

Portable Gas Detectors used in Confined Space and Other Industrial Atmospheric Monitoring Programs*

By Robert E. Henderson

Contents

Introduction.....	17
Atmospheric Hazards Associated with Confined Spaces.....	19
General.....	19
Aerosol Hazards.....	20
Measurement of Aerosols.....	20
Oxygen Deficiency and Enrichment.....	21
Causes of Oxygen Deficiency.....	22
Microbial Action.....	22
Displacement.....	23
Oxidation.....	23
Combustion.....	24
Absorption / Adsorption.....	24
Oxygen Detection.....	24
Fuel-Cell Type Oxygen Sensors.....	25
Oxygen Sensor Failure Mechanisms.....	28
Causes of Erroneously High Output.....	29
Solid Polymer Electrolyte (SPE) Oxygen s.....	30
Ignitable Gases and Vapors.....	31
Roll of Flashpoint in Monitoring of Ignitable Gases and Vapors.....	34
Catalytic (Hot Bead) Sensors.....	36
General Discussion.....	36
Relative Calibration.....	42
Sensor Poisons and Inhibitors.....	44
Loss of Sensitivity to Methane.....	45
Low Range Hydrocarbon Detection.....	46
High Range Flammable/Combustible Gas Detection.....	46
Thermal Conductivity Sensors.....	47
Oxygen Displacement.....	48
Dilution Fittings.....	48
Metal Oxide Semiconductor Sensors.....	49
Toxic Gases and Vapors.....	49
Measurement of Toxic Gases and Vapors.....	51

***Portions of this Chapter have been previously published in *Safety and Health in Confined Spaces*, McManus, Neil, Lewis Publishers, Boca Raton, FL, 1999. With permission.**

Badge-Type Dosimeters.....	51
Sorbent Tube Sampling.....	52
Colorimetric Measurement Techniques.....	52
Colorimetric Detector Tubes.....	52
Automated Colorimetric Measurement Systems.....	56
Colorimetric Badges and Dosimeter Tubes.....	57
Paper Tape and Metal Foil Devices.....	58
Electrochemical sensors.....	58
Metal Oxide Semiconductor Sensors.....	64
Ionization Detectors.....	65
General Discussion.....	65
Photoionization Detectors.....	66
Flame Ionization Detectors.....	69
Infrared Detectors.....	70
IR Spectrophotometers.....	72
Substance-Specific Infrared Instruments and Sensors.....	73
Photoacoustic Analyzers.....	73
Fourier Transform Infrared (FTIR) Analyzers.....	74
Gas Chromatography.....	74
Fixed Detection Systems.....	75
Hazard Management.....	75
Wirelessly Integrated Systems.....	77
The Way the New Technology Works.....	77
Using Real-Time Information to Improve Worker Safety.....	79
Future Developments.....	80
Criteria for Instrument Selection.....	80
Sample-Draw vs. Diffusion.....	82
Drawbacks of Diffusion Operation.....	82
Drawbacks of Sample-Draw Operation.....	82
Sensor Selection.....	83
Classification for Intrinsic Safety.....	84
ISO Registration.....	86
Batteries.....	86
Durability.....	89
Datalogging vs. Non-Datalogging Capability.....	89
Included Accessories.....	90
Warranty.....	90
Operability.....	90
Instrument Performance Specifications.....	91
Alarm Settings.....	93
Calibration.....	94
Bump Test.....	95
Lengthening the Interval Between Calibration Checks.....	95
Confined Space Monitoring.....	96
Summary.....	97
References.....	98

INTRODUCTION

Fatal industrial accidents which stem from dangerous atmospheric hazards encountered in the workplace are unfortunately common. It is a rare week that does not see the publication of a newspaper story describing a “fatal blast” at an industrial plant, or workers being overcome, or neighborhoods being evacuated by a release of “toxic vapors”. Several types of industrial worker activity, such as confined space entry, “hot work” or welding, and many other routine plant maintenance procedures, are highly associated with the potential for the development of dangerous atmospheric conditions, oxygen deficiencies or explosions. The root causes of most accidents which stem from dangerous atmospheric conditions are failure to recognize the potential existence of the hazards, failure to use the proper procedures to control or eliminate the hazards, and failure to take appropriate action at concentrations and under circumstances which allow workers to exit the affected area before conditions become life-threatening.

