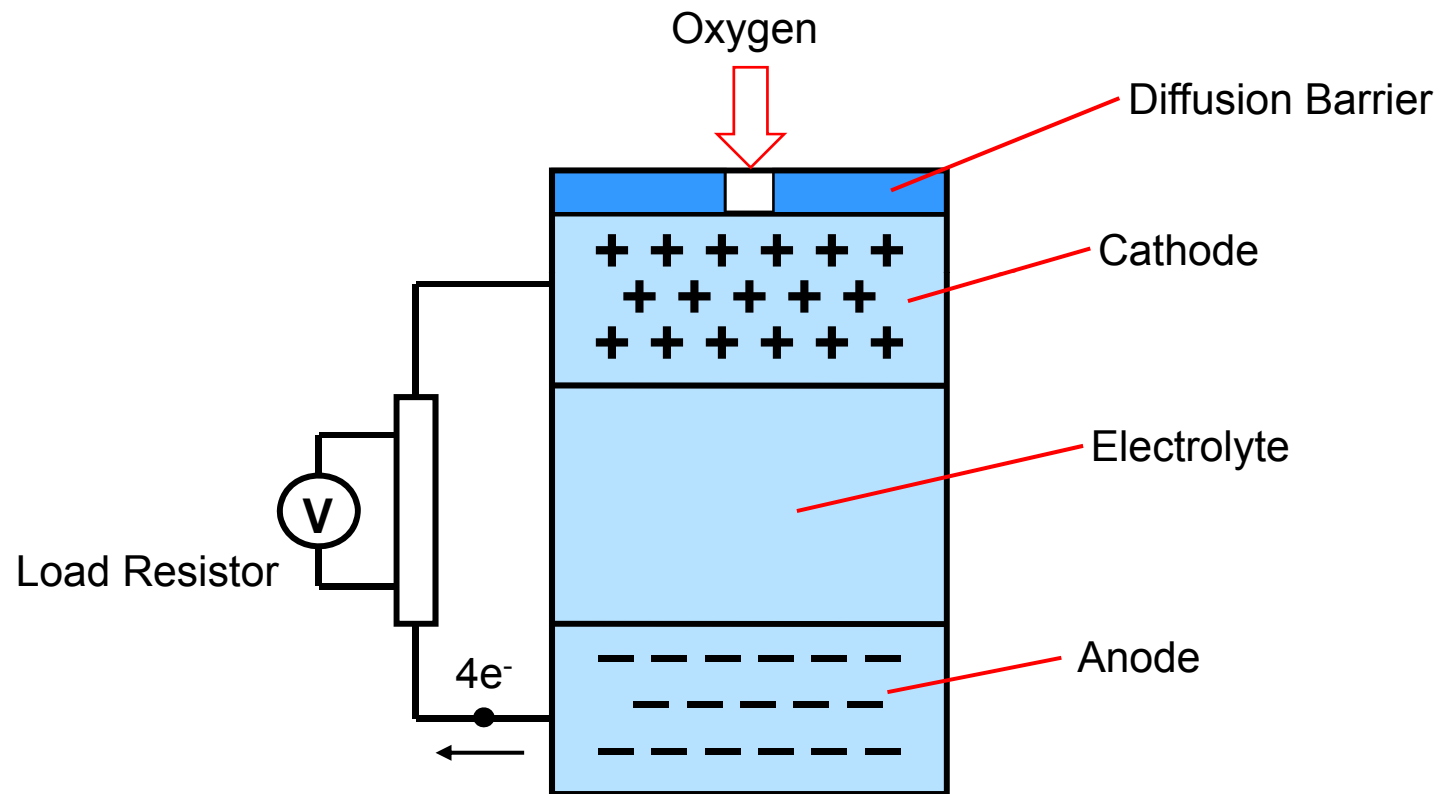
Honeywell

- Oxygen sensor performance
 - Sensor generates electrical current proportional to the O₂ concentration
 - Sensor used up over time (last approximately two years)

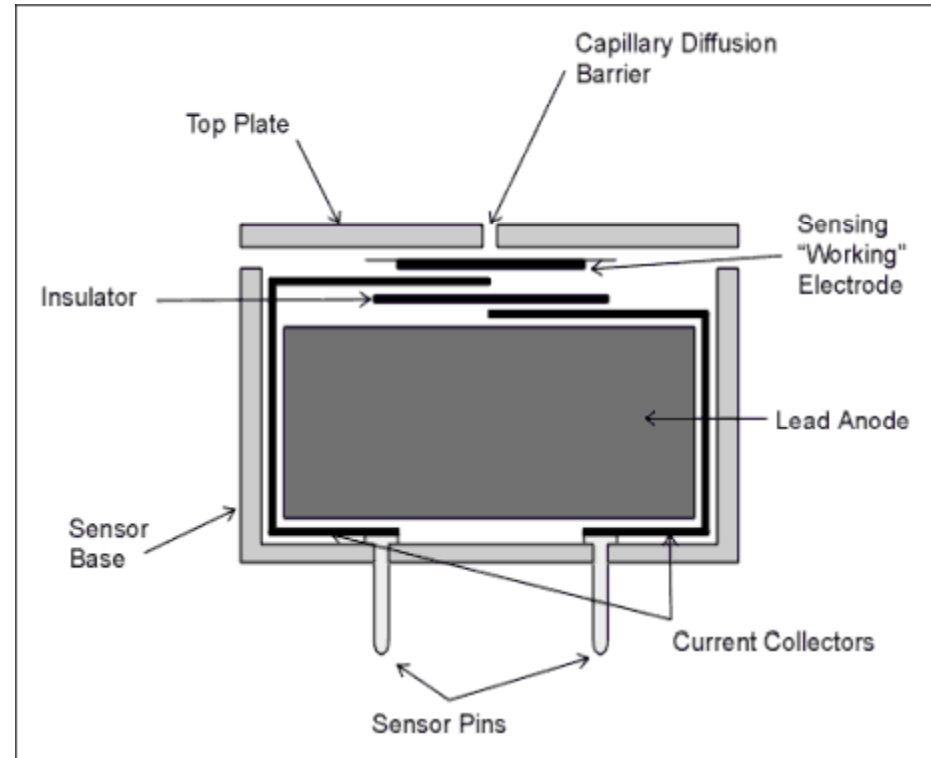
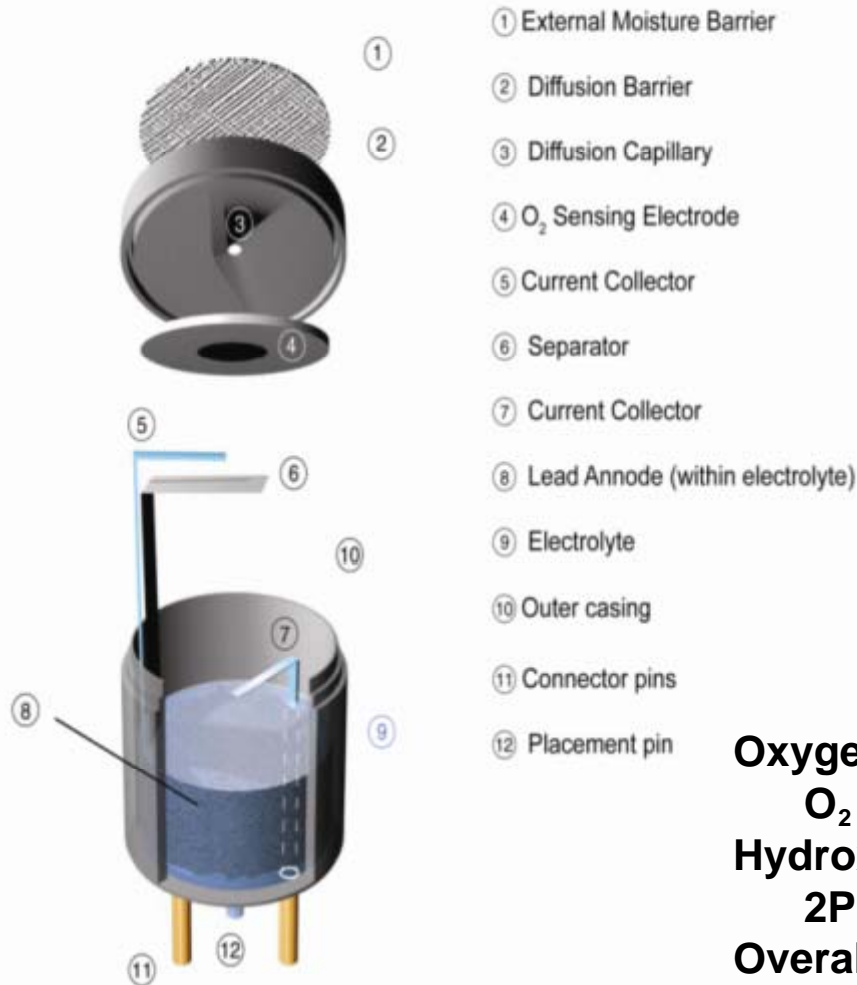


Oxygen Sensor

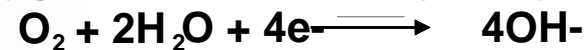
- Oxygen enters sensor through a capillary pore



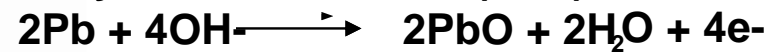
Oxygen Sensor



Oxygen is reduced to hydroxyl ions at the cathode:



Hydroxyl ions oxidize the (lead) anode:



Overall cell reaction:



Oxygen Sensor Operation

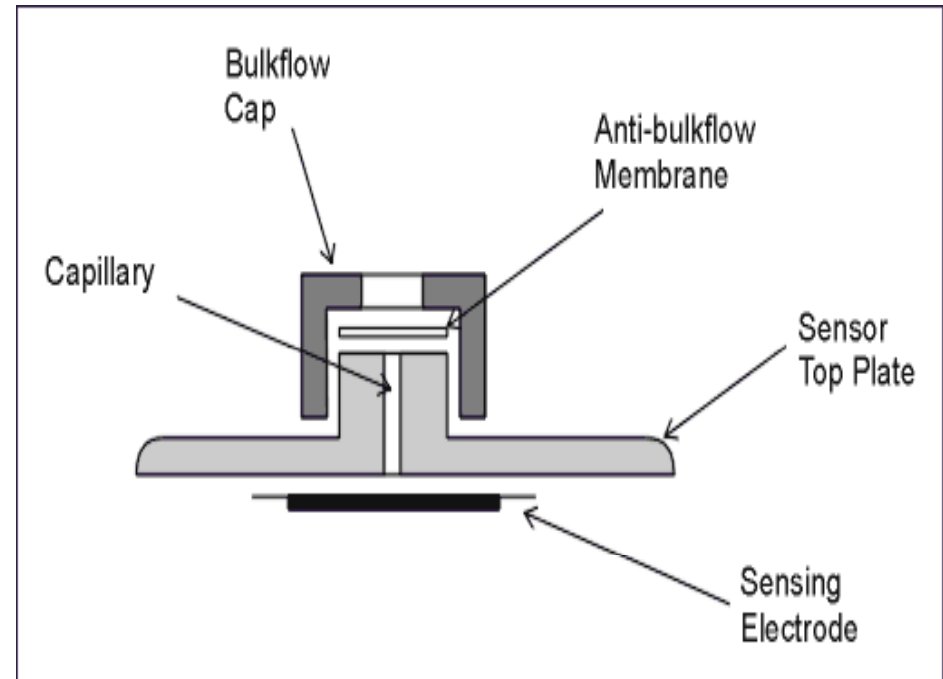
Honeywell



Capillary diffusion barrier

Honeywell

- Capillary diffusion barrier limits pressure transients, provides true percent volume readings
- When subjected to sudden pressure increase or decrease, gas is forced through the capillary barrier resulting in a current transient
- Transient quickly settles to zero once pressure pulse is complete
- City Technology sensors fitted with PTFE anti-bulkflow membrane that reduces effect of transients



Capillary Pore Benefits

Honeywell

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

O2 Sensor Failure Mechanisms

Honeywell

- Failure modes that lead to lower current output:
 - All available surface area of Pb anode converted to PbO
 - Electrolyte poisoned by exposure to contaminants:
 - High concentrations of acid gases - H₂S and CO₂
 - Solvents
 - Electrolyte leakage
 - Desiccation
 - Excessive heat and humidity
 - Blockage of capillary pore

