NEW HAMPSHIRE FIRE ACADEMY

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Division of Fire Standards & Training
And Emergency Medical Services

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RESCUE SKILLS
AIR MONITORING

February, 2009

Rescue Skills – Air Monitoring

PREPARATION

Motivation: This course of study has been prepared to provide the student with the basic skills necessary to safely conduct air monitoring for possible hazardous environment as may be encountered in rescue situations. It is one of a sequence of courses within the Introduction to Technical Rescue Skills Program needed to participate in advanced technical rescue programs.

Prerequisites: Certified Fire Fighter I

MATERIAL

Equipment: Power point projector, laptop and screen to accommodate presentation, easel pad with markers

Air monitoring equipment and supplies listed on page 28 in this manual.

PERSONNEL

Primary Instructor: One (1) Primary Instructor and two (2) Assistant Instructors knowledgeable in air monitoring skills to conduct the classroom (cognitive) portion and the skills (Psychomotor) portion of the program.

RECOMMENDED TIME TO COMPLETE TRAINING: Four (4) hours to conduct the classroom portion and two (2) hours for the skills portion

OBJECTIVES

TERMINAL OBJECTIVE

- Upon completion of **Introduction To Technical Rescue Skills – Air Monitoring**, The student, given the proper equipment, shall safely demonstrate monitoring atmospheres for oxygen level, combustibility and toxicity.

COGNITIVE OBJECTIVES

At the completion of this course the student will be able to:

- Utilizing the Risk based response, Identify 3 specific hazard areas.
- Identify protection level of Structural FF gear and SCBA as it relates to Hazardous Atmospheres
- Identify specific area of operation for utilization of air monitoring devices
- Describe how catalytic filament detectors operate and sample flammable/combustible gases.
- Describe how electro-chemical sensors operate and sample gases
- Describe flammable range
- Utilizing correction factors, convert meter readings to actual readings
- Identify levels of response and evacuation levels of gas percentages
- Describe Volatile organic compounds
- Define LEL, IDLH, TWA, STEL
- Describe how photo ionization detectors sample and analyze gases
- Describe how colorimetric tube samples gases
- Given an Unknown Material Identify/Classify by Hazard
- Given a meter reading, convert from percentages of gas to parts per million

PSYCHOMOTOR OBJECTIVES

At the completion of this course the student will be able to:

- Operate Four Gas Meter
- Use and Read pH Indicator and/or Meter
- Operate a PID meter

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Introduction
To Technical
Rescue
Skills

Air Monitoring

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Air Monitoring

Presented By:

New Hampshire Fire Academy

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Standards & Guidelines

NFPA 472 – Professional Competence of Responders to Hazardous Materials Incidents

NFPA 1006 – Rescue Technician Professional Competence

NFPA 1670 – Operations & Training for Technical Rescue Incidents

OSHA 29CFR 1910.120 – Hazardous Waste Operations & Emergency Response

OSHA 29CFR 1910.146 – Permit-required Confined Space

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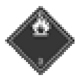
Risk Based Response Model

- Risk = Hazards + Probabilities

LEL



Toxic

pH

Route of Entry

Chem./Phys. Properties

Magnitude

Other Size-up

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Structural Firefighter Gear with SCBA

- **Excellent respiratory protection (PF $\geq$ 10,000)**
- **Limited liquid protection**
- **Estimated protection against skin absorption of vapors/aerosols (PF ~ 10)**

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Why Air Monitor ?

•<u>Tools</u> to assist

– **Classify <u>Hazards</u>!**

– **Assess <u>Probabilities</u>!**

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Where to Air Monitor ?

- **HazMat**
  - Perimeter Establishment & Maintenance
  - Leak Detection
  - Selection of PPE
- **Carbon Monoxide**
- **Confined Space Rescue**
- **Trench Rescue**
- **Building Collapse**
- **Firefighting**

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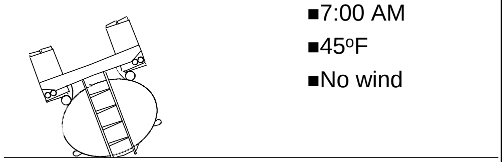
Perimeter Monitoring

Gasoline Tank Truck Rollover



- 7:00 AM
- 45ºF
- No wind

- TWA = 100 ppm

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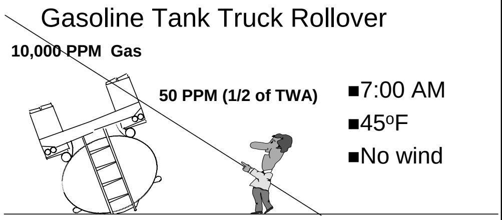
Perimeter Monitoring

Gasoline Tank Truck Rollover



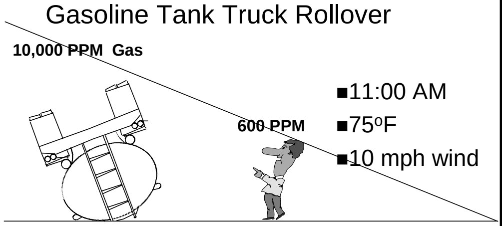
- 7:00 AM
- 45ºF
- No wind

- Perimeter = 100 feet

26

Perimeter Monitoring

Gasoline Tank Truck Rollover



- Perimeter now should be 300 feet
- Perimeter worker overexposed

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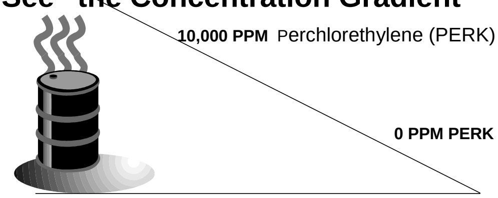
Leak Detection

“See” the Concentration Gradient



- Allows you to “see” concentrations
- As concentration increases you are closer to the source

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Initial PPE Assessment

- **Some “Incidents” may not be an “Incident” at all and many not require any PPE (Personal Protective Equipment)**
- **Some non-incidents are really “INCIDENTS” and require substantial PPE**

Air Monitoring Devices are an excellent AID in this decision making process

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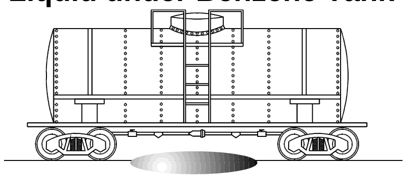
Initial PPE Assessment
Pool of Liquid under Benzene Tank Car



- Benzene (PEL = 1 ppm)
- Ambient conditions: 95ºF, 95% Humidity

How do you dress out?

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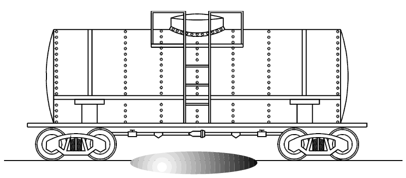
Initial PPE Assessment



- Level A is unnecessary if no Benzene
- Level A represents a Heat Stress Risk
- Car contents at 65ºF
- “Leak” really condensation

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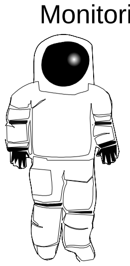
Air Monitoring for Decon

Monitoring helps answer questions:



- Is Worker Contaminated?
- Is Decon Complete?
- Is my turn out contaminated with Fuel Products?

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Effective Monitoring and Sampling

- **Corrosive risk - pH determination**
- **Oxygen determination**
- **Flammable/explosive level**
- **Toxic determination**
- **Radiation determination**

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Principles of Detection

- Catalytic Filament – Catalytic Bead
  - Wheatstone Bridge
- Electro-Chemical
- Colorimetric
  - PH Paper, Classifier Strips, Reagent Tubes
- Ionization
  - Photo
  - Flame
- Radiation

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Terminology

- Flammability
- Toxicity
  - Parts Per Million (PPM)
- Radiation
  - Alpha, Beta, Gamma

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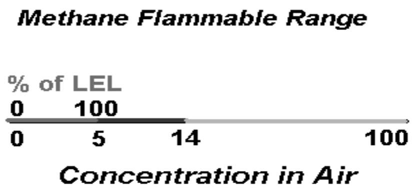
Flammability



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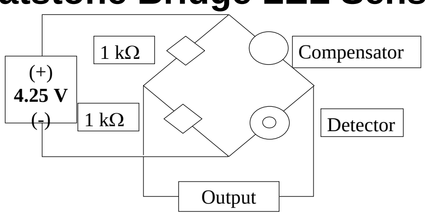
Wheatstone Bridge LEL Sensor



- **Measures change in resistance due to change in temperature of gas burning on detector**

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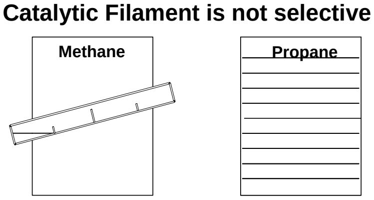
Selectivity Vs Sensitivity

- **Catalytic Filament is sensitive**
- **Catalytic Filament is not selective**



Ruler cannot tell difference between yellow and white paper

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Is the LEL Sensor Sensitive Enough?

LEL Sensors were designed to measure Methane

Gas/Vapor	LEL (%vol)	Sensitivity (%)
Acetone	2.5	45
Benzene	1.2	40
Diesel	0.8	30
Methane	**5.0**	**100**
MEK	1.4	38
Propane	2.1	53
Toluene	1.1	40

LEL Sensors are not suited for "cool burning" chemicals

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What is a Correction Factor?

- **Correction Factor (CF)** is a measure of the sensitivity of the Meter to a specific gas
- **Low CF** = high sensitivity to a gas
- **CFs** are scaling factors, they do not make a Meter specific to a chemical, they only correct the scale to that chemical.
- **Correction Factors** allow calibration on cheap, non toxic "surrogate" gas.
- Check Manufacturer's Literature **CF** listing.

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Actual Readings/Correction Factors

- Actual = Meter x CF

MEK

Actual = ?

Meter = 24

CF = 5

MEK

Actual = 25

Meter = ?

CF = 5

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Actual Readings/Correction Factors

- Actual = Meter x CF

Propane
Actual = ?
Meter = 10
CF = 1.9

Propane
Actual = 25
Meter = ?
CF = 1.9

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Action Levels / Relative Response

- Unknown Chemicals
  - 10% of the LEL
  - Meter Alarm Level
- Known Chemicals with Correction Factors
  - <25% of converted LEL = Ventilate
  - 25 59% LEL = Evacuate Civilians/Ventilate
  - 60% or greater = Evacuate all Personnel

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Most HazMat Incidents are:

Volatile Organic Compounds (VOCs)

Fuels (the majority of HazMats)

Greases, Oils, Degreasers

Paints, Solvents, Plastics, Resins

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Doesn't LEL measure VOCs?

- **LEL Measures** FLAMMABILITY **not** TOXICITY!
- **Many VOCs are toxic well below the sensitivity of an LEL sensor.**
- Using LEL to measure for Toxicity is like using a yardstick to measure the thickness of a sheet of paper!
- Wrong Tool for the Job!

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% Atmosphere to PPM

$\frac{\text{1,000,000 Parts}}{\text{1,000,000}}$ **= 100% = 1 ATM**

$\frac{\textbf{1,000,000 Parts}}{\textbf{100}} = \frac{\textbf{100\%}}{\textbf{100}}$ **= 1% ATM** ***= 10,000 PPM***

100% Methane LEL = 5% ATM = 50,000 PPM
1 % LEL of Methane = 500 PPM

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What is Toxicity?

Toxicity = Concentration x Exposure Period

- Acute **Toxicity will get you immediately (IDLH)**
- Chronic **Toxicity will get you over a longer period of time (TWA)**

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LEL Compared to PPM

- **LEL is more for acute toxicity**

  LEL gets you home tonight

- **PPM is more for chronic toxicity**

  PPM lets you enjoy retirement!

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Measures of Toxicity

- IDLH
  - **Immediately Dangerous to Life & Health**
    - **Escape within 30 Minutes**
    - **No Lasting Effects**
- TWA
  - **Time Weighted Average**
    - **Average 8 Hour day - 40 Hour week**
- STEL
  - **Short Term Exposure Level**
    - **15 minute exposure**
    - **Maximum 4 times/day**
    - **1 Hour of rest between exposures**

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We need to measure Toxicity

in

Parts Per Million (PPM)!

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How can we measure in PPM?

- Electro-Chemical Sensor
- Colorimetric Indicators
- Photo Ionization Detector (PID)

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Electro-Chemical Sensor

- **Oxygen**
- **Toxics**
  - CO
  - H_2S
- **Metal Oxide Sensors**

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Electro-chemical Sensors

- **Faster response than tubes**
- **Affordable ("Poor Man's PID")**
- **Sensitive to Temperature and Humidity leading to false alarms**
- **Can be poisoned & ruined by over-ranging**
- **Logarithmic output limits accuracy. Entry decisions cannot accurately be made based on PPM.**
- **Non-specific / Cross Sensitivity**

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Electrochemistry

Theory of Operation

- Chemicals react with a solution, coating or a solid
- Reactions are measured

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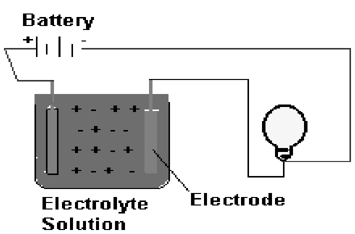
Electrochemistry



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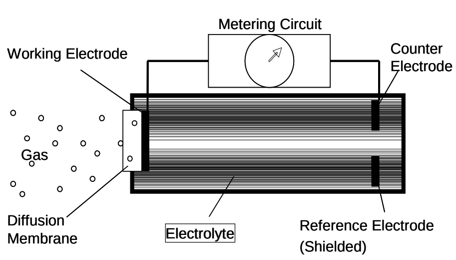
Electrochemistry



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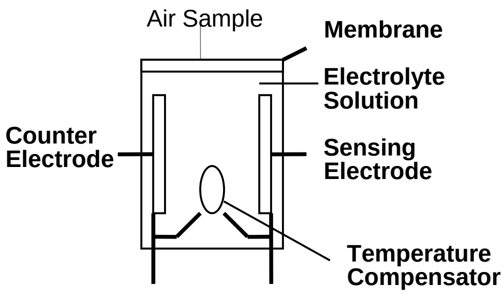
Electro-Chemical Sensor



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% Atmosphere to PPM

$\frac{\text{1,000,000 Parts}}{\text{1,000,000}}$ **= 100% = 1 ATM**

$\frac{\text{1,000,000 Parts}}{100} = \frac{100\%}{100\%}$ **= 1% ATM = *10,000 PPM***

Oxygen ≅ 21% of ATM or 1/5th of Atmosphere
1 % ↑↓ in Oxygen = 5% ATM = 50,000 PPM

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Multi Gas Meter

- Lithium Ion battery
- Measures 0-100% LEL of Calibration Gas
  - Conversion Factors for know VOC's
- Sensor Life
- Cross Sensitivity
- Calibration
  - "Prior to Use"
- Cleaning/Maintenance

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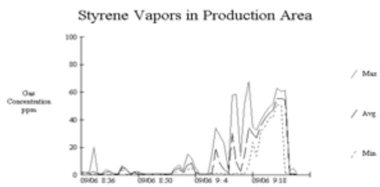
Data-Logging as a Tool

- Document Worker Exposures



- Provide Evidence to Justify Evacuations

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Colorimetric Tubes

- Proven technology
- “Snap Shots” only like a “Polaroid” camera, cannot provide continuous monitoring with alarms
- Potential of sampling error
- 25 35% accuracy
- Readings subject to interpretation
- Tubes expire and large stock is expensive
- Slow to respond

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What is a PID?

- PID = **Photo-Ionization Detector**
- Detects VOCs (Volatile Organic Compounds) and Toxic gases in low concentrations of 0.1 to 2000 ppm.
- Over 90% of HazMat incidents are fuel product related and are easily measured with a PID
- A PID is a very sensitive broad spectrum monitor, like a “low level LEL”

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PIDs Measure in PPM

- Fastest response
- Very Accurate (the “heart of a GC”). Entry decisions can be made directly based on PPM with confidence.
- Optical Technology not affected by contaminants
- Non specific

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What does a PID Measure?

Ionization Potential

- **IP** determines if the PID can “see” the gas
- If the **IP** of the gas is less than the **eV** output of the lamp the PID can “see” 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 manufacturer’s Literature, NIOSH Pocket Guide and many chemical texts.

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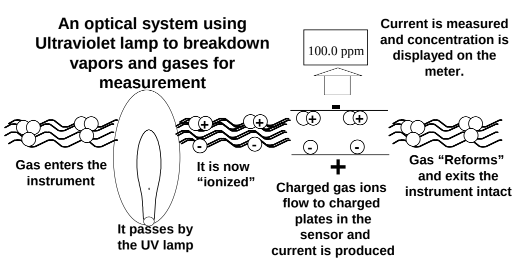
How does a PID work?