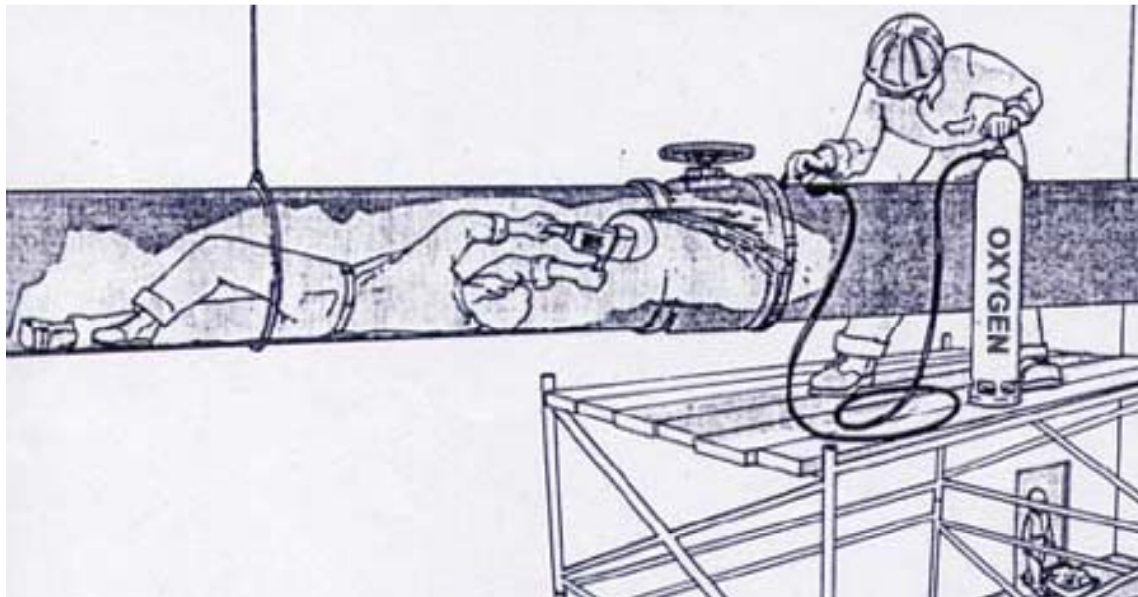
Oxygen Enrichment

Honeywell

- 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

Oxygen Enrichment

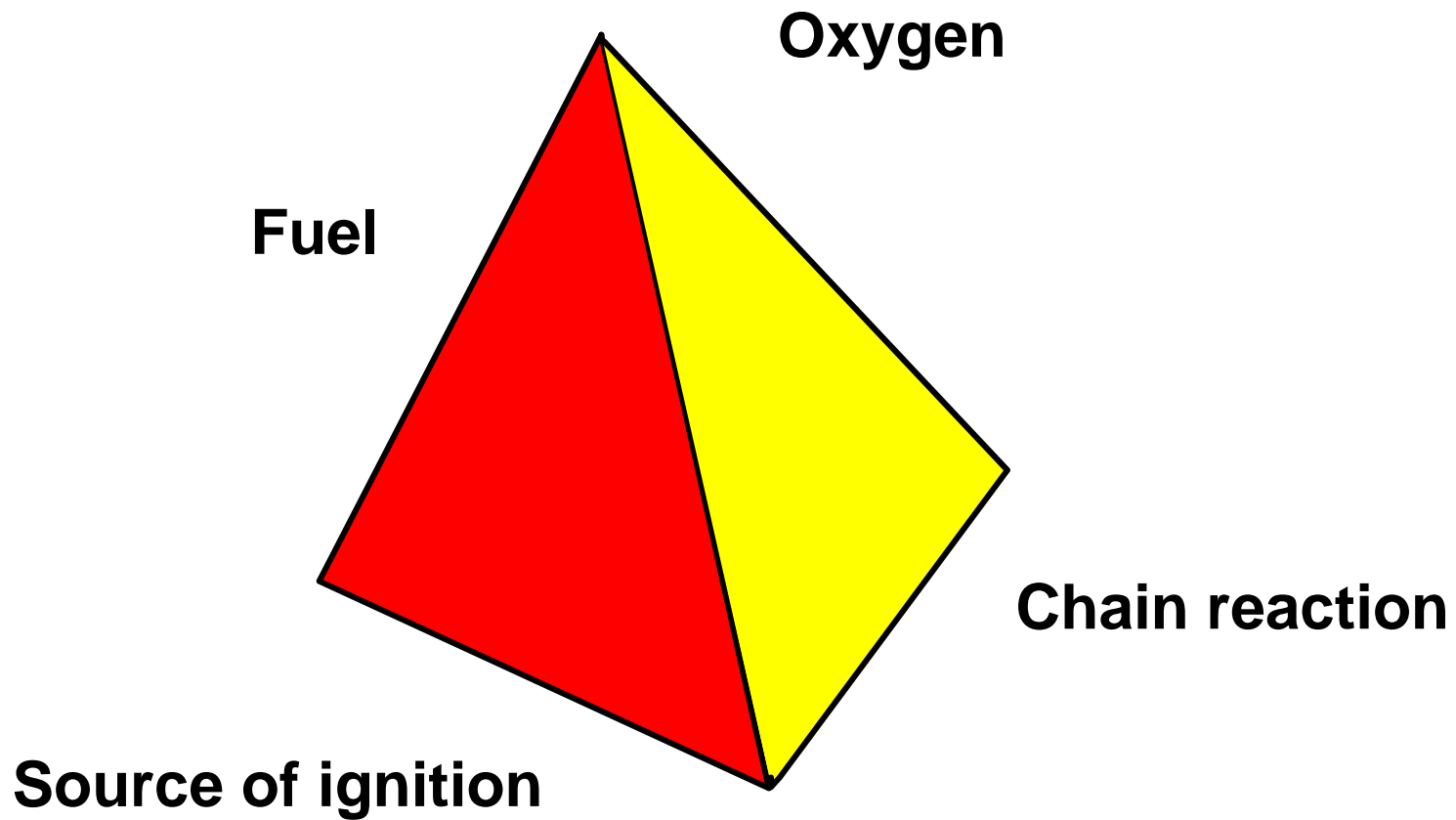
- Proportionally increases the rate of many chemical reactions
- Can cause ordinary combustible materials to become flammable or explosive





Explosive or Flammable Atmospheres

Fire Tetrahedron



Lower Explosive Limit (L.E.L.)

Honeywell

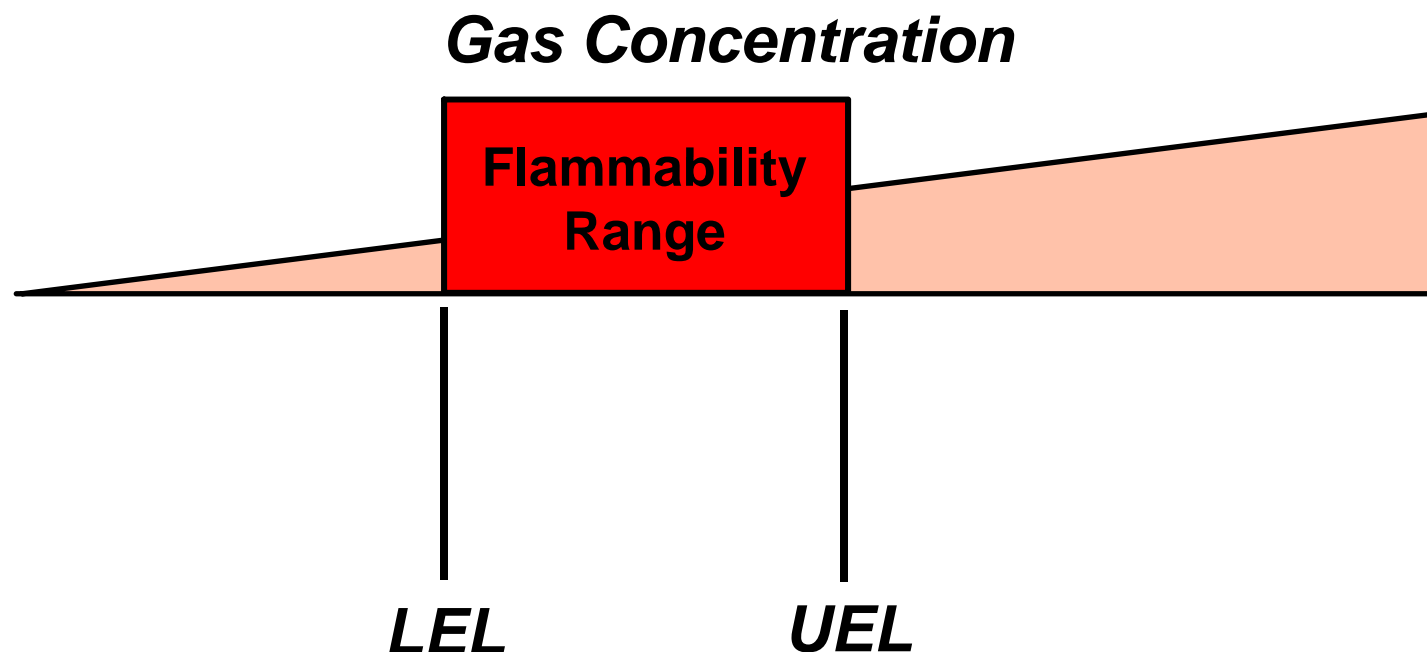
- Minimum concentration of a combustible gas or vapor in air which will ignite if a source of ignition is present

Upper Explosive Limit (U.E.L.)

Honeywell

- 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

Flammability Range



- Range between LEL and UEL of combustible gas or liquid
- Concentrations within flammable range will burn or explode if ignition source is present

Common Flammability Ranges

	LEL	UEL
Methane	5.0%	15.0%
Propane	2.2%	9.5%
Hydrogen	4.0%	75.0%
Butane	1.8%	8.4%
Pentane	1.4%	7.8%
Ethylene Oxide	3.0%	100.0%
Hydrogen Sulfide	4.3%	46.0%

Different gases have different flammability ranges

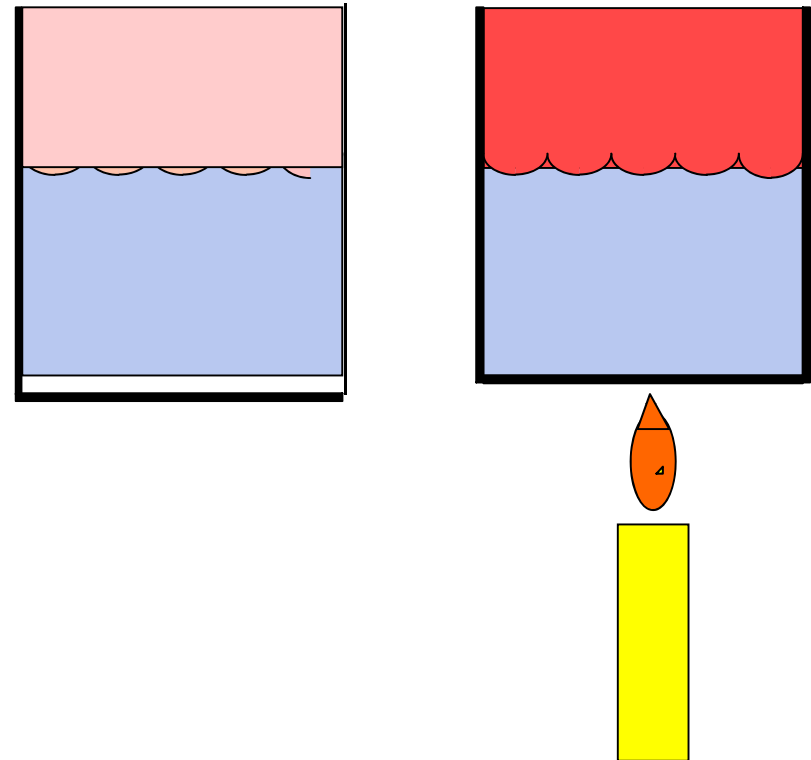
According to OSHA 1910.146

Honeywell

- 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 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



Flashpoint

- Temperature at which a combustible liquid gives off enough vapor to form an ignitable mixture
- Common Flashpoints (degrees F)
 - Gasoline (aviation grade) - 50 (approx.)
 - Acetone 0
 - Methyl ethyl ketone 24
 - Ethanol (96 %) 62
 - Diesel oil 100 - 190

OSHA 29 CFR 1910.106

- Flammable or combustible liquid classifications:

	Flash Point Temp °F	Boiling Point °F	Examples
Class 1A Flammable Liquid	Below 73°F	Below 100°F	Methyl ethyl ether Pentane Petroleum ether
Class 1B Flammable Liquid	Below 73°F	Above 100°F	Acetone Ethanol Gasoline Methanol
Class 1C 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		

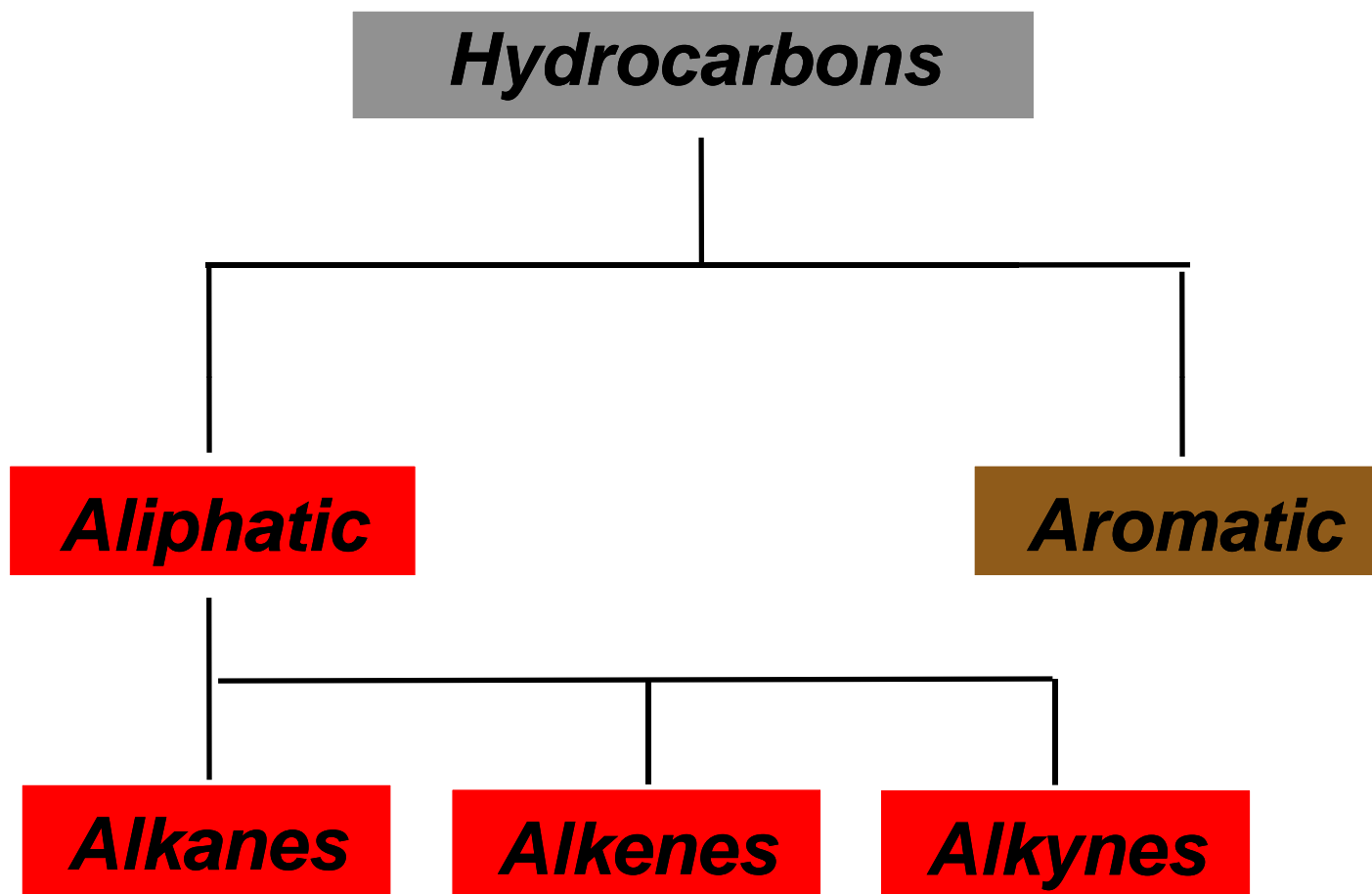
Flashpoints Vary

Honeywell

- Common Flashpoints (degrees F)
 - Gasoline (aviation grade) - 50 (approx)
 - Acetone 0
 - Methyl ethyl ketone 24
 - Ethanol (96 %) 62
 - Diesel oil 100 - 190
- General Guideline
 - Catalytic bead combustible gas sensors are not ideal for the detection of combustible liquids with flashpoints higher than 100 °F (38°C)

Classes of Hydrocarbons

Honeywell



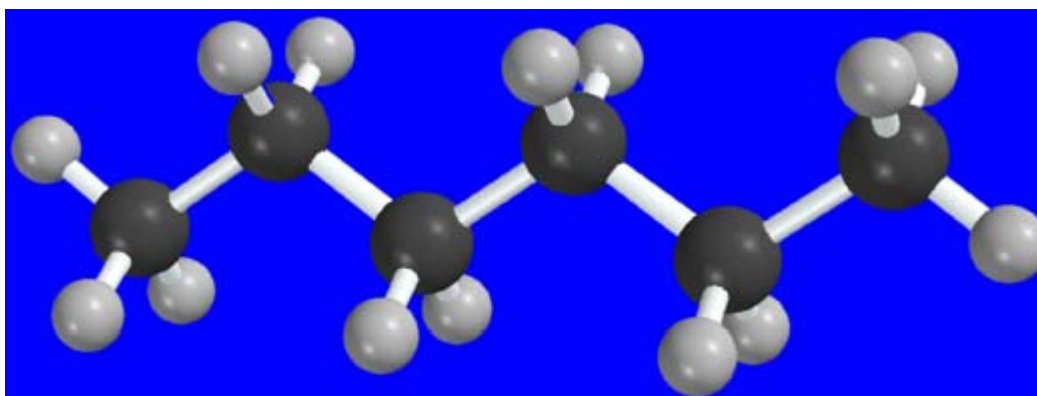
Names of Unbranched Alkanes

Honeywell

Methane	CH_4	1 Carbon
Ethane	CH_3CH_3	2 Carbon
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	3 Carbon
Butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	4 Carbon
Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	5 Carbon
Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	6 Carbon
Heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	7 Carbon
Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	8 Carbon
Nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	9 Carbon
Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	10 Carbon

Unbranched alkanes

- The most stable conformation of unbranched alkanes



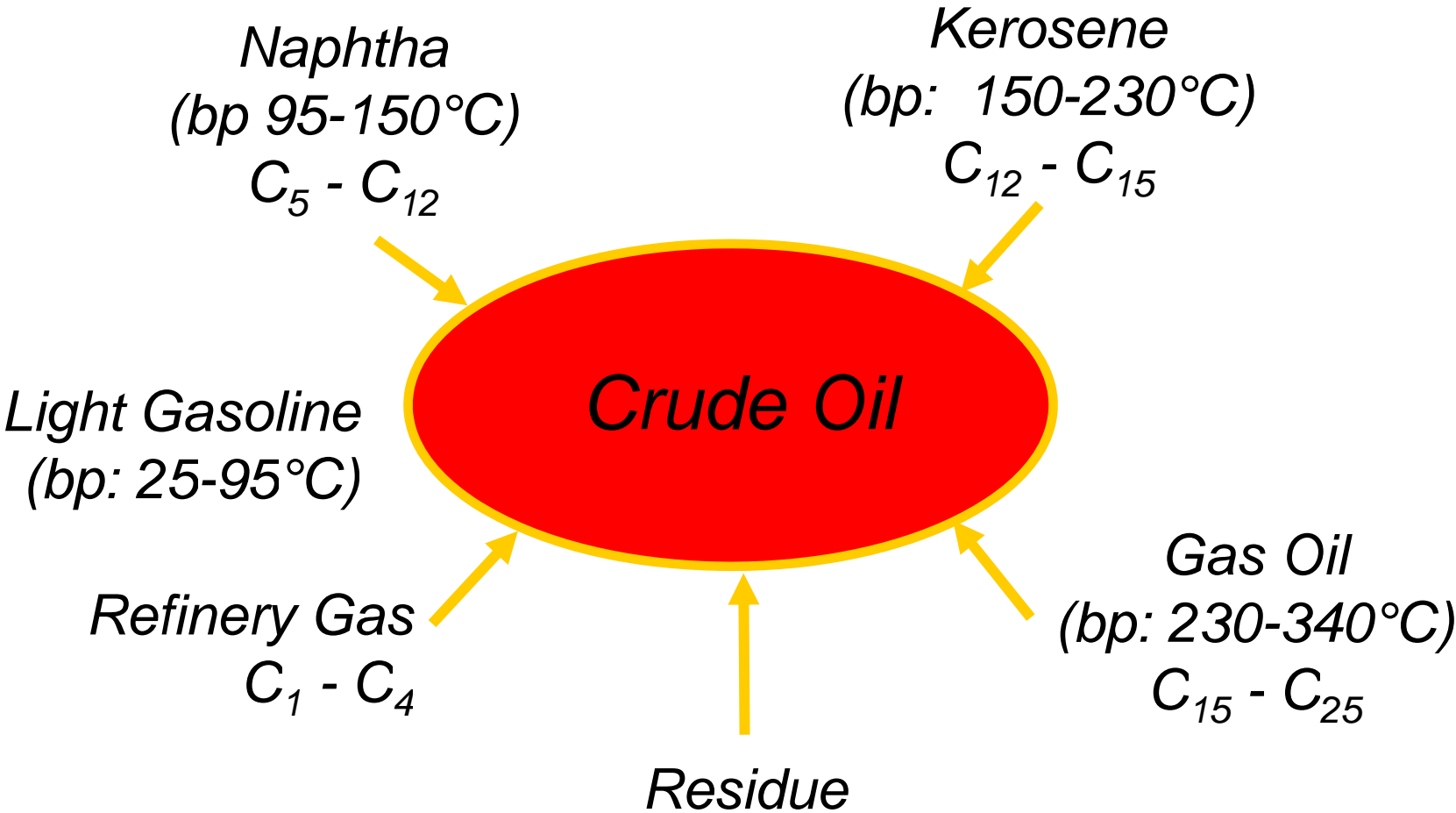
Hexane

Petroleum Refining

Honeywell

- 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



Petroleum Refining

Honeywell

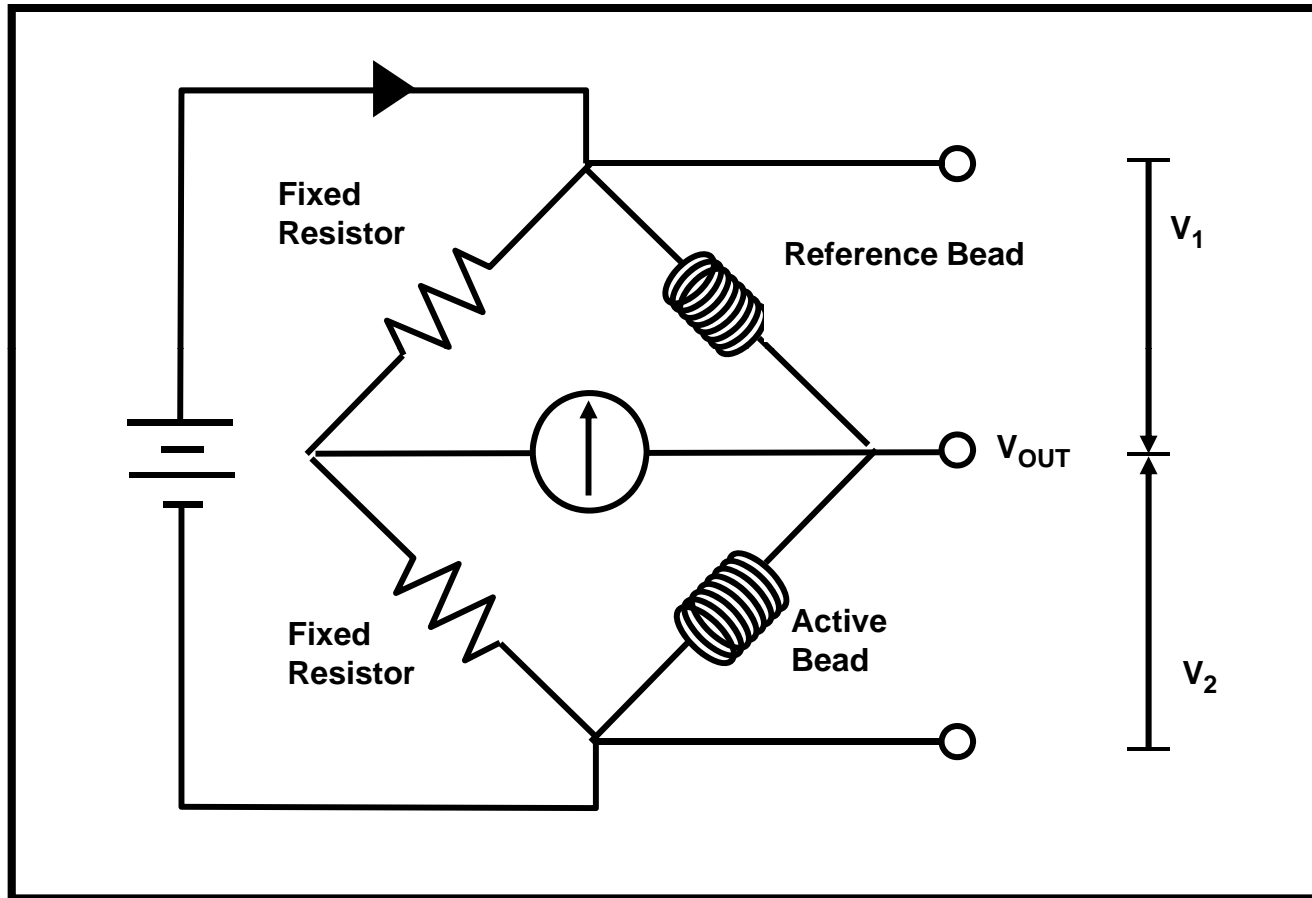
- Cracking
 - Converts high molecular weight hydrocarbons to more useful, low molecular weight ones
- Reforming
 - Increases branching of hydrocarbon chains branched hydrocarbons have better burning characteristics for automobile engines

Catalytic “Hot Bead” Combustible Sensor

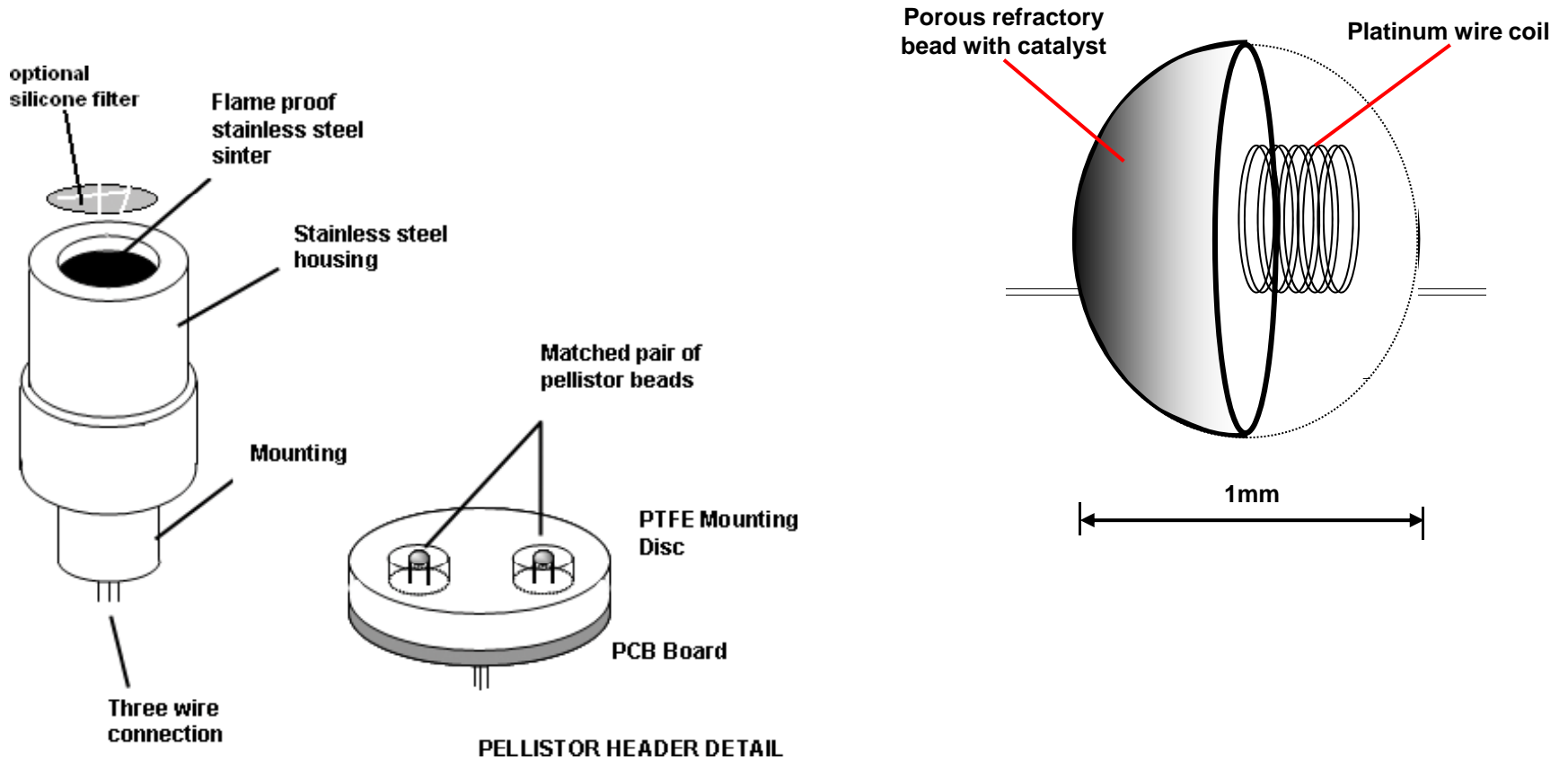
Honeywell

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

Balanced Wheatstone Bridge



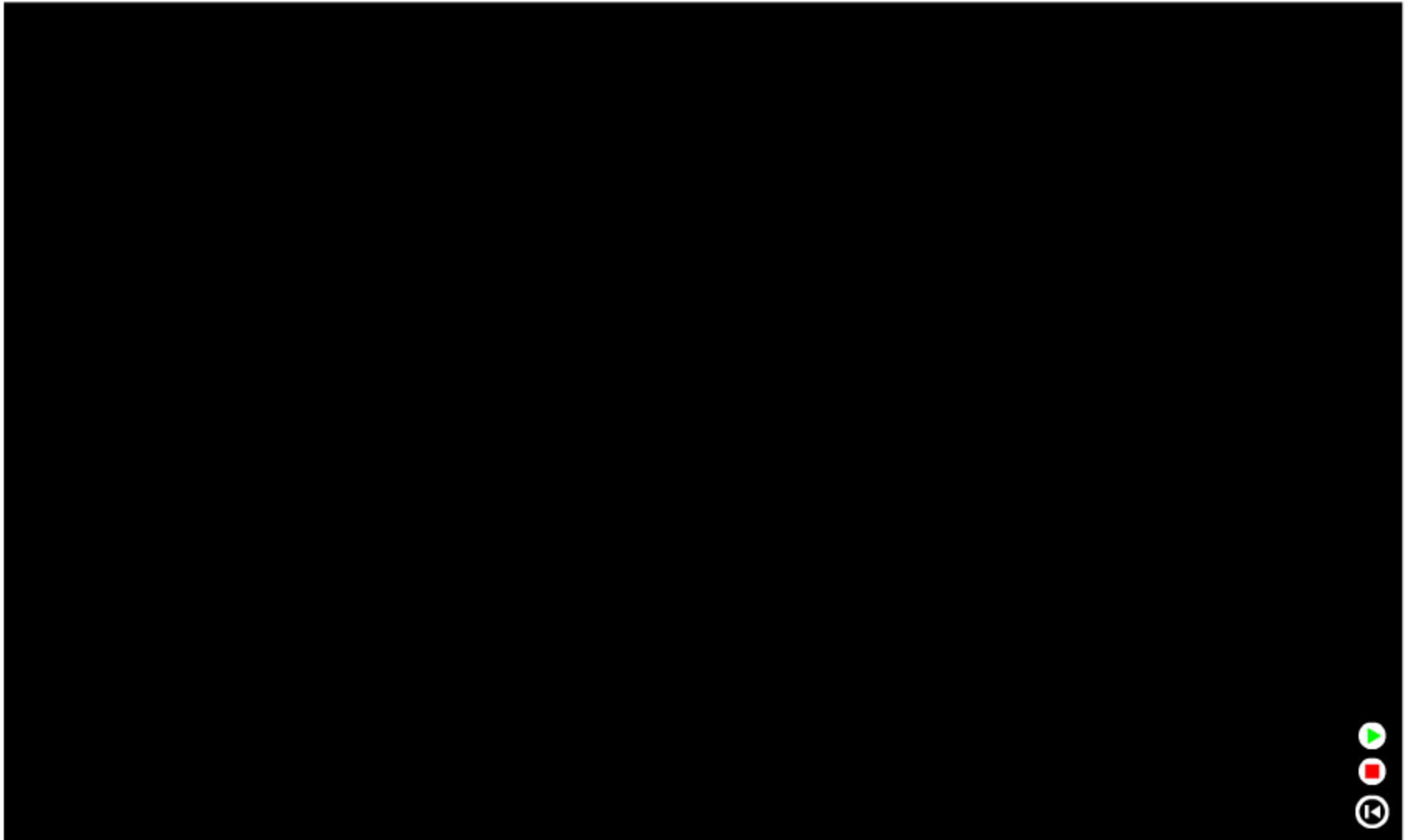
Combustible Sensors



Combustible sensors detect gas by catalytic combustion

Catalytic Sensor Operation

Honeywell



Over-Limit Protection

Honeywell

- 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 and instead of the LEL reading OL = (Over Limit) is displayed.