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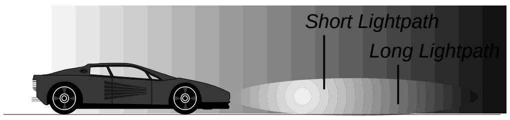
How Humidity Affects PID



- The closer to the headlights the easier it is to see something through fog.
- By reducing the distance the UV light travels in a PID the affects of humidity are drastically reduced

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Electrodeless Discharge PID lamp

- Extremely low power draw
  - cool lamp and small batteries
- No internal contamination
- Extremely rugged
  - Hermetically sealed lamp window with no metal to glass interfaces to fail (10.6eV)
- Virtually no RFI or EMI
  - Low-frequency electric field excites lamp like cooking a hotdog in a microwave
- Inexpensive to replace

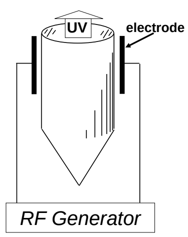

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Photo Ionization

Theory of Operation

- Uses ultraviolet light to ionize suspect agents
- Ions flow to negative or positive plates
- Current is measured; then gas reforms and exits
- Most common lamps are 9.8, 10.6, 11.7eV

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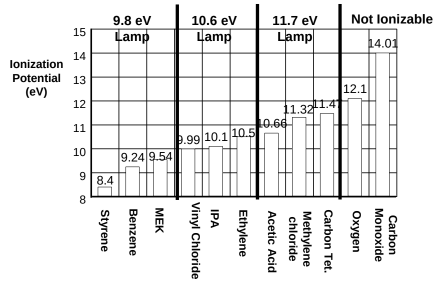
PID Lamps

Some Ionization Potentials (IPs) for Common Chemicals



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PID Lamps

Why not always use 11.7 eV Lamps?

- **9.8 & 10.6 provide more specificity**
- **10.6 lasts 12-24 months**
- **10.6 costs less ($195)**
- **10.6 is more accurate**
- **11.7 is required for high energy compounds like Methylene Chloride**
- **11.7 Lithium Fluoride crystal absorbs water and degrades faster**
- **11.7 lasts about 2-3 months**
- **11.7 costs more ($345 in ampule)**

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If the “wattage” of the gas or vapor is less than the “wattage” of the PID lamp then the PID can “see” the gas or vapor!

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What does a PID Measure?

- Organics: Compounds Containing Carbon (C)
  - **Aromatics** - compounds containing a benzene ring
    - BETX: benzene (9.24), ethyl benzene (8.76), toluene (8.82), xylene (8.56)
  - **Ketones & Aldehydes** - compounds with a C=O bond
    - acetone (9.71), methyl ethyl ketone or MEK (9.54), acetaldehyde (10.22)
  - **Amines & Amides** - Carbon compounds containing Nitrogen diethyl amine (8.01)
  - **Chlorinated hydrocarbons -** trichloroethylene (TCE)
  - **Sulfur compounds -** mercaptans
  - **Unsaturated hydrocarbons** - C=C & C C compounds
    - butadiene (9.07), isobutylene
  - **Alcohol's**
    - ethanol (9.51)
  - **Saturated hydrocarbons**
    - butane (10.63), octane (9.82)
- Inorganics: Compounds without Carbon
    - Ammonia (10.18)
    - Semiconductor gases: Arsine (9.89)

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What PIDs Do Not Measure

- Radiation
- Air
  - N_2
  - O_2
  - CO_2
  - H_2O
- Toxics
  - CO
  - HCN
  - SO_2
- Natural gas
  - Methane CH_4
  - Ethane C_2H_6
- Acids
  - HCl
  - HF
  - HNO_3
- Others
  - Freons
  - Ozone O_3

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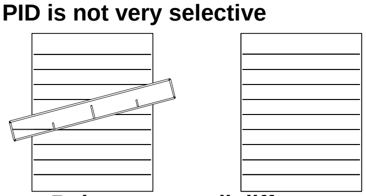
Selectivity Vs Sensitivity

- **PID is very sensitive and accurate**
- **PID is not very selective**



Ruler cannot tell difference between yellow and white paper

Selectivity Vs Sensitivity

Use your head for Selectivity and the PID for Sensitivity

- **PID is sensitive to chemicals not specific**
- **Correction Factors set correct PID scale**
- **PID should stay on Isobutylene (Calibration gas) until unknown is identified**

A PID is a Gas Chromatograph where the column is between your ears!

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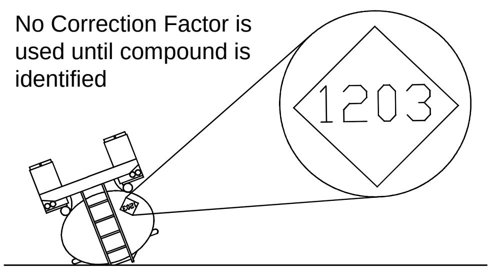
Selectivity Vs Sensitivity

No Correction Factor is used until compound is identified



Classify then Identify then Quantify!

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What is a Correction Factor?

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- Low CF = high sensitivity to a gas
- CFs are scaling factors, they do not make a Meter specific to a chemical, they only correct the scale to that chemical.
- Correction Factors allow calibration on cheap, non-toxic “surrogate” gas.
- Check Manufacturer’s Literature CF listing.

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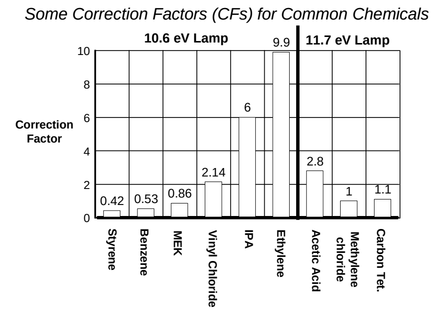
What is a Correction Factor?



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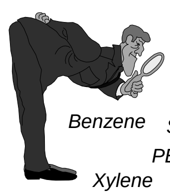
Air Monitor like a Magnifying Glass

A Magnifying glass lets a detective see fingerprints; an Air Monitor lets us "see" VOCs



Ammonia
Carbon Disulfide
Benzene *Styrene*
PERC *Jet Fuel*
Xylene

<u>Classify</u> then Identify !

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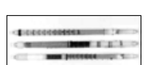
Colorimetric Indicators

- **pH Paper** 
- **Classifier Strips** 
- **Colormetric Tubes** 
- **Reagent Test Kits** 

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Corrosives

- pH Paper Utilization
  - Measures Acid & Bases
  - Useful for liquids and vapors
  - Use 1st in line of metering
- Use
  - On PPE for indication of exposure
  - Tape to end of pike pole to extend reach

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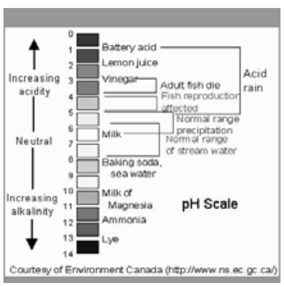
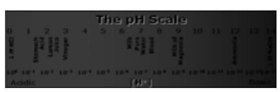
pH Scale



- Power of Hydrogen



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Carbon Monoxide Response

- **Carbon Monoxide is a toxic gas that can occur in homes and buildings. It is colorless, odorless, tasteless and non-irritating. CO is a poison and can be deadly at high levels. At low concentrations, CO can go undetected and contribute to nagging illnesses. It can compound pre-existing health problems and often times goes unblamed in premature deaths.**

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Carbon Monoxide Response

CO Levels

12,800ppm	*Death 1-3 minutes*
1,600ppm	*Nausea within 20 minutes death within 1 hour*
800ppm	*Nausea and convulsions within 2 hours*
400 ppm	*Frontal headaches 1 to 2 hours: life threatening after 3 hours.*
50ppm	*Maximum concentration for continuous exposure in any 8 hour period.*
9ppm	*Maximum acceptable level of CO in a living space.*

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Final Monitoring Practical

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Questions

Multigas Detectors

for the Fire Service…know the basics

by Ted Hardenbergh
Portable Instrument Product Line Manager
Instrument Division

The Need

Emergency response crews face two basic challenges when entering dangerous environments. They need to know if the air is acceptable for normal, unprotected breathing and safe from potential explosions. Portable multigas detectors can help meet this challenge.

A wide variety of gas detection equipment is available on the market today. Technology exists to meet almost any detection need from simple, single toxic gas detectors to portable analytical laboratories. However, one flexible product at the right price is the best choice for both daily use and emergencies. That product is the "multigas" detector: one unit that can sense several gases at the same time.

Gas detection needs are expanding. Increasingly, fire services are being called on to handle situations where hazardous substances may be present and proper detection equipment is necessary.

The Basics

Portable multigas detectors come in many styles and configurations. In most cases, they can simultaneously detect three to five gases and alert the user when the gas exposure level becomes a concern.

These detectors consist of multiple sensors in a single case. The electronics then change the sensor output into a numerical display showing the level of gas exposure. There are four basic types of portable gas sensors:

- Catalytic
- Electrochemical
- Infrared
- Photoionization Detectors

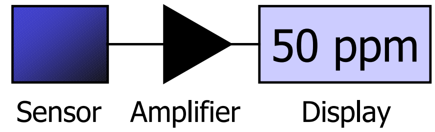

Figure 1
Basic detector operation

These sensors operate in different ways to enable them to detect certain gases. The two most common sensors are the catalytic and electrochemical sensors. Catalytic sensors detect flammable gases and electrochemical sensors detect many toxic gases. Infrared sensors and PID sensors are designed to detect either special gases or especially low gas levels, which cannot be detected by the other two technologies.