MicroPel Intrinsicly Safe Pellistor Sensor

Honeywell

- MICROpel40 an experimental design used in older MicroClips SR-WMP
- MICROpel 75 used in current MicroClips SR-WMP75
- MICROpel 75C used in MAX XT II and potentially in MicroClip
 - Sensor is silicone filtered



LEL Sensor Relative Response

Relative Response of a Flammable/Combustible Sensor

Combustible gas / vapor	Relative response when calibrated on pentane	Relative response when calibrated on propane	Relative response when 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

Relative Sensitivity 4P-90C

- Table below shows response variation of 4P-90C CiTipeL on exposure to a range of gases and vapors at the same %LEL concentration
 - Figures are experimentally derived and expressed relative to the Methane signal (=100)

Gas/Vapor	Relative Sensitivity	Gas/Vapor	Relative Sensitivity	Gas/Vapor	Relative Sensitivity
Methane	100	n-Hexane	40	Ammonia	125
Propane	60	Acetylene	80	Cyclohexane	50
n-Butane	60	Carbon Monoxide	105	Ethylene	85
n-Pentane	50	Hydrogen	100	1, 3 Butadiene	55

Each sensitivity has been rounded to nearest 5%

- Note:
 - Results are intended for guidance only
 - For the most accurate measurements an instrument should be calibrated using target gas

Correction Factors

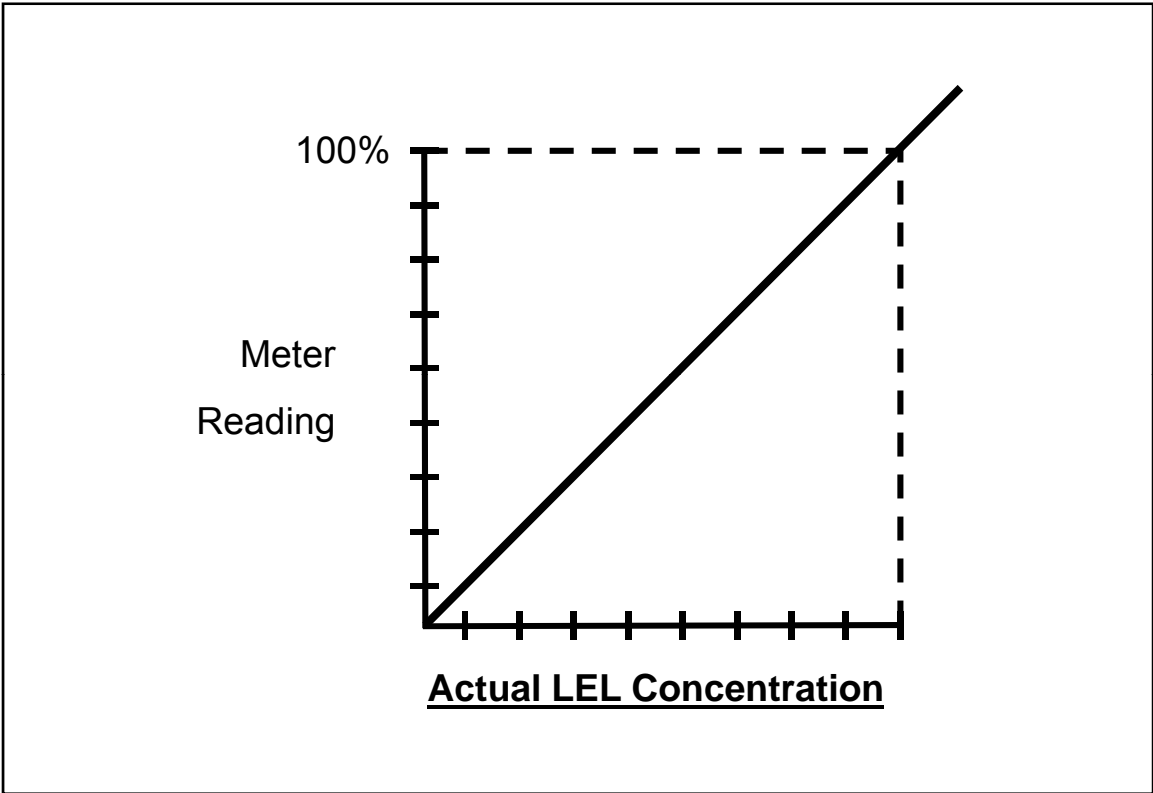
- Correction factor is reciprocal of relative response
 - Consider detector calibrated on methane, then used to monitor pentane
- When calibrated on methane, sensor shows a relative response to pentane of 0.5
 - In other words, readings will be 50% lower than actual
- Correction factor calculated as: $1 / 0.5 = 2.0$

Correction Factors

- Multiplying instrument reading by correction factor for pentane provides true concentration
 - Given correction factor for pentane of 2.0, and instrument reading of 40% LEL, true concentration calculated as:

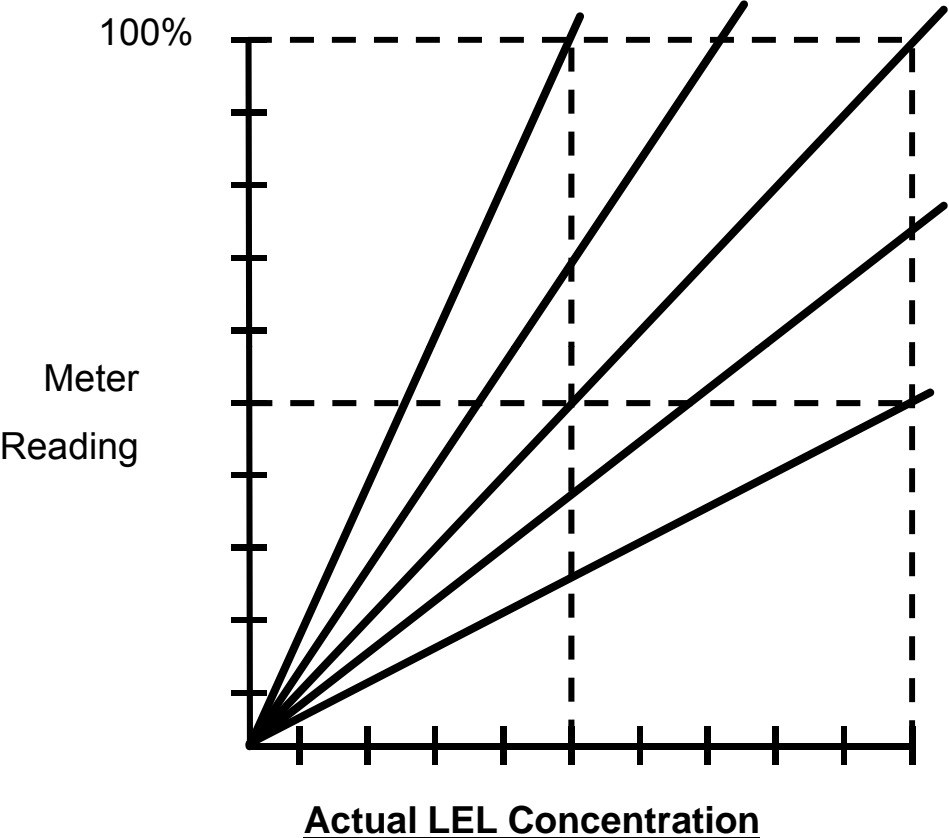
$$\begin{array}{ccccc} 40 \% \text{ LEL} & \times & 2.00 & = & 80 \% \text{ LEL} \\ \text{Instrument} & & \text{Correction} & & \text{True} \\ \text{Reading} & & \text{Factor} & & \text{Concentration} \end{array}$$

Linear Response



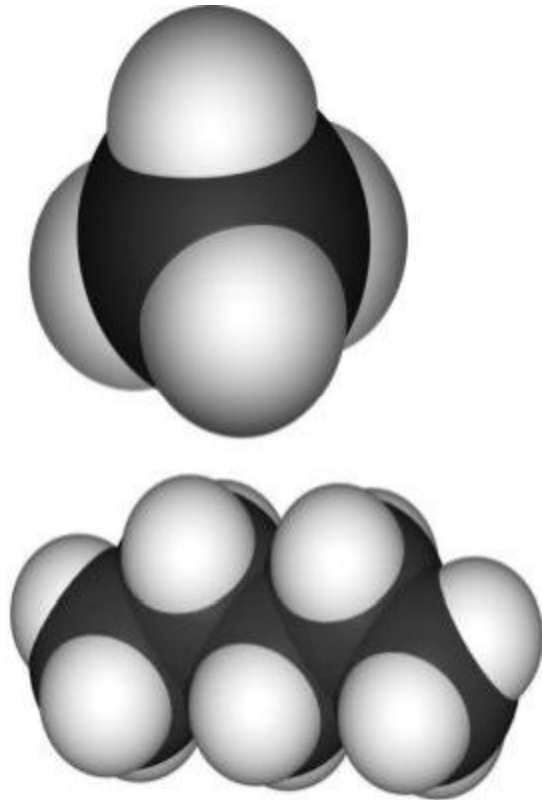
Calibration Standard

Relative Responses



LEL Sensors and Calibration

Honeywell



- BW Technologies by Honeywell chose to calibrate all LEL sensors to Methane
- Methane is a stable tetrahedron and requires more energy to oxidize than other hydrocarbons
- While it is true a monitor calibrated to pentane will alarm on the side of safety in a methane environment, poisoning and over exposure can lead to reduced sensitivity in an LEL sensor.
- An LEL sensor with reduced sensitivity may potentially respond to pentane and not to methane.
- The only way to be certain if an LEL sensor can detect methane is to challenge it with methane
- Alarm levels are set conservatively in order to compensate for the correction factor differences

Pentane equivalent methane mixture

Honeywell

- To provide pentane sensitivity and ensure that the catalytic bead sensor is capable of detecting methane BW provide a “pentane equivalent” quad gas mixture
- The pentane equivalent mixture contains 1.25% v/v methane gas
- The sensor is calibrated to 25% LEL gas but the span value is left at 50% giving the same sensor response you would have with a pentane calibrated sensor in a methane atmosphere

Combustible sensor Poisons

Honeywell

- Silicones
 - Lubricants such as WD-40
 - Rust inhibitors
 - Hand moisturizers
 - Hand sanitizers
 - Cleaners such as ARMOR ALL
- Hydrogen sulfide and other sulfur containing compounds
- Phosphates and phosphorus containing substances
- Lead containing compounds (especially tetraethyl lead)
- Over Exposure to combustible gases



Combustible sensor characteristics

Honeywell

- Inhibitors:
 - Halogenated hydrocarbons (Freons®), trichloroethylene, methylene chloride, etc.)
- Oxygen Deficiency:
 - If O₂ concentration less than 10% O₂, LEL sensor will not read properly. Safest approach is to include an oxygen sensor with any combustible sensor. In the event a user is attempting to monitor combustible gas in an oxygen deficient environment it is possible the LEL sensor will not respond to a potentially dangerous situation, but the O₂ sensor would warn of the oxygen deficiency
- Over Exposure:
 - sensor may be damaged by exposure to higher than 100% LEL concentrations (To prevent damage, sensor is switched OFF and instead of the LEL reading OL = {Over Limit} is displayed).
- Non-Specific:
 - Cannot determine the species of gas being detected
 - Some combustible gases are toxic at concentrations well below the detection capabilities of the catalytic bead sensor

Monitor Cleaning

Honeywell

- In addition to the use of a soft damp cloth as recommended in the BW User Manual the only approved cleaner is ACL Staticide
- Avoid exposing the sensor screens to moisture – do not use computer keyboard air dusters to clean debris from sensor filters
- BW do not recommend the use products such as EconoClean, citrus based cleaners or Armor All



Combustible sensor limitations

Honeywell

Contaminant	LEL (Vol %)	Flashpoint Temp (°F)	OSHA PEL	NIOSH REL	TLV	5% LEL in PPM
Acetone	2.50%	-4°F (-20 °C)	1,000 PPM TWA	250 PPM TWA	500 PPM TWA 750 PPM STEL	1250 PPM
Diesel (No.2) vapor	0.60%	125°F (51.7°C)	None Listed	None Listed	15 PPM	300 PPM
Ethanol	3.30%	55°F (12.8 °C)	1,000 PPM TWA	1000 PPM TWA	1000 PPM TWA	1,650 PPM
Gasoline	1.30%	-50°F (-45.6°C)	None Listed	None Listed	300 PPM TWA 500 PPM STEL	650 PPM
Hexane	1.10%	-7°F (-21.7 °C)	500 PPM TWA	50 PPM TWA	50 PPM TWA	550 PPM
Isopropyl alcohol	2.00%	53°F (11.7°C)	400 PPM TWA	400 PPM TWA 500 PPM STEL	200 PPM TWA 400 PPM STEL	1000 PPM
Kerosene/Jet Fuels	0.70%	100 – 162°F (37.8 – 72.3°C)	None Listed	100 mg/M3 TWA (approx 14.4 PPM)	200 mg/M3 TWA (approx 29 PPM)	350 PPM
MEK	1.40%	16°F (-8.9°C)	200 PPM TWA	200 PPM TWA 300 PPM STEL	200 PPM TWA 300 PPM STEL	700 PPM
Turpentine	0.8%	95°F (35°C)	100 PPM TWA	100 PPM TWA	20 PPM TWA	400 PPM
Xylenes (o, m & p isomers)	0.9 – 1.1%	81 – 90°F (27.3 – 32.3 °C)	100 PPM TWA	100 PPM TWA 50 PPM STEL	100 PPM TWA 150 PPM STEL	450 – 550 PPM

Silicone Filtered vs Unfiltered Response

Honeywell

- City Technology 4P-90C and MICROpel75c combustible sensors have an external silicone filter—the 4P-90 and MICROpel75 versions do not
 - Filter removes silicone vapor – a profound sensor poison
 - Filter also reduces response to heavier hydrocarbons such as pentane, hexane, benzene, toluene, xylene, cumene, etc.
 - The heavier the compound, the greater the reduction in response. Nonane cannot be detected
 - The MICROpel75c is suitable for hydrocarbons up to heptane
 - The 4P-90C is suitable for hydrocarbons up to hexane
 - Effective Jan 2008, all new LEL sensor equipped BW instruments equipped with the 4P-90C sensor
 - The MAX XT II will be equipped with the MICROpel75C, There are plans to adapt this change into the MicroClip
 - The 4P-90 and MICROpel75 sensors are still available for customers who need it
 - The silicone filter on the 4P-90C used the GasAlertMicro and Micro5 can be easily removed
 - Customers monitoring for heavy hydrocarbons should consider removing the filter, and calibrating their instruments with “PENTANE EQUIVALENT” calibration gas