How Catalytic Combustible Sensors Work

To detect flammable gases, a heated wire is used. Basically, a special wire coil is heated by applying power to it.

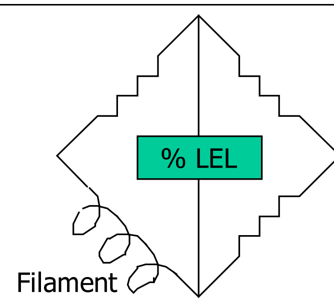

Figure 2
Combustible gas circuit

The wire filament is selected or specially treated so that the surface will react and will readily burn (oxidize) gases that come in contact with it. If this coil is exposed to combustible (oxidizable) gases, the gas molecules react on the wire surface. This reaction releases heat and increases the temperature of the wire. As the wire temperature increases, the electrical resistance of the wire increases and is measured by a simple "Wheatstone Bridge" circuit which accurately measures this change. The result is then converted to a display reading on the face of the instrument (see Figure 2).

Since the catalytic combustible gas sensors act like small heaters, they use a lot of power and regularly require fresh or recharged batteries for the combustible gas detector. To increase sensitivity and reduce power consumed by these sensors, many manufacturers form a ceramic bead around the wire coil. This bead is also treated with special chemicals to make it more reactive. The bead increases sensitivity by providing more surface area for the reaction to occur.

What Catalytic Combustible Sensors Detect

In order for a flame to exist, three conditions must be met. You must have:

1. A source of fuel such as methane or gasoline vapors.
2. Enough oxygen to oxidize or burn the fuel.
3. A source of heat to start the process.

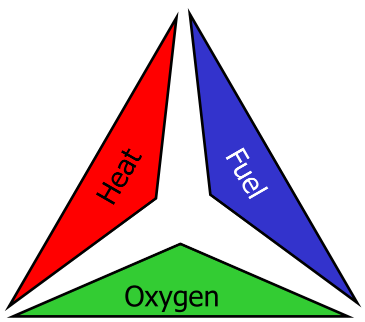

Figure 3
The Fire Triangle: Oxygen, Fuel and a Heat Source

Explosive Limits

Generally, for flame to occur, the fuel must be in a gas form to mix with air (the oxygen source). For instance, with gasoline, the liquid does not burn but the vapor given off by the liquid creates a dangerous situation. If a liquid does not give off enough vapors, it will not burn easily under normal conditions.

In general, any flammable substance with a flashpoint (the minimum temperature at which a liquid gives off vapor in sufficient concentration to ignite) of less than 100°F may be detected. (NFPA 325 lists the flashpoint of many common substances). Liquids such as diesel and jet fuels, have high flashpoints and cannot be readily detected by catalytic sensors since they do not give off enough vapors at normal temperatures to support combustion.

Too much gas can also displace the oxygen in an area and fail to support combustion. Because of this, there are limits at both low-end and high-end gas concentrations where combustion can occur. These limits are known as the Lower Explosive Limit (LEL) and the Upper Explosive Limit (UEL). They are also referred to as the Lower Flammability Limit (LFL) and the Upper Flammability Limit (UFL). Figure 4 graphically demonstrates these limits relative to gas concentration.

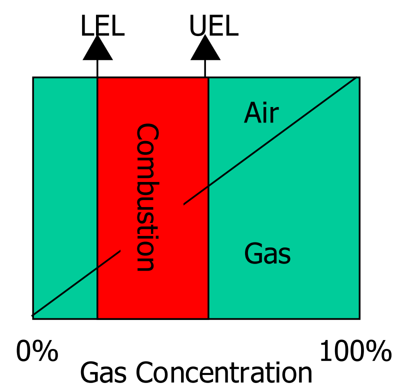

Figure 4
Lower and Upper Explosive Limits

To sustain combustion, the correct mix of fuel and oxygen (air) must be availaible. The LEL indicates the lowest quantity of gas which must be present for combustion and the UEL indicates the maximum quantity of gas. The actual LEL level for different gases may vary widely and are measured as a percent by volume in air. These LEL numbers are also published in NFPA 325.

Gas Type	LEL (% gas by volume)	UEL (% gas by volume)
Methane	5.0%	15.0%
Hydrogen	4.0%	75.0%
Propane	2.1%	9.5%
Acytelene	2.5%	100%

Table 1
Explosive limits for some common gases

Most combustible gas instruments measure in the LEL range and gas readings are shown as a percentage of the LEL. For example: a 50% LEL reading means the sampled gas mixture contains half the gas necessary to support combustion.

Combustible Gas Response Factors

Catalytic combustible gas sensors can detect a wide variety of potentially flammable gases. From natural gas leaks to gasoline spills, this sensor is very good at helping to determine if there is danger.

However, it should be noted that different combustible gases react at different rates with the sensor. For instance, the same "%LEL" levels of two common flammable gases such as methane and pentane will yield different sensor outputs and different readings on the instrument display. To ensure an appropriate response on average, a mid-range response gas such as pentane is often used for calibrating the instruments.

Gas Type	Actual % LEL	Actual Gas Concentration	Typical Display Reading (%LEL)
Pentane	50%	0.70%	50%
Methane	50%	2.50%	100%
Propane	50%	1.05%	63%
Styrene	50%	0.55%	26%

Table 2
Comparison of actual LEL and gas concentrations with typical instrument readings

Table 2 shows four typical flammable gases and the resulting displays of a combustible gas detector calibrated to read pentane. There is a wide variation in the typical catalytic sensor response to these gases. Since you do not know what you will be called on to detect, the most common approach is to select a "middle-of-the-road" gas, such as pentane, as your calibration gas.

Catalytic combustible gas sensors have met the needs of many industries for many years. In supporting the fire service's requirements for proven, reliable and cost-effective hazard analysis, this workhorse technology will continue to be a key factor for years to come.

Electrochemical Toxic Gas Sensors

In addition to detecting combustible gases, multigas instruments can help determine if the atmosphere is acceptable for breathing. These instruments can answer two basic questions:

1. Is there enough oxygen present for me to breathe? and
2. Are there any other toxic gases present which can harm me?

Once again, portable gas detectors can handle the majority of common air-monitoring situations. Many can be ordered with a combustible sensor, an oxygen sensor and up to two or three toxic gas sensors, depending on your application.

How Electrochemical Toxic Gas Sensors Work

Toxic gas sensors measure one type of gas at a time. The two toxic gases most commonly encountered on the job are carbon monoxide (CO) from furnace leaks or car exhaust and hydrogen sulfide (H_2S) from sewer gas.

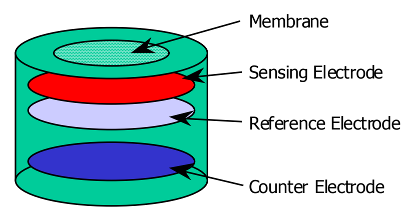

Figure 5
Electrochemical Toxic Gas Sensors Basic Construction

An electrochemical sensor is similar to a small battery. One chemical component required to produce the electric current is not present in the sensor cell. The target gas, such as CO, diffuses into the membrane at the top of the sensor. The CO then reacts with the chemicals on the sensing electrode and generates an electrical current to be measured and displayed as in Figure 1. If no CO is present, no reaction occurs and no current is generated.

Electrochemical sensors are typically available for a wide variety of gases, from carbon monoxide to chlorine. Check with your safety products supplier to see what is available to meet your specific needs.

Cross-Sensitivity

Since sensor output is driven by chemical reactions, there are many circumstances where gases other than the ones we are interested in will cause a reading on the instrument display. This is known as "cross-sensitivity" and chemical engineers designing the sensors do their best to limit this phenomenon. They attempt to make the reaction very specific or install filters to screen out common "interferants" when possible.

As an example, most electrochemical CO sensors also respond to alcohol vapors and unsaturated hydrocarbons, such as ethylene or acetylene. When exposed to these substances, the instrument displays an upscale reading and can produce a "false alarm" for CO. Fortunately, these compounds are present only in limited quantities in fire service situations.

It pays to know what types of gases you are likely to encounter on your calls. If you are calling mostly on homes, oxygen, CO and H_2S may be all you need to monitor. Calls to industrial facilities, however, present the possibility of a much wider range of deadly gases, so you must be careful to fully understand the risks of each response situation.

Oxygen Sensors

Oxygen sensors operate on the same basic principles as other electrochemical sensors. Oxygen from the air diffuses into the sensor and reacts to produce an electrical current. Typically, oxygen sensors use the oxidation of lead as the basis for their detection. As lead is consumed (oxidized), sensor life diminishes.

Our surrounding atmosphere contains an average of 20.8% oxygen. Since oxygen is present in the air at all times, oxygen sensors are slowly being consumed, even as they sit "unused." Manufacturers are responding by slowing the reactions in the sensors. Just a few years ago, these sensors typically lasted a year; some now last well over two years.

Although you may want to place your oxygen sensor in a box containing no oxygen to increase the life of the sensor, this may damage your sensor permanently. Be sure to follow the manufacturer's instructions on proper storage for your instruments.

Infrared Sensors

Some gases are not very reactive and require detection by other means. Carbon dioxide (CO_2) is an example of an important gas that cannot be detected using typical electrochemical cells.

Infrared (IR) sensors, which are commonly used to detect CO_2, approach gas detection in a completely different way. With IR sensors, the amount of gas is determined by how much the gas absorbs light, not by some type of chemical reaction to detect the gas. No chemical reaction occurs.

Gases absorb certain wavelengths of light and certain gases absorb certain frequencies. For instance, astronomers determine the composition of distant stars and galaxies by noting which wavelengths of light are missing from the spectrum of light coming from the object.

Figure 6 shows the basic layout of a portable instrument IR sensor. A special "source" emits light that passes through a filter. This filter screens out all but a very specific set of light wavelengths, typically in the infrared part of the spectrum (just slightly longer wavelengths than the eye can detect).

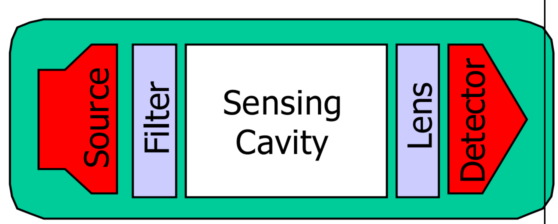

Figure 6
Infrared Sensor Basics

The wavelength of light allowed to pass through must match the wavelength that is easily absorbed by the gas you want to detect. The amount of light energy received at the detector decreases as more of the "target" gas passes into the sensing cavity.

For CO_2, (common in fermentation processes such as brewing), this is the best means of detection available in portable instruments today. The industry is also experimenting with the use of infrared sensors for combustible gas sensing as a replacement for catalytic technology.

The main issues here are cost. IR sensors are more complex and costly; yet, they have the potential to last longer. As the technology matures, it is possible that IR sensing technology may overtake catalytic technology as the choice for combustible gas detection.

Volatile Organic Compounds and Photoionization Detectors

One last large group of compounds relevant to portable gas detection is volatile organic compounds (VOCs). This class of typically industrial compounds (which includes toluene and isobutylene) is sometimes present during emergency spill response actions.

VOCs can be toxic at relatively low concentrations over the long term; this has caused significant concerns in industries where worker exposure must be limited.

While many VOCs are also flammable and can be detected with a catalytic sensor, the levels of concern are typically at the parts-per-million (ppm) level. For example, toluene has an LEL of 1.2% and a permissible 8-hour exposure of 50 ppm. Exposures to LEL levels are 240 times higher than the shift exposure level (1.2% is 12,000 ppm). Clearly, a different technology is needed to protect workers and determine if there are hazards present.

Enter photoionization detectors (PIDs). PIDs rely on specific chemical properties of the VOCs. Instead of absorbing light, a PID uses a light source (in this case in the ultraviolet [UV] spectrum – wavelengths just shorter than we can see) to "ionize" or bump electrons off gas molecules (see Figure 7).

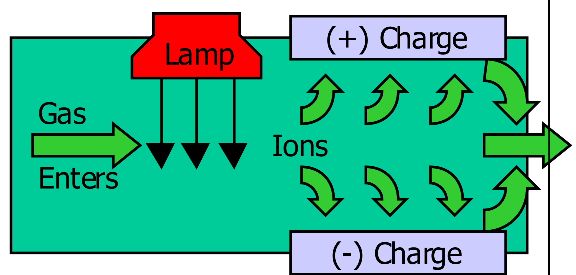

Figure 7
Photoionization Detector Basics

Once the gas is ionized, it passes through two charged plates, which separate the gas ions and the now "free" electrons. As the gas ions flow towards the plates, a current (which can be measured) is generated between the two plates. This current is sensitive to the amount of ionized molecules (the more gas present, the more gas is ionized and the higher the current). The instrument then converts this output into a reading that is displayed on the face of the instrument.

PID sensors, however, are not at all specific; they will indicate that some VOCs are present, but not what type. Many instruments with PID sensors have built-in conversion factors; if you know what type of VOC you are measuring, you can obtain a direct ppm reading on your display.

While PID sensors are excellent tools for the specific requirement, they are not necessarily the best choice for everyone. They add cost and complexity to the gas detector and require more complex maintenance. Be sure to carefully weigh your applications when considering what type of detector to purchase; often, a standard unit will meet the majority of your gas detection needs.

Calibration and Calibration Checks

No gas detection presentation is complete without some discussion of the required sensor maintenance. While most digital instruments come equipped with electronic self-diagnostics, sensors must be checked directly.

It is usually obvious when an oxygen sensor is inoperative since it should read near 20.8% under normal circumstances. If it is malfunctioning, it will likely not be able to read properly in clean, ambient air.

Other sensors, however, normally have no output (instrument display will read "zero"). To verify proper operation, it is important that you institute a program where each gas sensor is exposed to a known level of gas before each day's use. Without this check, you could falsely assume the atmosphere is safe when it actually contains deadly gases.

This does not mean that you must fully calibrate your instruments each day. You must, however, be sure they are operating within the manufacturer's specified limits.

Tying it all Together: Packaging and Software

The sensors form the heart of any gas detection instrument, but their operation should be as easy as possible.

Portable multigas detectors come in many shapes and sizes, from small handheld instruments to larger units which may be placed on the ground. In general, though, emergency response teams have more than enough gear to carry, making instrument size very important.

Figure 8
Typical, Compact Portable Gas Detector

The ability to rapidly assess gas readings in emergency situations is key to the safe operation of any instrument. Physical features such as an easily seen display and alarm lights should be carefully considered when making your decision.

Software Keeps it Simple

In addition to the physical features, instrument operation can be critical to its proper use and maintenance. Today's advancements in processing power allow sophisticated software to operate in even the smallest instruments. Be sure to trial-run any instrument before you buy; it may look easy enough when the salesman is in your station, but will you and your team be able to operate it effectively when the support isn't there?

Fire Service Applications

There are many applications for multigas detectors in the fire service, many of which you will be called on to perform on a regular basis – so it pays to be prepared. Some of these applications include:

- Confined space entry
- Home CO alarm calls
- Natural gas leaks
- Gasoline spills
- Odor calls
- Overhaul

Confined Space Entry

There are many situations when emergency response teams may be called in to perform emergency services or rescues in confined spaces. While mainly industrial in nature, a confined space is usually defined as any enclosed area not typically meant for human habitation.

A multigas detector can provide the appropriate measures to help ensure the confined space atmosphere is safe *before* your team enters and *while* working in the area.

Home Calls

With the advent of carbon monoxide monitoring in the home, the number of calls to fire departments regarding CO alarms in the home has risen dramatically.

You need to be prepared to verify the complaint upon arrival and determine if the premises are safe for habitation. You may even be called upon to help locate the source of the gas (often a car in the garage or a leaky furnace vent).

A multigas detector can help determine if the premises are safe. In addition, they often provide the leak detection necessary to locate the source of the problem.

You may also be called in for natural gas leaks or "bad smells". Having the capability to measure several gases at once becomes a distinct advantage in these situations.

Overhaul

During overhaul operations, you can never be certain of the conditions when you enter a damaged structure. A gas detector can let you know when it is necessary to don your breathing apparatus.

Conclusion

Multigas detectors are available to meet most of your gas detection needs. From standard catalytic and electrochemical sensors to advanced IR and PID sensors, they can detect a great variety of gases and vapors which can pose a threat to your team as they perform their duties.

In general, a standard four-gas unit with a combustible, oxygen, carbon monoxide and hydrogen sulfide sensor is adequate for many needs. These units, readily available from most safety products or fire service distributors nationwide, can help ensure everyone goes home safely at the end of the shift.

Gas detection is fundamental to emergency response; make sure you "know before you go."

Ted Hardenbergh is the portable instrument product line manager for the MSA Instrument Division. If you have any questions about multigas detectors or would like information on products available from MSA, please call us at 1-800-MSA-2222.

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Chapter 3

Catalytic Combustible Gas Sensors

Catalytic bead sensors are used primarily to detect combustible gases. They have been in use for more than 50 years. Initially, these sensors were used for monitoring gas in coal mines, where they replaced canaries that had been used for a long period of time.

The sensor itself is quite simple in design and is easy to manufacture. In its simplest form, as used in the original design, it was comprised of a single platinum wire. Catalytic bead sensors were produced all over the world by a large number of different manufacturers, but the performance and reliability of these sensors varied widely among these various manufacturers. A catalytic bead sensor is shown in Figure 1.