High Range Combustible Gas

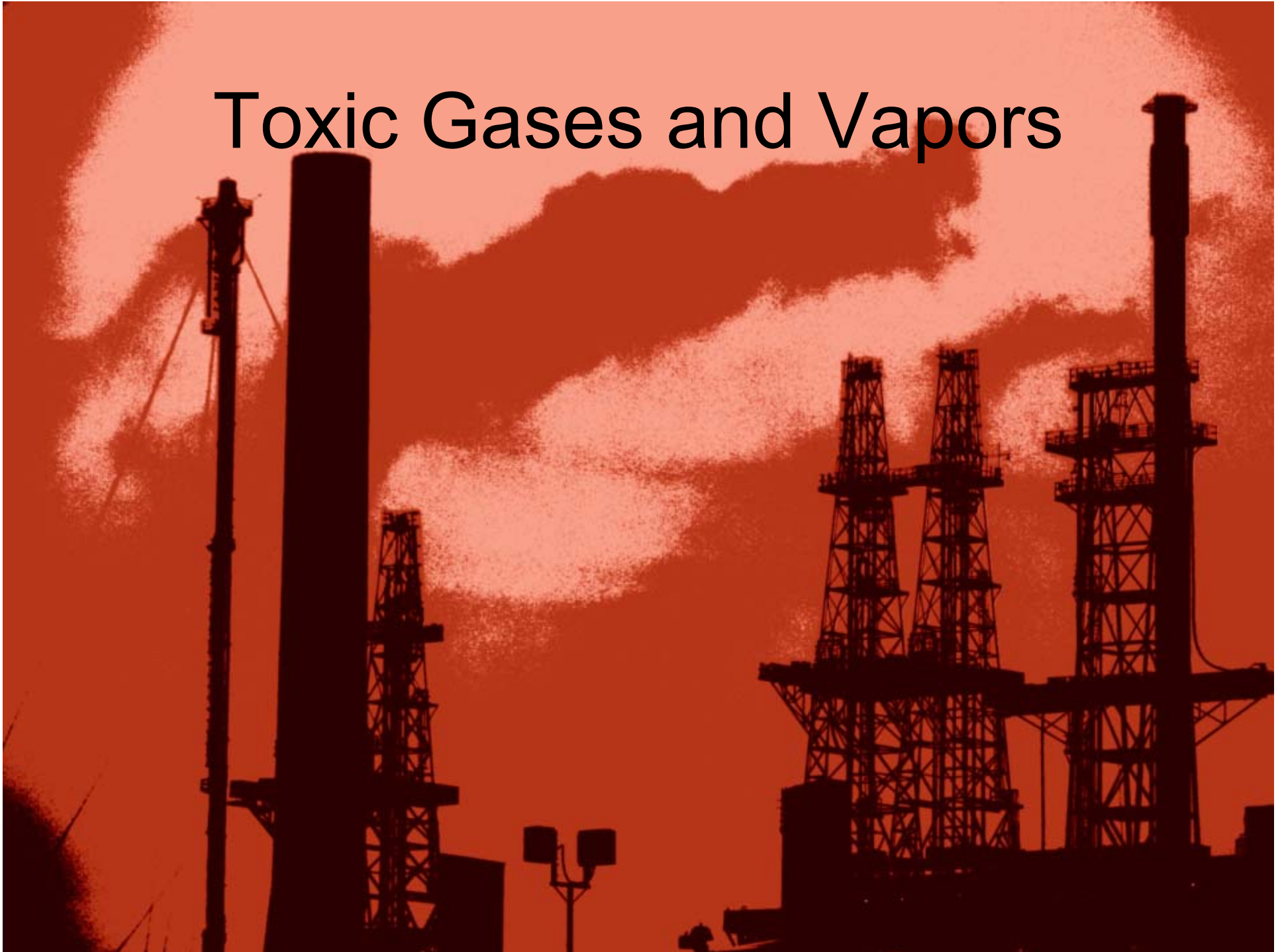
Honeywell

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

Since catalytic bead combustible sensors do not function in the absence of oxygen we recommend the use of an oxygen sensor in conjunction with an LEL sensor to prevent suffocation due to excessive explosive gas environments!

Toxic Gases and Vapors



Toxic atmospheres come from

Honeywell

- Microbial action on material in CS
- Products or chemicals stored in CS
- Work being performed in CS
- Areas adjacent to Confined Space

Toxic Gases and Vapors

Honeywell

- Detection technologies:
 - Electrochemical Sensors
 - Photoionization detectors
 - Non-dispersive infrared (NDIR)

Toxic Exposure Limits

Honeywell

- OEL is maximum concentration of airborne contaminant to which unprotected worker may be exposed
- 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

Permissible Exposure Limit (PEL)

Honeywell

- Determined by 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

Permissible Exposure Limits

Honeywell

- “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

NIOSH Recommended Exposure Limit (REL) Honeywell

- Determined by National Institute of Occupational Safety and Health (NIOSH)
- Guidelines 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

Threshold Limit Value (TLV)

Honeywell

- Determined by American Conference of Governmental Industrial Hygienists (ACGIH)
- Guidelines for control of potential health hazards
- Intended as recommendation
- Usually more conservative than Federal OSHA PEL, frequently more conservative than NIOSH REL
- Incorporated by adoption in some states, (e.g. California) where it has force of law
- Also incorporated by adoption as part of US Coast Guard, Certified Marine Chemist Association, Mine Safety and Health Administration and other specific federal standards
- Force of law in Canada!

Exposure Limits defined

Honeywell

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

TWA is projected value

Honeywell

- 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:

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

- 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
4hrs	100 ppm	50 ppm
8hrs	100 ppm	100 ppm
12 hrs	100 ppm	150 ppm

Ceiling Limit

Honeywell

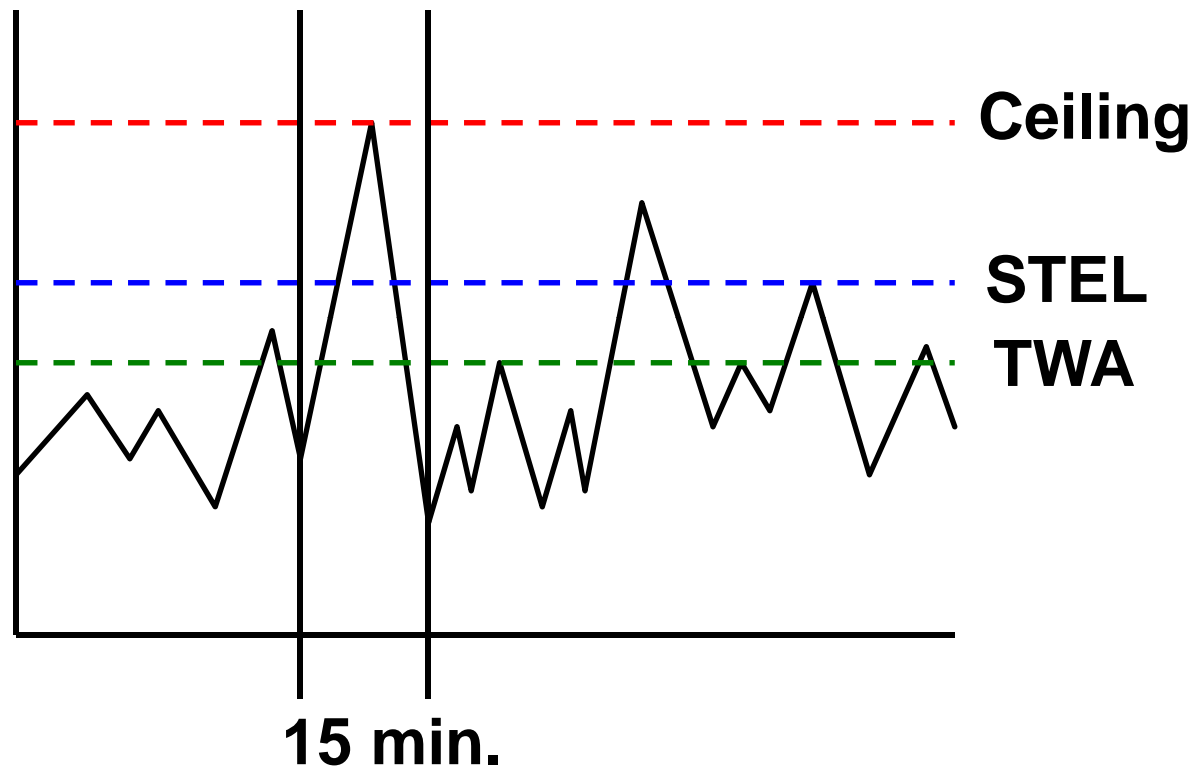
- Ceiling is the maximum concentration to which an unprotected worker may be exposed
- Ceiling concentration should never be exceeded even for an instant

Short Term Exposure Limit (STEL)

Honeywell

- 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

Short Term Exposure Limit (STEL)



Exposure Limits and Data-Logging

Honeywell

- How are Exposure limits affected by Data-Logging?
- They're not!
 - PEL calculations are continuously updated by the instrument
 - The data-logging 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

Immediately Dangerous to Life and Health

Honeywell

- 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

Converting PPM to mg/m³

- ACGIH / NIOSH use following formulae:

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

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

- So for chlorine:

Cl₂ gram molecular weight = 70.9 g/mole

Cl₂ TLV = 0.5 ppm

TLV in mg/m³ calculated:

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

Carbon Monoxide

- *Bonds to hemoglobin in red blood cells*
- *Contaminated cells can't transport O₂*
- *Chronic exposure at even low levels harmful*

Carbon Monoxide

Honeywell

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

Characteristics of Carbon Monoxide

Honeywell

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

Symptoms of Carbon Monoxide Exposure

Honeywell

- 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)

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

Exposure Limits for Carbon Monoxide

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

AlphaSense and SureCell CO Sensors

Honeywell

- BW is incorporating the use of sensors from a variety of manufacturers' including City Technology, Surecell and Alphasense, Dynamant, E2V, BW Technologies



Characteristics of Hydrogen Sulfide

- *H₂S is a 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 to H₂S occurs primarily by inhalation, but can also occur by ingestion (contaminated food) and skin (water and air)*
- *Once taken into the body, it is rapidly distributed to various organs, including the central nervous system, lungs, liver, muscle, as well as other organs*

Hydrogen Sulfide

Honeywell

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

Characteristics of Hydrogen Sulfide

Honeywell

- 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

Honeywell

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

Toxic Effects of H₂S

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 H₂S

Honeywell

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

North America GasAlert Extreme

Honeywell

- Factory default alarm settings

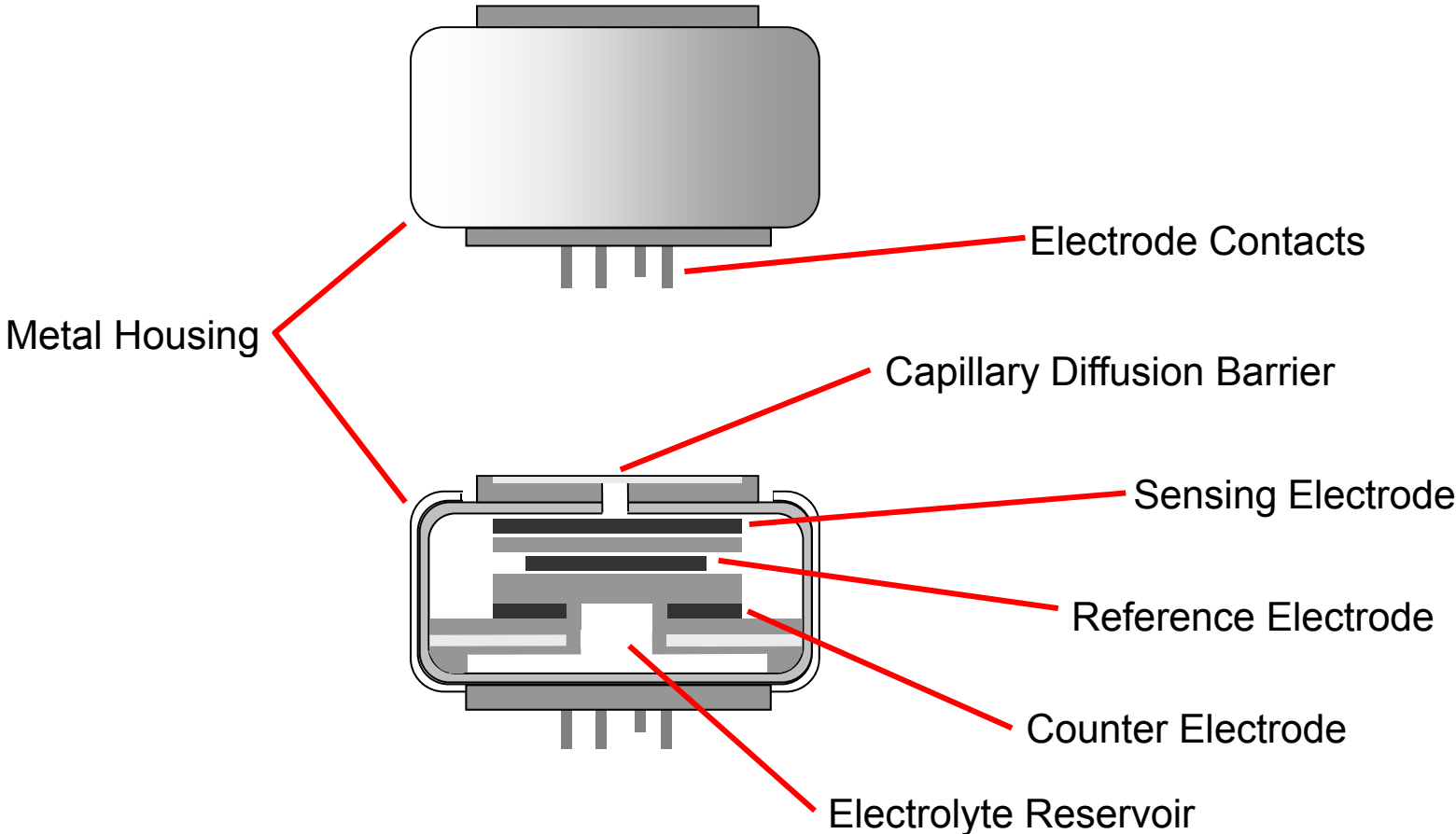
	TWA	STEL	Low	High
Hydrogen Sulfide	10 ppm	15 pm	10 ppm	15 ppm
Sulfur Dioxide	2 ppm	5 ppm	2 ppm	5 ppm
Hydrogen Cyanide	4.7 ppm	10 ppm	4.7 ppm	10 ppm
Carbon Monoxide	35 ppm	200 ppm	35 ppm	200 ppm
Chlorine	0.5 ppm	1.0 ppm	0.5 ppm	1.0 ppm
Nitrogen Dioxide	2 ppm	5 ppm	2 ppm	5 ppm
Ammonia	25 ppm	35 ppm	25 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	0.1 ppm	0.1 ppm	0.1 ppm	0.2 ppm
Oxygen	N/A	N/A	19.50%	23.50%