Fig. 1 A Catalytic Bead Sensor

Principle of Operation

Combustible gas mixtures will not burn until they reach an ignition temperature. However, in the presence of certain chemical media, the gas will start to burn or ignite at lower temperatures. This phenomenon is known as a *catalytic combustion*. Most metal oxides and their compounds have these catalytic properties. For instance, volcanic rock, which is comprised of various metal oxides, is often placed in gas burning fireplaces. This is not only decorative, but it also helps the combustion process and results in cleaner and more efficient burning in the fireplace. Platinum, palladium, and thoria compounds are also excellent catalysts for combustion. This explains why the automobile exhaust system is treated with platinum compounds and is called a catalytic converter. This kind of gas sensor is made on the basis of the catalytic principle, and therefore is called the *catalytic gas sensor.*

A gas molecule oxidizes on the catalyzed surface of the sensor at a much lower temperature than its normal ignition temperature. All electrically conductive materials change their conductivity as temperature changes. This is called the *coefficient of temperature resistance* (Ct). It is expressed as the percentage of change per degree change in temperature.

Platinum has a large Ct in comparison to other metals. In addition, its Ct is linear between 500°C to 1000°C, which is the temperature range at which the sensor needs to operate. Because the signal from the sensor is linear, this means that the concentration of gas readings are in direct proportion to the electrical signal. This improves the accuracy and simplifies the electronic circuitry. Also, platinum possesses excellent mechanical properties. It is physically strong and can be transformed into a fine wire which can be processed into small sensor beads.

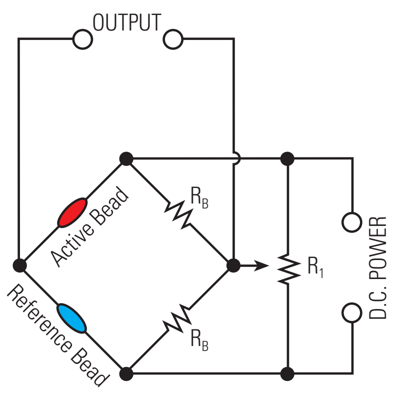

Fig. 2 A catalytic bead sensor Wheatstone bridge–a circuit for measuring an unknown resistance by comparing it with known resistances.

Furthermore, platinum has excellent chemical properties. It is corrosion resistant and can be operated at elevated temperatures for a long period of time without changing its physical properties. It is capable of producing a constant reliable signal over an extended period of time.

The electrical circuit used to measure the output of catalytic sensors is called a *Wheatstone bridge,* in honor of English physicist and inventor Sir Charles Wheatstone (1802-75). Wheatstone bridges are commonly used in many electrical measurement circuits. As shown in Figure 2, four circuit branches are arranged in a square. The source of the electrical current is connected, and between the other pair of opposite corners, the output measurement circuit is connected.

In operation, R_1 is the trim resistor that keeps the bridge balanced. A balanced bridge has no output signal. Resistor value R_B and trim pot R_1 are selected with relatively large resistance values to ensure proper function of the circuit. When the gas burns on the active sensor surface, the heat of combustion causes the temperature to rise, which in turn changes the resistance of the sensor. As the bridge is unbalanced, the offset voltage is measured as the signal. It is important that the reference sensor or bead maintains a constant resistance during the exposure to the combustible gas; otherwise, the measured signal will be inaccurate.

Evolution of the sensor. The original catalytic sensor was a coil-shaped platinum wire. The coiled shape, illustrated in Figure 3, was used to obtain a compact geometry for efficient heating and to produce a strong enough signal to function as a gas sensor. Unfortunately, despite the excellent physical and chemical properties of platinum, it is a poor catalyst for combustion of hydrocarbon gases.

Fig. 3 Hot Wire Sensor

For the proper detection of hydrocarbon gases, the sensor requires a heated surface temperature between 900°C and 1000°C so that the sensor can properly react with gases at a sufficiently high and stable rate. At this temperature, however, the platinum starts to evaporate. The evaporation rate increases as the gas molecules start to react with the sensor and as the sensor temperature increases. This causes a reduction in the cross-section of the platinum wire, and, as a result, the resistance increases. This affects the sensor's operating temperature, which shows up as *zero* and *span drifts.*

The reference wire ideally should be the same as the active wire, with the same geometry and operating temperature, but should be nonreactive with the gas. This is not practically possible, however. A compromise is made by operating the reference wire at a temperature that is substantially lower so that no oxidation takes place in the presence of hydrocarbons. In addition, the reference wire is chemically treated to reduce the catalytic property of the platinum. This may also be achieved by coating platinum wire with a non-catalytic metal, such as gold.

Another problem with hot platinum wire is that it becomes very soft at a temperature of 1000°C. Therefore, it is difficult to maintain its coil shape. Also, the coefficient of thermal resistance becomes less linear as the temperature increases. This situation also results in poor zero and span quality of the sensor, as well as a relatively short operating life.

One way to improve stability of the sensor is to coat the platinum wire with suitable metal oxides. Thus, the final step is to treat the finished sensor or bead with a catalyst, such as platinum, palladium or thoria compounds. Figure 4, shows the sensor bead.

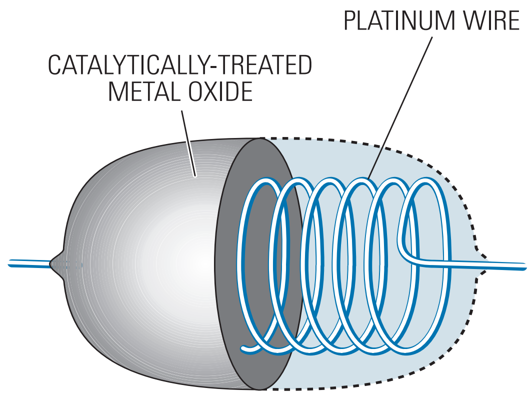

Fig. 4 A Catalytic Bead Sensor

The construction of the catalytic sensor bead is analogous to constructing a building by using reinforced concrete. The coating makes the sensor physically very rugged. The sensor becomes a very small mass which helps make it resistant to shock and vibrations. Most importantly, the catalyst coating reduces the temperature needed to achieve a stable signal for hydrocarbons between 400°C and 600°C.

The use of fine diameter wire not only reduces the size of the sensor, but it also increases the signal, because finer wire has a higher magnitude of resistive value and the signal output is the percentage change of total wire resistance. This also reduces power consumption.

The reference sensor can be constructed in the same way as the active sensor, with the exception that the catalyst chemical is eliminated. The bead can be further treated with chemicals, such as potassium, to prevent the reference bead from reacting with the gas. A near perfectly compensated pair of sensors is now possible. The sensor is called a "catalytic" sensor because the use of the catalyst is the main ingredient involved in the proper functioning of the sensor. The catalytic sensor is stable, reliable, accurate, and rugged, and has a long operating life. The output is linear because the platinum wire has a good linear coefficient of thermal resistance.

Characteristics

The sensor's output is directly in proportion to the rate of oxidation. The maximum output of the signal occurs at about the stoichiometric[1] mixture of the gas, or it is based on the theoretical combustion reaction formula. Methane, for example:

$$CH_4 + 2O_2 + 8N_2 \rightarrow CO_2 + 2H_2O + 8N_2$$

It takes 10 moles of air for one mole of methane to complete the reaction, assuming there is one part of oxygen and four parts of nitrogen in air.

Therefore, for a theoretical combustion to take place, one part of methane will require 10 parts of air

[1] Pertaining to substances that are in the exact proportions required for a given reaction.

to complete the combustion, or theoretically 9.09% of methane in a mixture of air.

For a sensor to detect methane, the signal output will respond linearly from 0–5% of methane (which is 100%LEL). As the concentration reaches close to the stoichiometric value of 9%, the signal increases very rapidly and peaks at around 10%. The signal starts to drop slowly as the concentration of gas passes approximately 20%; after 20% it drops straight down to a level that reflects no output as the concentration of gas reaches 100%. Figure 5, illustrates this effect.

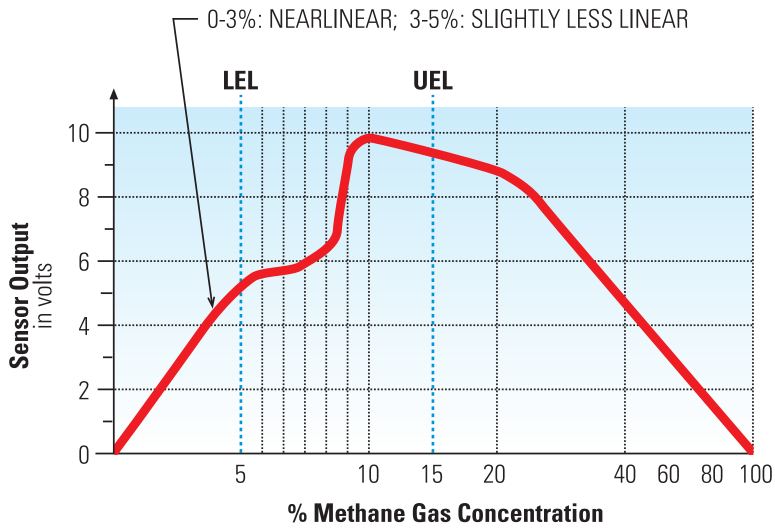

Fig. 5 Sensor Output vs. Gas Concentration

Consider another example, propane. The reaction formula for propane is:

$$C_3H_8 + 5O_2 + 20\ N_2 \rightarrow\ 3CO_2 + 4H_2O + 20N_2$$

or one part of propane per 25 parts of air for theoretical combustion of propane. The actual theoretical combustion concentration for propane is 3.85%.

The LEL for methane is 5% and for propane is 2.1%. This value is near half of the theoretical combustion value. There is a safety factor of 2 added to ensure safety.

Sensor Operation Factors

There are several factors affecting the operation of the catalytic sensor.

1. Catalyst Poisoning: There are chemicals which will deactivate the sensor and cause the sensor to lose sensitivity and eventually become totally nonresponsive to gases. The most common chemicals that can poison catalytic sensors are those that contain silicon, such as the common oil and lubricants with silicon compounds used as additives in machinery. Sulfur compounds, which are often released with gases, chlorine, and heavy metals also cause the poisoning of the sensor.

The exact cause of this poisoning is very difficult to identify. Some chemicals, with very small concentrations, will totally destroy the sensor. There have been instances in which the silicon contained in simple hand lotions has caused problems with catalytic sensors.

2. Sensor Inhibitors: Chemicals such as halogen compounds, which are used in fire extinguishers and Freon used in refrigerants, will inhibit the catalytic sensor and cause it to temporarily lose the ability to function.

Normally, after 24 or 48 hours of exposure to ambient air, the sensor starts to function normally. These are just a few typical chemicals that inhibit the sensor performance and are by no means to be considered as the sole possible inhibitors.

3. Sensor Cracking: The sensor, when exposed to excessive concentration of gases, excessive heat, and the various oxidation processes that take place on the sensor surface, may eventually deteriorate. Sometimes this will change the zero and span setting of the sensor.

4. Correction Factors: Catalytic sensors are most commonly calibrated to methane for 0-100% LEL full scale range.

The manufacturers generally provide a set of *correction factors* that allow the user to measure different hydrocarbons by simply multiplying the reading by the appropriate correction factor to obtain the reading of a different gas. The reason for using methane as the primary calibration gas is that methane has a saturated single bond that requires the sensor to operate at the highest temperature in comparison to other hydrocarbons. For instance, a typical catalytic sensor for methane gas may require a 2.5-volt bridge voltage to obtain a good signal, while the same sensor will only need 2.3 volts for butane gas. Therefore, if the sensor is set to read butane, it will not read methane properly.

In addition, methane gas is a very common gas and is often encountered in many applications. Furthermore, it is also easy to handle and has the ability to be mixed into different concentrations easily. However, it should be noted that the correction factors are a set of numbers that should be used with great care. The correction factors can vary from sensor to sensor, and they can even change on the same sensor as the sensor ages. Therefore, the best way to obtain precise readings for a specific gas is to actually calibrate the sensor to the gas of interest directly.

5. Percent LEL for Mixtures of Hydrocarbons: For combustion to take place, the following requirements must be present:

a. Combustible mixture

b. Oxygen

c. Ignition source

This is sometimes referred to as the combustion triangle. But in real life, the process of igniting a combustible mixture is much more complicated. The en-

Relative Sensitivity

As an example for a typical sensor calibrated for 100% LEL methane gas, the relative sensitivity to other gases is as follows:

Gas	Reading
Methane	*100%*
Propane	60%
n-Butane	60%
n-Pentane	50%
n-Hexane	45%
Methanol	100%
Ethanol	70%
iso-Propyl Alcohol	60%
Acetone	60%
Methyl Ethyl Ketone	50%
Toluene	45%

vironmental conditions, such as pressure, temperature, temperature of the ignition source, and even humidity can have an affect on the combustible mixture concentration.

If two or more chemicals are involved, it is not even possible to calculate and determine the combustion range of the mixture. Therefore, it is best to consider the worst-case scenario and calibrate the sensor accordingly. Furthermore, a sensor calibrated at a percentage LEL for one gas cannot necessarily be used for other gases. Many instruments on the market today have a scale unit as a percentage of LEL without indicating that the unit is calibrated on methane. Therefore, if the unit is used for some other gas or mixture of gases, the data can be totally meaningless.

For example, a catalytic sensor calibrated on methane produces lower readings when exposed to hydrocarbons of higher carbon content, while infrared instruments will produce much higher readings if exposed to a higher carbon content gas. This is a very common mistake made by many users of gas detection equipment.

Summary

A catalytic sensor is relatively easy to manufacture. However, the quality of the sensor varies quite drastically from one manufacturer to another.

The overall technology of making a sensor for the market is more of an art than a predictable scientific event. This is particularly true in selecting, preparing and processing all the chemicals needed to make the final sensor. There are too many variables in the process that inhibit the making of a predictable final product. Therefore, most users of catalytic sensors select their sensors based on the reputation of the manufacturer.

Typical Specifications for Catalytic Sensors

Sensor Type: Diffusion catalytic bead

Temperature Range: –40°C to +60°C

Response Time: 10 to 15 sec. to 90% of reading

Accuracy: ±5%

Repeatability: 2%

Drift: 5–10% per year

Life Expectancy: Up to 3 years; depending on application

Sensors can be remotely mounted up to 2,000-3,000 meters, depending on the manufacturer and cable size used to wire the sensor.

Photoionization Detectors (PIDs)

[Theory, Uses and Applications for First Responders, Law Enforcement Agents, HazMat and Fire Service Professionals]

Photoionization Detectors (PIDs)

For years, fire departments, law enforcement agents, HazMat teams, and now more than ever First Responders, have been concerned about detecting and identifying hazardous compounds in emergency situations. Several techniques and technologies are used such as:

- Catalytic sensors
- Electrochemical sensors
- Gas chromatography
- Flame ionization
- Photoionization
- Ion Mobility Spectrometry
- Surface Acoustic Wave
- Color-changing detectors

While each of the above technologies have their advantages, photoionization detectors offer the ideal combination of speed-of-response, ease-of-use and maintenance, size, ability to detect low levels (in the ppm range) of many hazardous compounds, and affordability. PIDs are capable of effectively detecting and monitoring several hundred, if not thousands, of hazardous substances for maximum benefits and safety to users.

What Does Ionization Mean?

When the gas being sampled absorbs the energy from the PID lamp, it becomes "excited" and its molecular content is altered. The compound loses an electron (e-) and becomes a positively charged ion. Once this happens, the substance is considered to be "ionized." This is what happens inside the PID.

Pictorially, we see photoionization at work in Figure 1.

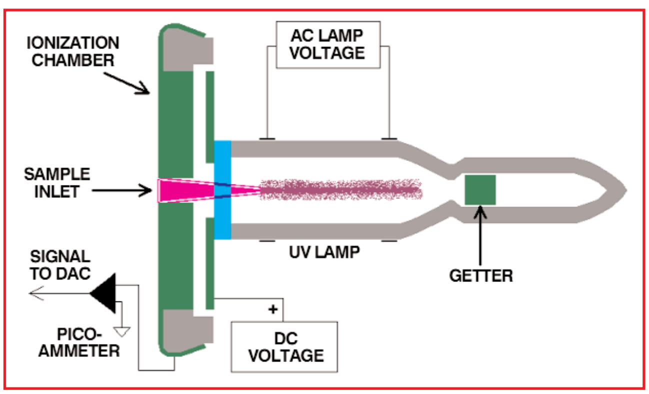

Figure 1. Block diagram of photoionization at work.

Theory of Operation

PIDs rely on ionization as the basis of detection. Most substances can be ionized; some more easily than others. The ability of a substance to be ionized is measured on an eV (electron volt) energy scale. The scale generally runs from a value of 7 to a value of approximately 16. Substances with an eV rating of 7 are very easy to ionize. Substances with an eV rating between 12 and 16 are extremely difficult to ionize. The eV ratings of some common substances include:

Substance	eV	Substance	eV
Benzene	9.24	Methyl ethyl ketone (MEK)	9.53
Hexane	10.18	Chlorine Dioxide	10.36
Toluene	8.82	Phosphine	9.87
Styrene	8.41	Ammonia	10.18

When chemicals being monitored have been ionized inside the instrument, a current is produced and the concentration of the compound is displayed as parts-per-million on the meter. PIDs utilize an ultraviolet (UV) lamp to ionize the compound to be monitored. The lamp, often the size of a common flashlight bulb, emits enough ultraviolet energy to ionize the compound.

There are different lamps available for PIDs. Two examples follow:

A 9.8 eV lamp puts out enough energy to ionize any compound whose eV rating is less than 9.6:

- Toluene ....8.82 eV
- Benzene ....9.25 eV
- Propylamine ....8.78 eV
- Styrene ....8.40 eV
- Vinyl acetate ....9.19 eV

A 10.6 eV lamp puts out enough energy to ionize any compound that a 9.8 eV lamp can detect, plus any compound whose eV rating is less than 10.6.