Substance Specific Electrochemical Sensors Honeywell

- 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

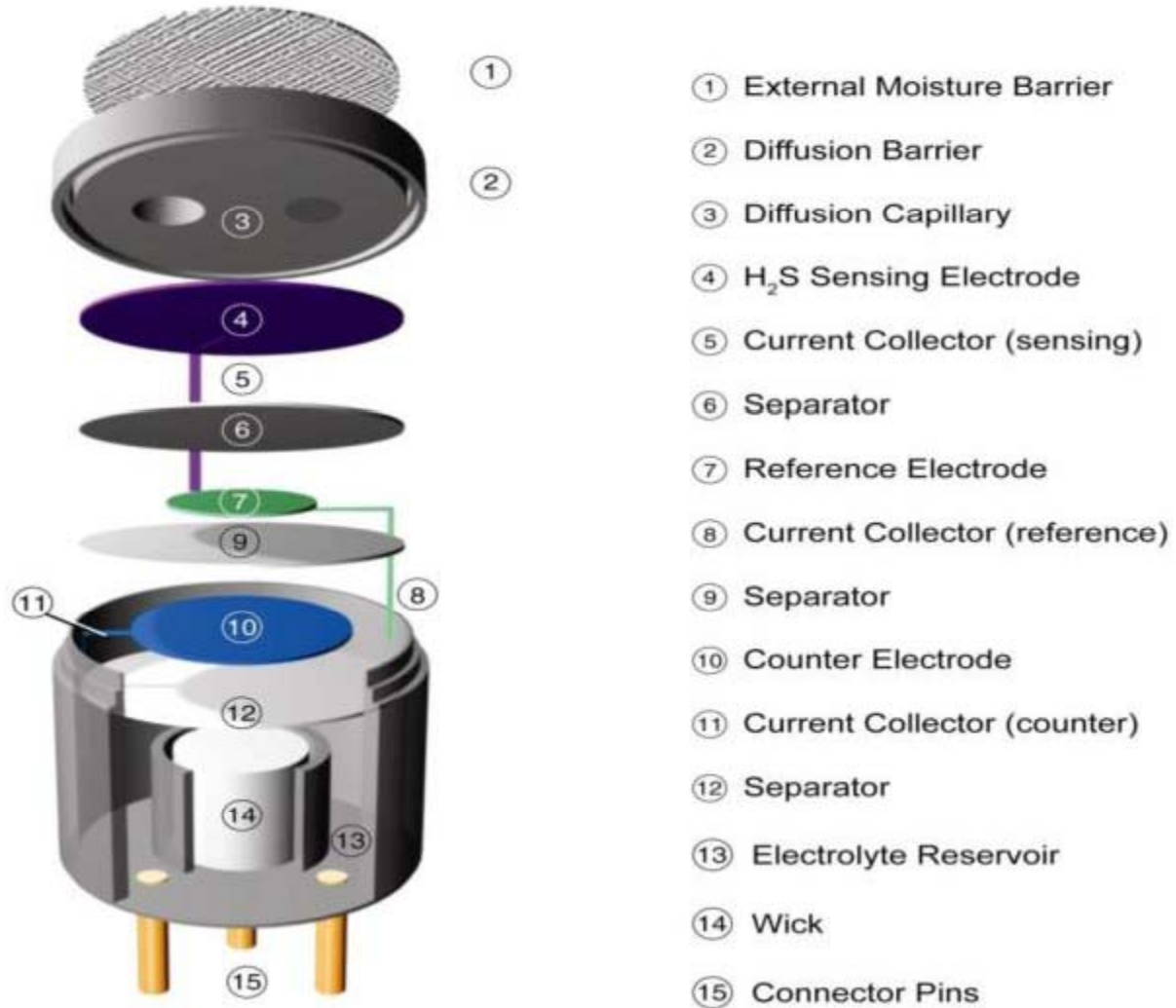


Electrochemical Toxic Sensor



Electrochemical H₂S Sensor

Honeywell



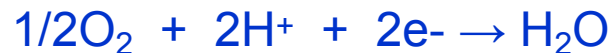
CO and H2S Sensor Detection Mechanism

Honeywell

Carbon monoxide is oxidized at the sensing electrode:



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



And the overall reaction is: $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$

4CF Signal Output: $0.07 \mu\text{A} / \text{ppm CO}$

Hydrogen sulfide is oxidized at the sensing electrode:



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



And the overall reaction is: $\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$

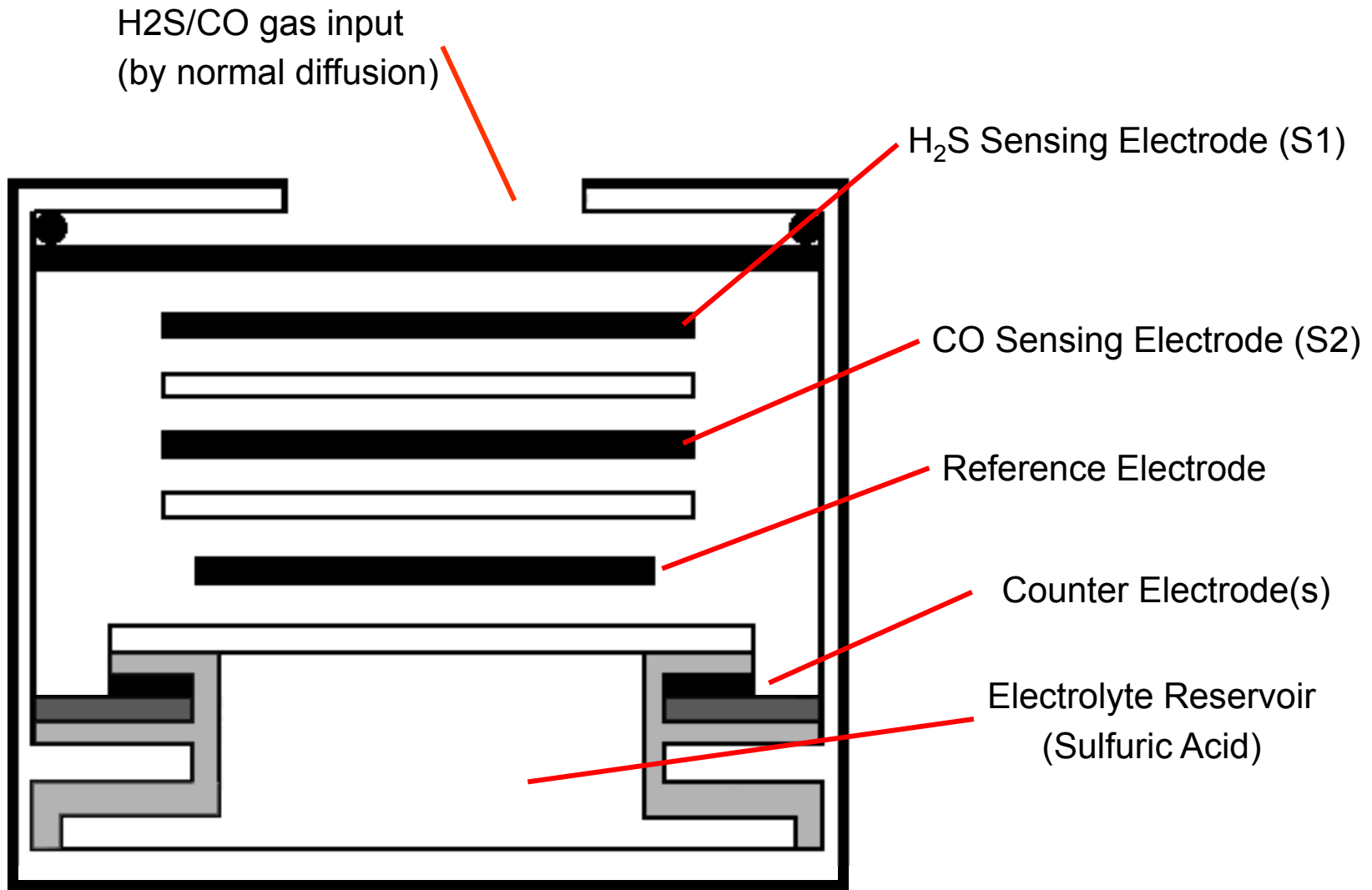
4HS Signal Output: $0.7 \mu\text{A} / \text{ppm H}_2\text{S}$

H2S Sensor Performance

Honeywell



COSH Sensor



COSH Sensor

Honeywell

H₂S Gas Reaction:

H₂S Sensing Electrode Reaction: $\text{H}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^-$

H₂S Counter Electrode Reaction: $2\text{O}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2\text{O}$

Overall reaction: $\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$

CO Gas Reaction:

CO Sensing Electrode Reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$

CO Counter Electrode Reaction: $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