- Propy alcohol ....10.22 eV
- Phosphine ....9.96 eV
- Vinyl chloride ....10.00 eV
- Acetaldehyde ....10.22 eV

Substances that PIDs Can Detect

PIDs measure organic compounds such as benzene, toluene, and xylene, and also certain inorganics such as ammonia and hydrogen sulfide. As a general rule, if the compounds being measured or detected contain a carbon (C) atom, a PID can be used. However, this is not always the case, as methane (CH_4) and carbon monoxide (CO) cannot be detected with a PID.

Following are some of the common substances that a PID can detect and monitor:

- Benzene
- Toluene
- Vinyl chloride
- Hexane
- Ammonia
- Isobutylene
- Jet A fuel
- Styrene
- Allyl alcohol
- Mercaptans
- Trichloroethylene
- Perchloroethylene
- Propylene oxide
- Phosphine

Substances that PIDs Cannot Detect

PIDs cannot be used to measure the following common substances:

- Oxygen
- Nitrogen
- Carbon dioxide
- Sulfur dioxide
- Carbon monoxide
- Methane
- Hydrogen fluoride
- Hydrogen chloride
- Fluorine
- Sulfur hexafluoride
- Ozone

Response Factors

The optimal way to calibrate a PID to different compounds is by using a standard of the gas of interest. However, this is not always practical as it requires that a number of different and sometimes hazardous gases be kept on hand for this purpose. To address this issue, response factors are used. A response factor is a measure of the sensitivity of a PID to a particular gas. With response factors, a user can measure a large number of compounds using a single calibration gas – typically isobutylene. The user simply multiplies the instrument reading (calibrated for isobutylene) by the response factor to get the corrected value for the compound of interest.

The instruction manuals for most PIDs list the response factors. Some PIDs have response factors for common gases programmed into the software of the unit so that all response factor calculations are performed automatically. If the compound at a test site is known, the instrument can be set to indicate a direct reading for the target compound.

Threshold Limit Values (TLVs) and Permissible Exposure Limits (PELs)

The default low and high alarm values are set for isobutylene. If the user wants to monitor a different gas, they must determine the TLVs for the gas and then change the instrument's alarm level accordingly. The instrument manual should be referenced to ensure correct instructions are followed. Chemical limit values can be found by referencing ACGIH, NIOSH, or OSHA.

Indicator Versus Analyzer

A common misconception about PIDs is that they are analyzers. Many expect that a PID will tell them exactly what the vapor is at a spill site. This is not true. While PIDs are extremely sensitive and effective tools, they are not analyzers and cannot determine if the spill is benzene, jet fuel or iodine, for example. A PID can detect that something is present and can alert you to potentially hazardous situations, but additional steps will be necessary to properly identify what the substance is and how much of that substance is present.

Below is a sample procedure to identify the concentration of a substance at a spill site:

1. Set the PID to isobutylene
2. Detect and record a reading
3. Identify, via a placard or MSDS, what the specific substance is

If the placard or MSDS tells you that the substance is vinyl chloride, set the PID response factor to vinyl chloride so that you can get a direct reading of the actual vinyl chloride level.

PID Applications

Homeland Security

Potential terrorist chemical attacks may include industrial chemicals such as chlorine dioxide and ammonia. First Responders can use PIDs to confidently determine whether one of these chemicals is present and, if so, to accurately measure the concentration.

No single technology alone is adequate for First Responders to rely on completely, but PIDs used in conjunction with other tools such as SAW or IMS devices can assure that the most appropriate response is taken in a homeland security incident.

Three ways in which response factors are used with PIDs

Method	Example
Method #1: Preprogrammed Response Factors *Typically, PID detectors are calibrated for 100 ppm isobutylene. Other gases, for which there are hundreds, have corresponding correction values known as response factors. Numerous corresponding response factors are preprogrammed into the PID instrument. After a user selects the desired gas to measure from the instrument menu, the unit will automatically calculate the corrected gas concentration reading for the gas of interest. The direct reading will now measure the selected gas' concentration.*	The instrument is calibrated to read in isobutylene equivalents, for a reading of 100 ppm with 10.6 eV lamp. Ethylbenzene is the target gas, with a response factor of 0.62. Select the pre-programmed response factor and the instrument now reads about 62 ppm when exposed to the same gas, reading directly in ethylbenzene concentration values.
Method #2: Customized Response Factors *Typically, PID detectors are calibrated for 100 ppm isobutylene. If a user does not find a desired gas in the preprogrammed instrument menu list, the user can program a custom gas and response factor into the unit. If the user does not know the corresponding response factor, they can call MSA and request a customized response factor be calculated specific to their application.*	Tetrahydrofuran is the target gas. The response factor for tetrahydrofuran is 2.1 with 10.6 eV lamp. When calibrating the instrument with 100 ppm isobutylene, enter 2.1 times 100, or 210, when prompted for the calibration gas concentration. The instrument now reads directly in tetrahydrofuran concentration values.
Method #3 Manually Calculated Response Factors *Typically, PID detectors are calibrated for 100 ppm isobutylene. If a user chooses to read an isobutylene's direct reading for a different gas and does not want to utilize either the preprogrammed or customized response factors, the user may manually calculate the desired gas' direct reading. If the user knows the response factor of the desired gas, they can manually multiply the isobutylene reading by the known response factor. The result of this equation can be recorded externally to the instrument.*	The instrument is calibrated with isobutylene to isobutylene equivalents, for a reading of 10 ppm with 10.6 eV lamp. Cyclohexanone is the target gas, with a correction factor of 0.82. Multiply 10 by 0.82 to produce an adjusted cyclohexanone concentration of 8.2.

Leak Detection

Often the level of a leak is so small that it cannot be smelled by humans. PIDs are used to detect these low-level leaks. PIDs can detect compounds at levels below 1 ppm.

Not only can PIDs be used to detect leaks, they can also be used to locate sources of leaks. Higher concentrations of gases are found at or near the source of a leak. Once the user detects a substance, the user, wearing adequate personal protective equipment, should move in the direction of higher concentrations if trying to identify the source of the leak.

Perimeter Monitoring

At HazMat sites, perimeters are set to contain a hazardous area. PIDs can be used to set and, if necessary due to changing environmental conditions, change the perimeter line. For example, the concentration of toluene is 5 ppm at Perimeter Line A at 10:50 a.m. At 11:05 a.m., the reading at Line A changes to 10 ppm due to the wind direction. This tells the HazMat worker that the perimeter line may need extended.

Spill Delineation

Because water and foam are often used at HazMat sites, there can be a variety of liquids on the ground in addition to any material that was inadvertently spilled. A PID is effective in locating the hazardous substance while "ignoring" the foam and water. The PID will not respond to the water or foam.

Remediation

Often times, HazMat spills can contaminate bodies of water or soil, which poses long-term environmental concerns. PIDs are extremely useful in taking samples from soil to determine if remediation is necessary in conjunction with applicable environmental regulations.

Arson Investigation

PIDs are often used to detect accelerants at a post-fire scene. PIDs can detect low levels of substances used to accelerate fires. Once a reading is detected on the PID, a sample from that specific area can be taken to a laboratory to be analyzed. In this application, it is recommended that the PID be set to the isobutylene response factor for general-purpose indications.

Diesel Fuel TLV Monitoring

Marine chemists are now following new TLV limits for diesel fuel which have been determined by the ACGIH (American Conference of Governmental Industrial Hygienists). The presence of diesel fuel in the workplace and its associated exhaust has long been connected with being carcinogenic and a source of particulate pollution associated with lung disease. The new TLV is 15 ppm of diesel vapor. This is very conservative, and all marine chemists are expected to comply with this new TLV. Sampling for diesel fuel vapors and recording the results are important aspects of their inspections. Surveys are conducted in fuel tanks, cargo spaces and engine rooms.

Determining the Level of Personal Protective Equipment (PPE) Required

One of the most fundamental questions at a potential HazMat incident is, "What type of PPE should be used?" Is the site truly hazardous? Is Level A clothing or self-contained breathing apparatus (SCBA) necessary throughout the whole incident? A PID can help determine appropriate levels of PPE.

Decontamination

After the incident is over, PIDs can be used to help determine if any of the HazMat responders need to be decontaminated by checking the protective clothing for contamination. This can help HazMat teams decide if they can reuse a piece of clothing rather than discarding it – allowing a potentially significant cost savings to the HazMat team.

Conclusion

PIDs are extremely valuable tools for Homeland Security, Law Enforcement Agents, Fire Service and HazMat response. Their sensitivity, low levels of detection, and ability to detect many different compounds enable PIDs to be used in many different applications. Simply stated, PIDs can help make the difficult jobs of First Responders, Law Enforcement Agents, Fire Service and HazMat professionals easier.

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