Overall reaction: $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$

H₂S signal output: 775 nA / ppm

CO signal output: 80 nA / ppm

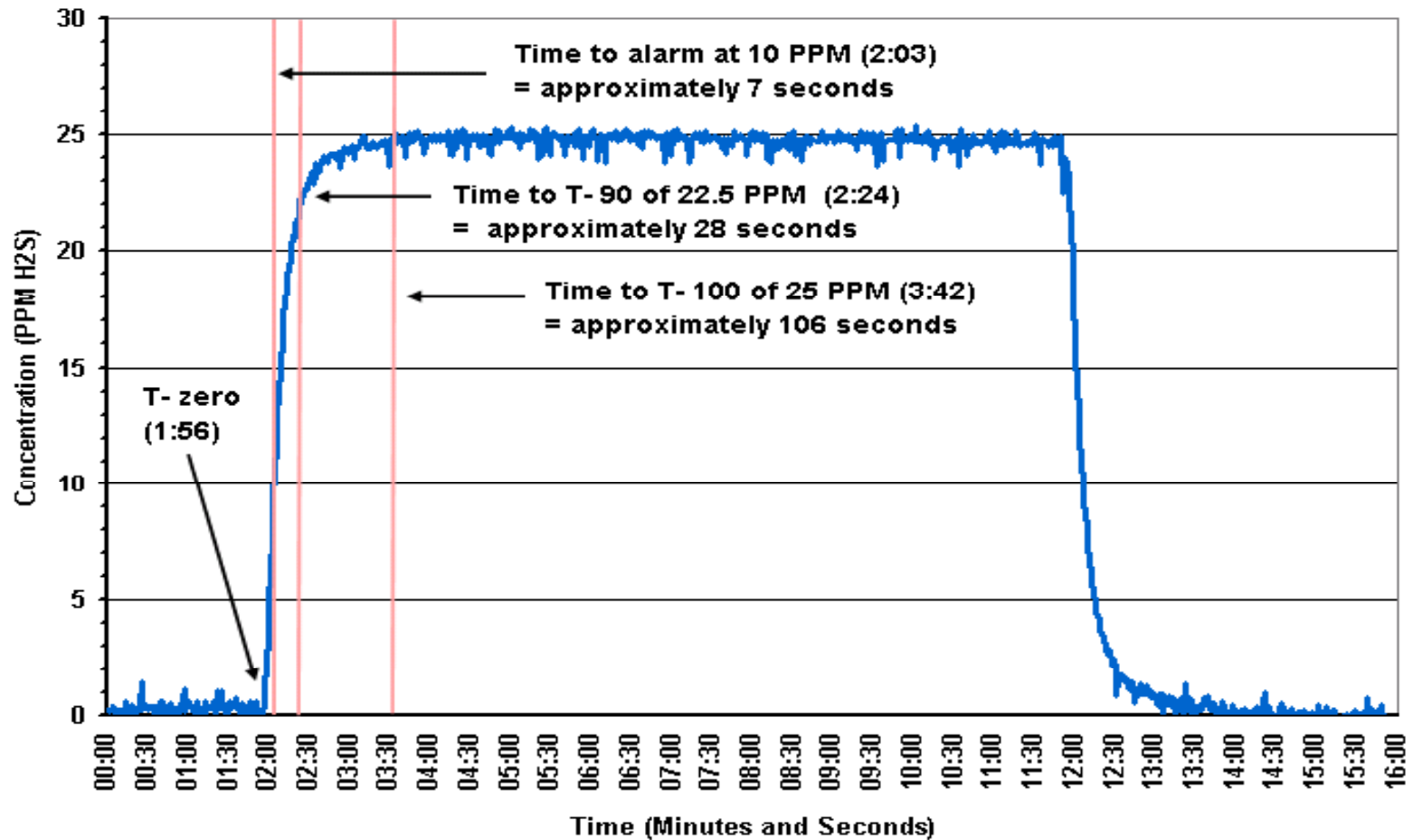
COSH Sensor Performance

Honeywell



Electrochemical Sensor Performance

Response of H2S Sensor When Exposed to 25 PPM Gas





HA University

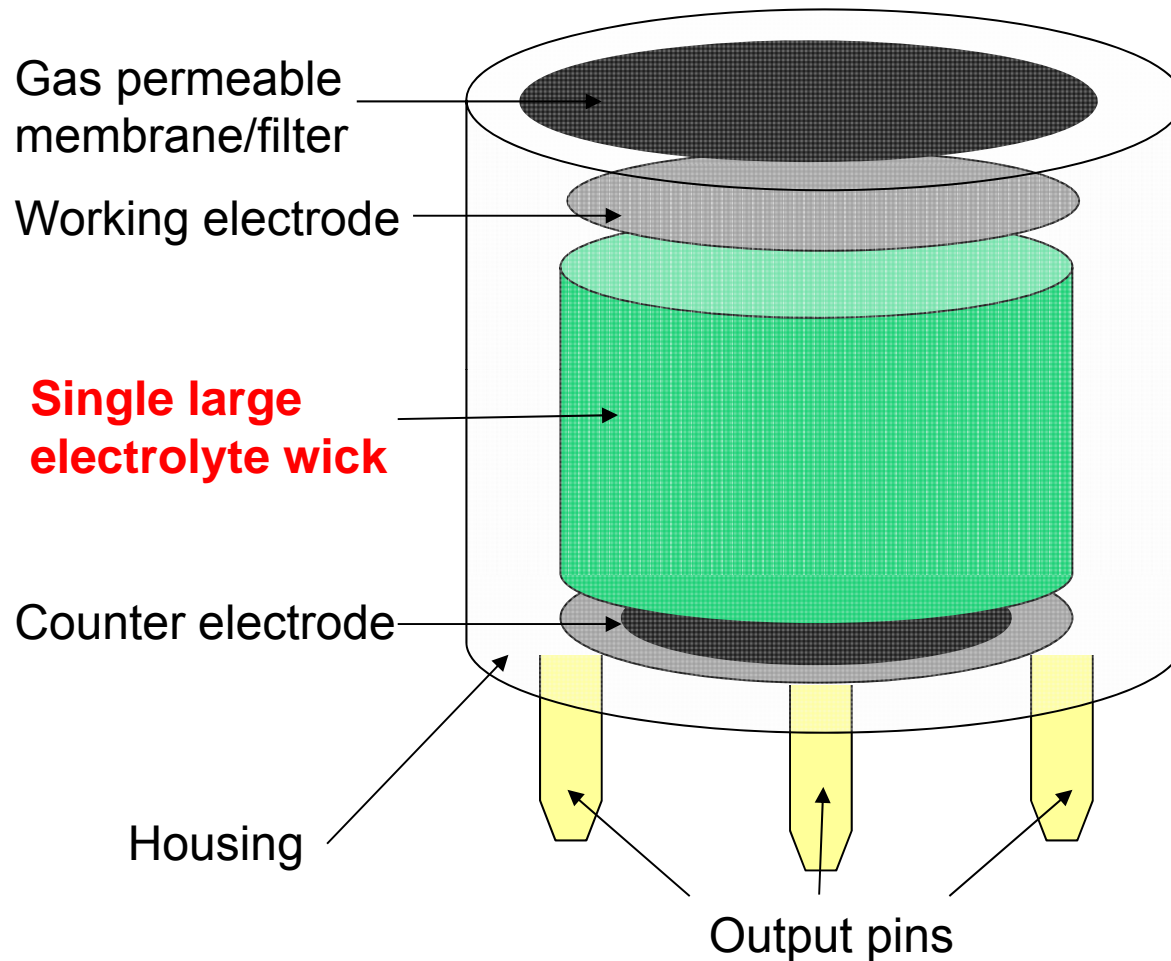
Honeywell SureCell Technology



Honeywell

Standard electrochemical sensor design

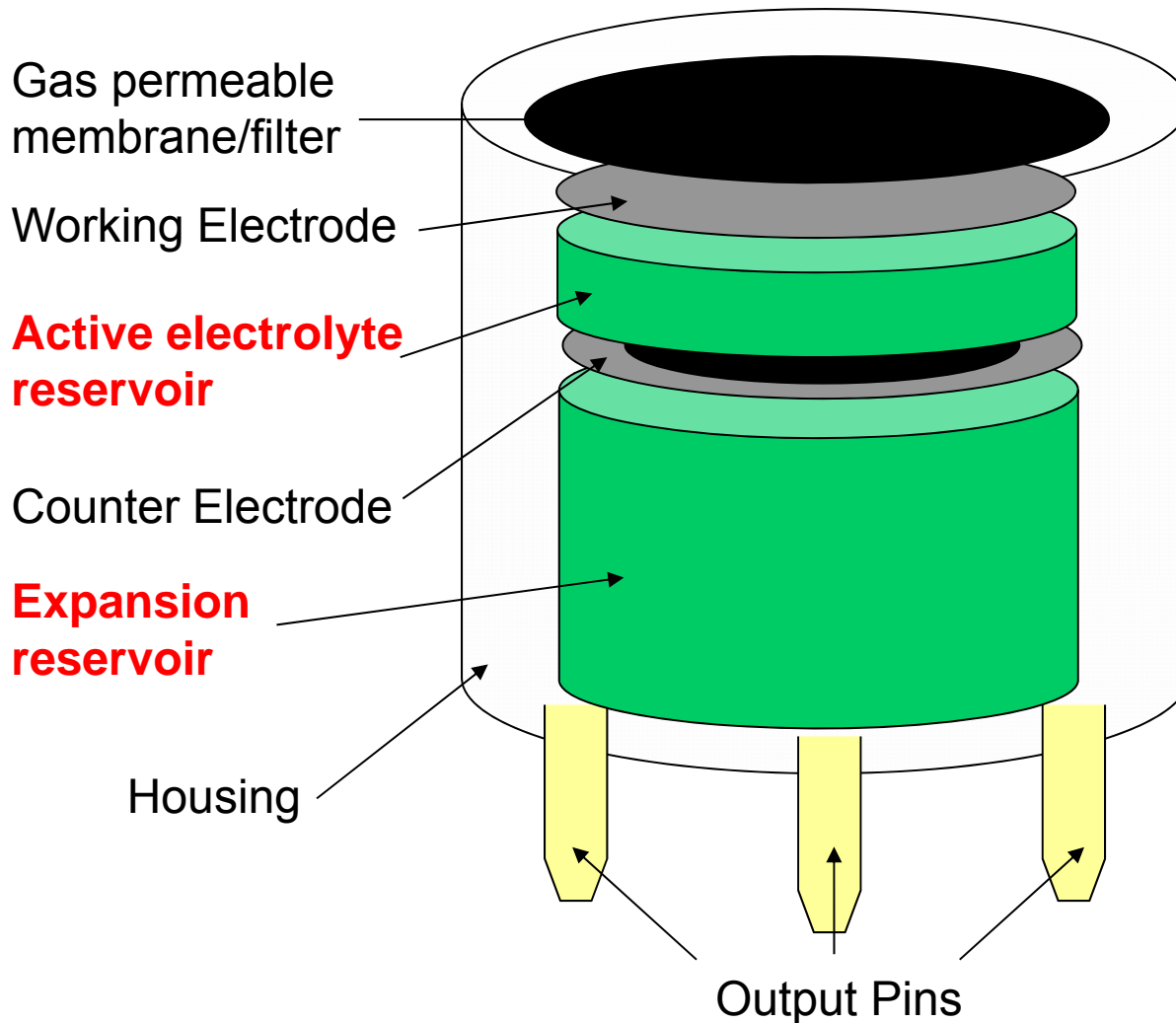
Honeywell



- **How does it work?**
Chemical reaction generates electrical current
- **Why Do We Use It?**
 - *No Mechanical Parts*
 - *Linear response to gas concentrations*
 - *Generally reliable and economical*
- **Challenges**
 - *Sensitive to temp and humidity extremes*
 - *Speed of response*
 - *Cross sensitivity*
 - *CO2 sensor requires constant bias*

Honeywell SureCell electrochemical design

Honeywell

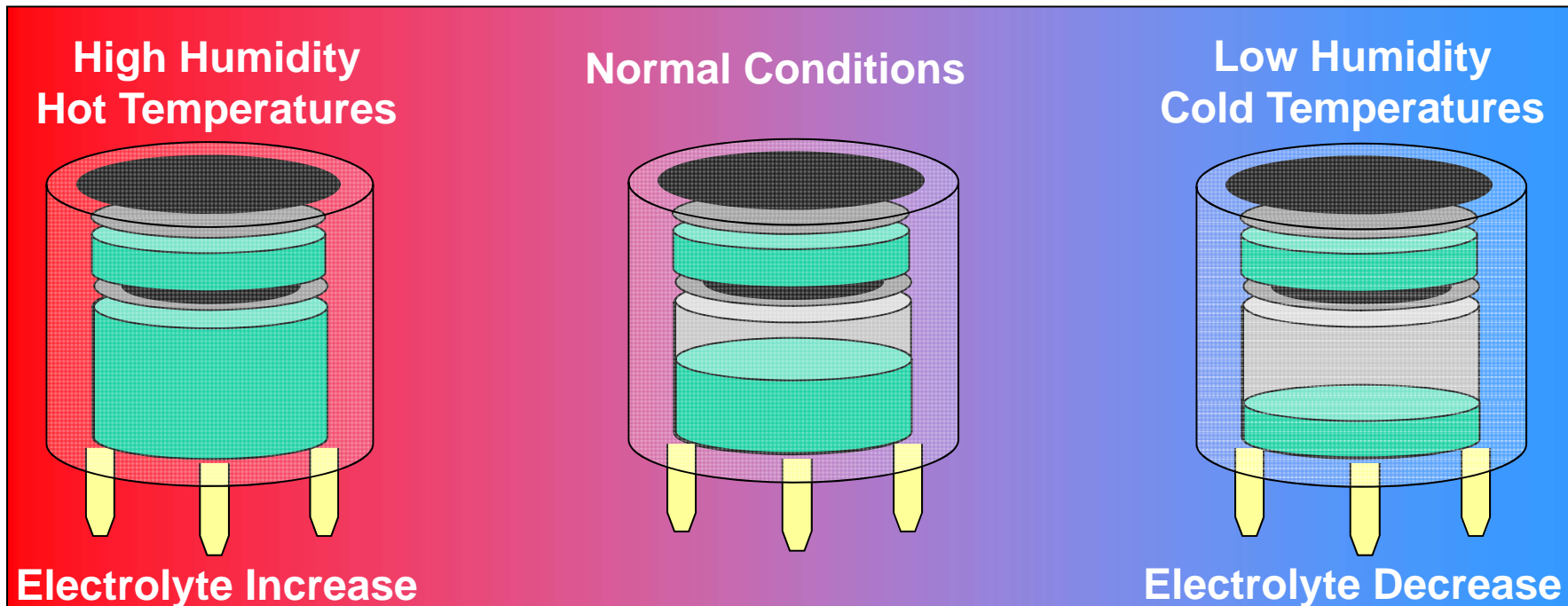


- **Advantages**

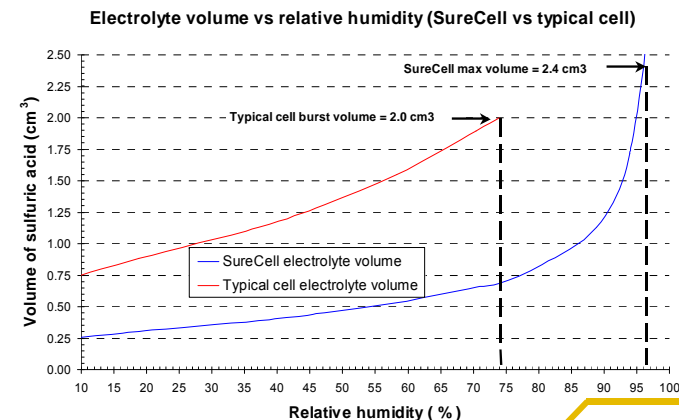
- *Separate electrolyte reservoirs allow for expansion and contraction under extreme conditions*
- *Faster speed of response*
- *Better linearity*
- *Longer calibration intervals*

SureCell advantages

Honeywell



- Prevents cell bursting/leakage in high temperature and humidity environments
- Prevents dehydration in low temperature & humidity environments
- Produces faster and more reproducible response times
- Decreases warm-up time
- Reduced Cross interference's to VOCs



Electrochemical sensor cross sensitivity

Honeywell

Gas	Carbon Monoxide (CO)	Hydrogen Sulfide (H ₂ S)	Sulfur Dioxide (SO ₂)	Chlorine (Cl ₂)	Hydrogen Cyanide (HCN)
CO	100	< 10	0	0	< 5
H ₂ S	< 10	100	0	~ - 33	~ 1100
SO ₂	< 10	~ 20	100	0	~ 395
NO	< 30	< 0	0	0	0
NO ₂	< 15	~ - 20	~ - 120	120	~ - 120
Cl ₂	< 10	~ - 20	< 5	100	~ - 140
H ₂	< 60	< 5	0	0	0
HCN	< 15	0	< 50	0	100
HCl	< 3	0	0	0	~ 65
NH ₃	0	0	0	0	0
Ethylene	~ 50	0	0	0	0

Cross sensitivity

- Example:
 - While wearing an H2S Clip, a worker entered a 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 H2S Clip immediately went into alarm
 - The worker left the area, picked up an SO2 Clip, a real-time H2S detector manufactured by Draeger, and went back into the area
 - All three instruments went into alarm
 - Unfortunately, this time the worker collapsed
 - Worker was rescued, but had to spend significant time in the hospital

Cross sensitivity to VOCs actually benefit to customers

Effect of citrus solvents on H2S and COSH

Honeywell

- 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 very high concentration for the H2S sensor to go into alarm
- In most cases this is actually a benefit for our customers
- Although H2S GasAlertClip Extreme is not designed to function as a general VOC detector, the fact that it responds to high concentrations of VOC has saved the life of at more than one worker

Other Toxic Sensors and Considerations

Honeywell

- NH_3 sensor is only warranted for 12 months; background concentrations of ammonia will shorten the sensor life
- For calibration of O_3 and ClO_2 an appropriate generator must be used; gas generators are not compatible with the MicroDock system; Cl_2 is commonly used to bump test ClO_2 and O_3 .
- So response time is not impaired O_3 monitors do not use sensor filters
- Chlorine: Chlorine is a “sticky” gas and requires a 1LPM regulator for calibration, and can only be bumped not calibrated in the MicroDockII
- H_2S impairs the Cl_2 sensor response; when calibrating a detector that has both Cl_2 and H_2S sensors, it is important to calibrate H_2S first!
- Alcohols effect the performance of H_2S and COSH sensors



Photoionization Detectors

Honeywell

- Measuring Solvent, Fuel and VOC vapors in the workplace environment

Volatile Organic Compounds (VOCs)

Honeywell

- 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, Butadien, Hexane, Toluene, Xylene, Many others

Volatile Organic Compounds (VOCs)

Honeywell

- 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

VOC Toxicity

Honeywell

- 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

Honeywell

- 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

Honeywell

- Toxic substances tend to 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 fully manifest for years
 - Respiratory tract irritation (acute or chronic)
 - Dizziness, headaches (acute or chronic)
 - Long-term neurological symptoms: diminished cognition, memory, reaction time, hand-eye and foot-eye coordination
 - Mood disorders including 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)

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

Honeywell

- 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

Honeywell

- 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

Honeywell

- Percent LEL sensors have poor sensitivity to the large molecules found in found in fuels, solvents and other VOCs, with flashpoint temperatures higher than 38°C (100°F)
- 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 human toxicity levels are 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:

$$0.10 \times 11,000 \text{ ppm} = 1,100 \text{ ppm to trigger an alarm}$$

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

New VOC Exposure Limits

Honeywell

- Several newly 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, new TLVs® receiving much attention around the world
- 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!

Real-time measurement of VOCs

Honeywell

- Commonly used techniques used to measure VOC vapors:
 - Colorimetric detector tubes
 - Passive (diffusion) badge dosimeters
 - Sorbent tube sampling systems
 - Combustible gas monitors with catalytic "Hot Bead" sensors (percent LEL or PPM)
 - Photoionization detectors (PIDs)
 - Flame ionization detectors (FIDs)
 - Infrared spectra-photometers
- Most widely used instrument for VOC measurement is compact multi-sensor monitor with O₂, LEL, electrochemical toxic and miniaturized photoionization detector (PID)

LEL vs. PID Sensors

Honeywell



- Catalytic hot-bead combustible sensors and photoionization detectors complementary detection techniques
- Catalytic hot-bead sensors excellent for measurement of 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 to VOC measurement is to use a multi-sensor instrument capable of measuring all the atmospheric hazards that may be potentially present

PID - Operating Principle

Honeywell

- 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

How does a PID work?



Ultraviolet light used to remove electron from neutrally charged target molecules creating electrically charged fragments (ions)

Ionization Potential

Honeywell

- 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 detect the 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
- IP is sometimes referred to as IE (ionization energy)

Ionization Potential Values

Substance	Ionization Energy (eV)	Substance	Ionization Energy (eV)
Carbon Monoxide	14.01	n-hexane	10.18
Carbon Dioxide	13.77	Ammonia	10.16
Methane	12.98	Hexane	10.13
Water	12.59	Acetone	9.69
Oxygen	12.08	Benzene	9.25
Chlorine	11.48	Butadiene	9.07
Hydrogen Sulfide	10.46	Toluene	8.82

Characteristics of PID Lamps

- Sealed borosilicate 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

- Window material and filler gas determine output characteristics as well as operational life of lamp

Nominal Lamp Photon Energies	Gas in Lamp	Major Emission Lines		Relative Intensity	Window Crystal	Crystal 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 (MgF ₂)	115-7000
		10.03	123.6	650		
9.8eV	Krypton	10.03	123.6	650	Calcium Fluoride (CaF ₂)	125-8000

Technical Advances in PIDs

Honeywell

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



Critical PID Performance Issues

Honeywell

- Condensation and contamination on lamp window and sensor surfaces can create surface conduction paths between the sensing and counter electrodes
- If present, these currents cause false readings and / or add significant noise that masks intended measurement
- Buildup of even minor contamination provides nucleation points for condensation, leading to surface currents
- Most PID designs are forced to depend on active pumps, “ozone scrubbing”, or frequent cleaning of the lamp and detector to minimize the effects of contaminants and humidity condensation on PID readings

Critical PID Performance Issues: Humidity Effects & Contamination

PID Performance

Honeywell

Detector assembly

- Electrodes: sensing, counter and (in some designs) fence
- Lamp: 10.6 eV

BW PID

- 7 Series formatted miniaturized PID
- Fence electrode: electro statically collects charged fragments, prevents accumulation on window and collector electrodes
- Replaceable electrode stack: very inexpensive consumable component
- Easy to use lamp cleaning kit



Function of Fence Electrode

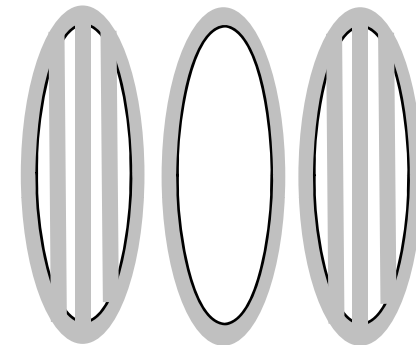
Honeywell

- Provides “short circuit path” that prevents surface currents due to particulate contaminants from reaching the sensing electrode
- Provides “short circuit path” that prevents surface currents due to humidity condensation from reaching the sensing electrode
- Provides “short circuit path” to prevent interference due to “photoelectron ejection”
- Electrostatically collects charged particulates and ionic fragments, prevents from accumulating on window, sensing and counter electrodes

How the fence electrode works

- Fence electrode is third electrode placed between sensing and counter electrodes
- Fence electrode is at same potential as sensing electrode
- Both fence and sensing electrodes are positive with respect to counter electrode
- Counter electrode is negative with respect to fence and sensing electrodes
- Surface currents cannot flow directly between counter and sensing electrode because they are blocked by fence electrode

Fence electrode (+)



Sensing electrode (+)

**Counter electrode
(- 200 V negative with respect to sensing and counter electrodes)**

PID Operating Characteristics

Honeywell

- Accurate, sensitive measurement to PPM levels (or lower)
- Able to detect most VOCs with:
 - Boiling Point <200o C.
 - Vapor Pressures (Pv) > 1.0 mm Hg at 20o C
 - VOCs with ionization energy up to 10.6eV
- Limitations:
 - Non-specific
 - Performance in high RH
 - Requirement for lamp cleaning

PID Operating Characteristics

Honeywell

- 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 Relative Humidity
 - High CH₄
 - High O₂

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 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

Honeywell

- 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

Honeywell

- Most VOCs with:
 - Boiling Point $< 200^{\circ}\text{C}$.
 - Vapor Pressures (P_v) > 1.0 mm Hg at 20°C
- Detect some inorganics (e.g. NO, NO₂, NH₃)
- Hydrides (arsine, phosphine)
- Do Not Detect:
 - CO, CO₂, SO_x,
 - Metals
 - Semi-Volatiles - PAH, higher phenols
 - Non-Volatiles - PCBs, pesticides

PID detectable compounds

- 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: Perchloroethylene, Trichloroethylene (TCE)
 - *Alkanes (saturated hydrocarbons C3 and higher5): Pentane, Hexane*
 - Unsaturated hydrocarbons (double or triple carbon-carbon bonds): Butadiene, Isobutylene
 - *Alcohols (-OH): Ethanol, Isopropanol*
- Sulfides and compounds containing sulfur: Mercaptans, Hydrogen sulfide
- Inorganics (compounds without carbon): Ammonia, Chlorine
- Hydrides: Arsine, Phosphine

Compounds not detectable by PID

Honeywell

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

Inorganic toxics: Carbon Monoxide, Hydrogen Cyanide, Ozone (O₃)

Hydrocarbons and VOCs w/ionization energies higher than 11.7eV: Methane, Natural Gas

Acids: Sulfuric Acid (H₂SO₄), Hydrochloric Acid (HCl), Nitric Acid (HNO₃)

Radiation

Aerosol droplets and particulates

PID as “Broad Range” Sensor

Honeywell

- 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

Honeywell

- 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

Honeywell

- 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

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

Honeywell

- 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 ≤ 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

Honeywell



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



Decision making with a PID

Honeywell

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

Correction Factors

10.6 eV Correction Factors

	RAE	BW	ION		RAE	BW	ION
Acetaldehyde	5.5	4.7	4.9	Jet fuel (J.P.8)	0.6	0.6	0.7
Acetone	1.1	1.1	0.7	Kerosene	n/a	1.1	0.8
Ammonia	9.7	11.2	8.5	Methylethylketone	0.9	0.9	0.77
Benzene	0.5	0.5	0.5	Naptha (iso-octane)	1.2	1.1	1.1
Butadiene	1	0.9	0.85	Styrene	0.4	0.46	0.45
Diesel fuel	0.8	1	0.75	Toluene	0.5	0.53	0.51
Ethanol	12	13.3	8.7	Turpentine	0.4	0.45	0.45
Ethylene	10	10.1	8	Vinyl chloride	2	2	2.2
Gasoline	0.9	0.7	1.1	Xylene	0.4	0.5	0.43
n-Hexane	4.3	4.3	3.3				

Single Chemical Mixtures

Honeywell

- 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

What about benzene?

- Benzene is almost never present all by its by itself
- Benzene is usually minor fraction of total VOC present
- ACGIH TLV = 0.5 ppm; OSHA PEL = 1.0 ppm – not able to detect at levels of concern
- Test for total hydrocarbons (TVOC), especially if the mixed product has an established PEL/TLV
 - Diesel 15 ppm
 - Kerosene 30 ppm
 - Jet Fuel (JP-8) 30 ppm
 - Gasoline 300 ppm

Non-dispersive Infrared Gas Sensors

Honeywell

- 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



Infrared Detectors

Honeywell

- 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

Infrared Detectors

Honeywell

- 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

Wavelength vs wavenumber

- 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 $100,000 \text{ cm}^{-1}$ (100,000 per centimeter)

- Example: The absorbance peak for CO_2 is = $4.26 \mu\text{m}$

$$4.26 \mu\text{m} = .000426 \text{ cm}$$

$$1 \text{ divided by } .000426 \text{ cm} = 2174 \text{ cm}^{-1}$$

$$\text{Wavenumber} = 2174 \text{ cm}^{-1}$$

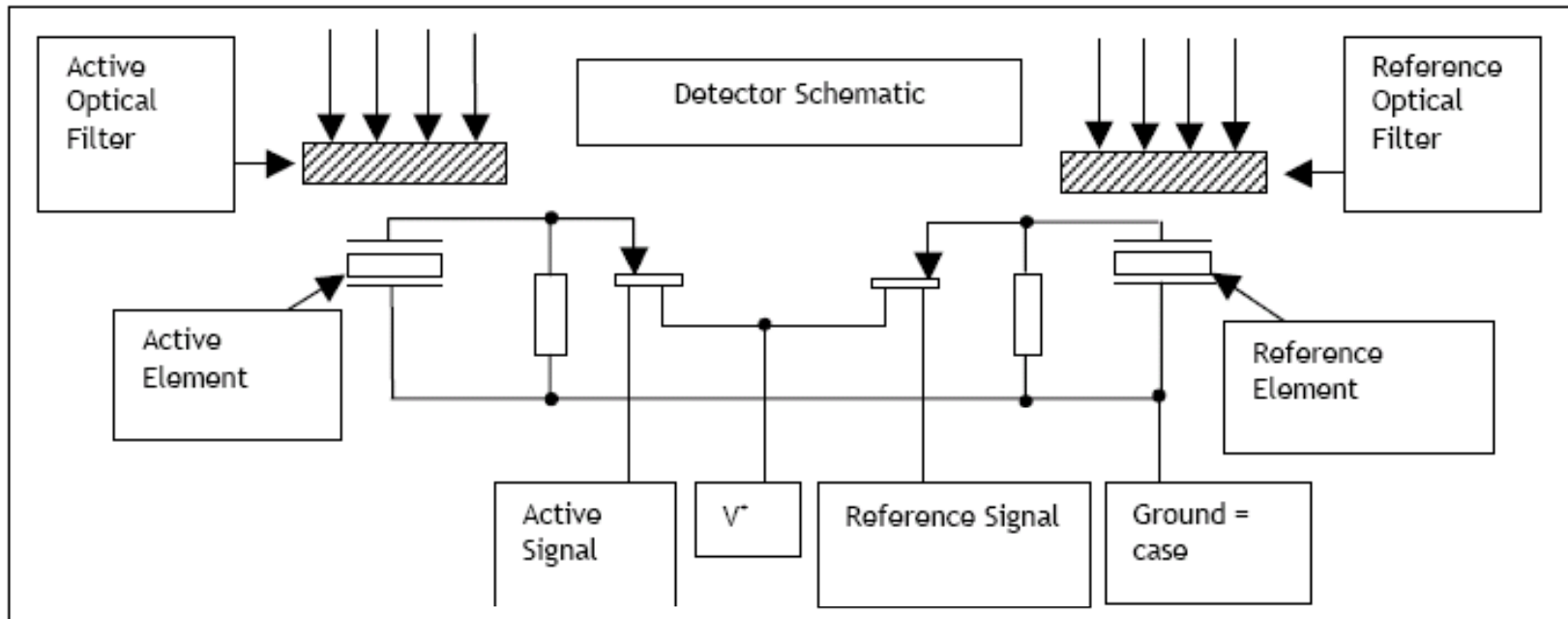
Infrared Detectors

- 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)



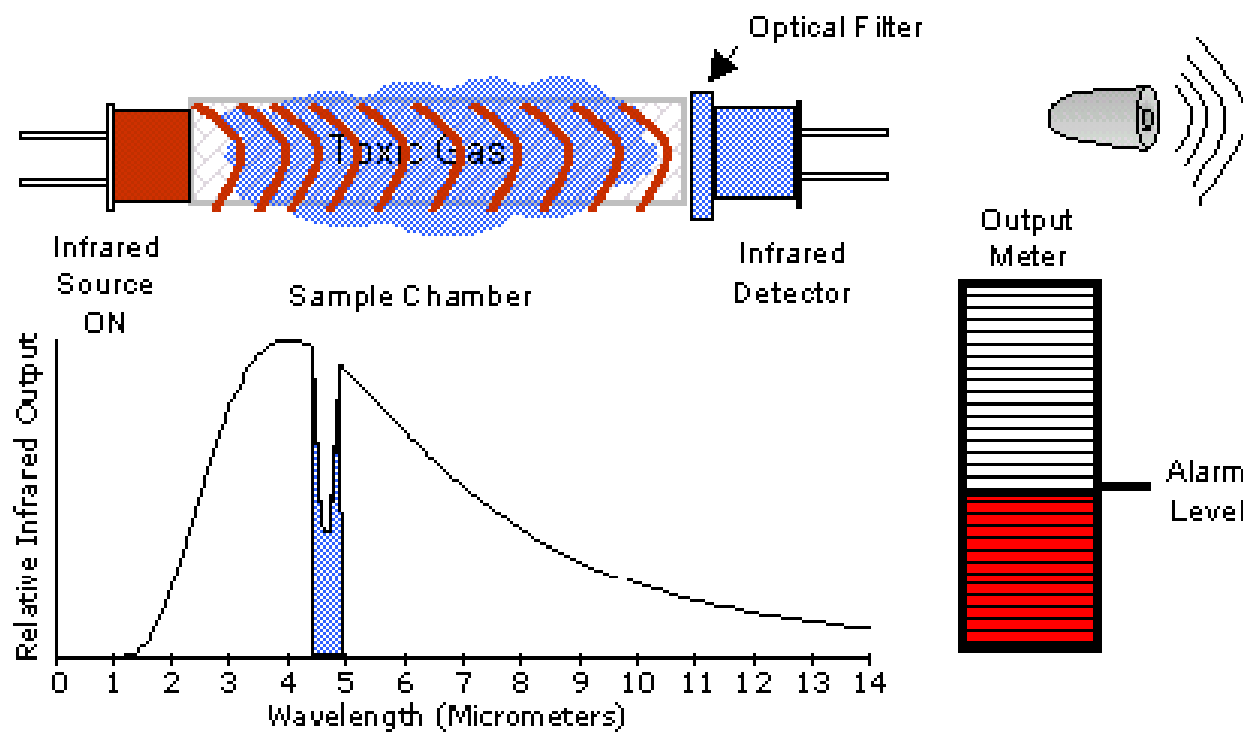
Infrared Detectors

The detector is a dual pyroelectric detector with each individual detector element optically filtered by integral windows to respond to specific bands of infrared radiation. The detector elements are individually buffered by on-chip FET transistors to provide a useable output. A schematic of the detector is shown below:



Infrared Detectors

- NDIR detector measures absorbance at specific wavelength to determine concentration of target gas



Non-Dispersive Infrared (NDIR) CO2 Sensor **Honeywell**

- Infrared absorption of CO2 molecules at a specific wavelength of 4.26 μm
- Sensor consists of IR source, light path, active detector and reference detector
- Concentration of CO2 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

Carbon dioxide

Honeywell

- 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

Carbon dioxide

Honeywell

- 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

CO₂ Exposure Symptoms

Honeywell

- 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

CO₂ - Toxic Contaminant

- 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-hr 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

CO₂ - Toxic Contaminant

- Chronic exposure to elevated indoor CO₂ concentrations linked with the following 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

- Even moderately elevated indoor concentrations produce symptoms

CO₂ - Toxic Contaminant

Honeywell

- Exposure to very high concentrations (e.g. exposure to 6% volume CO₂ for several minutes or 30% volume CO₂ for 20-30 seconds), linked to permanent heart damage
- Concentrations greater than 10% capable of causing loss of consciousness within 15 minutes or less

Concentrations of 40,000 ppm or higher should be regarded as IDLH



HA University

Selection and Use of Gas Detectors

BW
Technologies
by Honeywell

Honeywell

Classification for Intrinsic Safety

Honeywell

- 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
<p>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</p>	<p>Class I, Zone 0: Where ignitable concentrations are present continuously or for long periods of time</p>
<p>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</p>	<p>Class I, Zone 1: Where ignitable concentrations are likely to exist under normal operations; may exist frequently because of repair, maintenance or leakage; may exist due to breakdown of equipment in conjunction with an electrical failure; or adjacent to Class I, Zone 0 locations.</p>
	<p>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.</p>

European Cenelec / ATEX Product Markings **Honeywell**

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

Temperature Codes

- Auto-ignition temperature in °C, 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

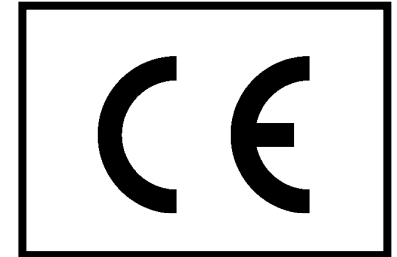
Temperature Codes

- Temperature code groups can also be expressed as a range of temperatures
- Gases with low auto ignition 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 auto ignition 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 Mark

- “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”



Ingress Protection

Honeywell

- 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

First No.	Degrees of Water Protection
0	No special protection
1	Water drops falling vertically must not have any harmful effect
2	Water drops falling at any angle up to 15° from the vertical must not have any harmful effect
3	Water hitting the object any angle up to 60° with the vertical must not have any harmful effect
4	Water splashing against the object from all directions must not have any harmful effect
5	A jet of water sprayed from all directions must not have any harmful effect
6	Water from a temporary floods, such as heavy seas, must not enter in any harmful quantity
7	If the object is dipped into water under the defined conditions of pressure and time, water must not enter it in any harmful quantity
8	If the object is submerged in water, water must not enter in any harmful quantity

Sample-Draw vs. Diffusion

Honeywell

- Ideal confined space entry gas detection package should include
 - Detector with an electronic pump for pre-entry testing and sentry/attendant monitoring
 - Small diffusion safety gas detectors for each individual working in a confined space

Sample-Draw vs. Diffusion

Honeywell

- Sample lag time
- Stabilization time
- Potential for leakage in system
- Potential for pump malfunction

Battery Type

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



Datalogging vs. Non-datalogting

Honeywell



Included Accessories

Honeywell



Calibration, Bump Testing and Verification

Honeywell

- Calibration: The adjustment of an instrument's response to match a desired value compared to a known concentration of test gas.
- Bump test: Briefly applying gas to check that each sensor responds to target gas and that the alarms are working.
- Calibration Verification: - A bump test utilizing a known concentration of a challenge gas to demonstrate that an instrument's alarms are activated and the response to the gas is within acceptable limits.
- DOCUMENT ALL TESTING.....IF IT WASN'T DOCUMENTED IT DIDN'T HAPPEN



Make sure instrument has been calibrated!

Honeywell

- Follow manufacturer recommendations at a minimum
- “Zero” instrument in fresh air prior to use
- Verify Accuracy Daily!
- Functional “bump” test sufficient
- Adjust “span” only if necessary
- Replacing a sensor requires calibration and a 5 min. stability check.

Loss of sensitivity can be due to:

Honeywell

- 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

Bump Testing

Honeywell

- The safest course of action is to expose the sensors to known concentration test gas before each day's use!
- Prudent to perform a bump test anytime a detector changes custody
- Bump test any time a sensor has been exposed to a gas concentration that exceeds the detection range
- Bump test any time there is doubt regarding the response of a safety gas detector
- This test is very simple and takes only a few seconds to accomplish!

When to Calibrate?

Honeywell

- 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
- The BW Technologies by Honeywell factory default calibration interval is 180days

Don't be afraid of calibration!

- Modern designs make calibration easy and automatic
 - All-In-One Calibration Mixtures Make Calibration and Functional Testing Easy!
 - MicoDockII stations take all the guess work out of calibration, bump testing and record keeping



Is calibration dangerous?

Honeywell

So, is it dangerous to use a cylinder that contains 25 ppm H₂S?

34 liters = 1.2 cubic feet @ 25 ppm H₂S

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 H₂S



Record Keeping

Honeywell

- 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!

Am I safe?

Honeywell

- Atmospheric hazards are frequently invisible to human senses
- You don't know whether it's safe until it's been tested with a properly operating gas detector!

Questions?

Honeywell

Questions?

Answers.