Studies published by the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) have found that the root cause of the majority of fatal confined space accidents is hazardous atmosphere associated with the space. The hazardous atmosphere may develop prior to the entry, or may be associated with work activity. (NIOSH 1979, NIOSH 1994, OSHA 1982, OSHA 1985, OSHA 1988, OSHA 1990). A high proportion of these accidents were characterized by failure to test prior to the entry, or during the conduct of work. These findings strongly suggest that atmospheric testing prior to and during entry should be a major component in a hazard management program.

Miners were among the first to become aware of the need for a device to detect hazardous gases. (AIHA 1980) The atmosphere in mines can be subject to a variety of hazardous conditions. Toxic gases encountered in this environment include carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide and others. The atmosphere in mines can also become oxygen-deficient. In some circumstances methane may be present in explosive concentrations. Since methane has no warning properties, a fully explosive concentration could accumulate before a worker would realize the potential risk. Any source of ignition, including the original miner's lamp, could readily cause an explosion. The first combustible gas indicator, the Davy lamp, therefore, provided a significant step forward in mine safety. The visible characteristics of the flame of the Davy lamp informed the experienced user about more than just the presence of methane. Variations and refinements of the original Davy lamp design are still used today in some programs.

Carbon monoxide was a particularly important concern to miners. Again, the absence of warning properties meant that miners could be exposed to lethal concentrations without their knowledge. The usage of small animals, birds, or the famous "Miner's Canary" was a poor substitute for a quantifiable method for the measurement of this hazard. The colorimetric indicator tube designed to measure carbon monoxide became available shortly after the turn of the century, and soon saw wide usage in mines and other environments subject to contamination by this hazard. Soon to follow was the percent oxygen indicator tube.

Atmospheric hazards associated with enclosed spaces on ships has been another spur to the development of modern atmospheric testing devices. In 1926, a string of oil tanker and ship tank explosions led the Standard Oil Company of California to sponsor the research and development of a direct reading indicator for explosive gas. As a result of this sponsorship, Oliver W. Johnson developed and in 1927 introduced a portable, explosive gas indicator based on the catalytic oxidation of flammable gas on a platinum filament wire. Seventy years later, the sensors used in the majority of today's confined space gas detectors continue to be based (with many modern refinements) on this basic detection principle. In the 1960's, development of the first generation of electrochemical oxygen sensors allowed the incorporation of oxygen measurement into real time direct reading portable instruments. Today's practitioner has the choice of indicator tubes, dosimeters, and portable real-time instruments based on a wide variety of detection principles. Indeed, one of the great challenges facing the practitioner is which detection technique to use when testing a particular environment!

Management of air quality during entry and work in confined space reflects two basic requirements: proper assessment of existing or potential atmospheric hazards, and strategies to eliminate, control or maintain safe atmospheric conditions for potentially affected workers. Before developing any strategy, assessment of all potential atmospheric hazards which may be related to the confined space or entry procedures is required.

Traditional monitoring strategies have focused on the detection of only those chemicals or conditions suspected to be present. This approach is most useful when there is a high level of knowledge about the nature of the hazard. In many cases this is the most appropriate approach. A tightly focused measurement technique usually provides the most accurate readings and is

least subject to sources of error, such as cross-interference from other substances simultaneously present. For example, a substance-specific electrochemical sensor designed for detection of hydrogen sulfide shows very little response to most other contaminants. The major pitfall in the use of highly specific measurement techniques is the potential for overlooking or missing an existing hazard.

In some confined spaces, such as sewers, the level of knowledge concerning hazards that may be present is relatively low. A sewer is a very large, interconnected confined space. Achieving complete control, and rendering the atmosphere safe throughout an entire sewer system prior to entry generally is not possible. This means, in most cases, that only the atmosphere in the area where entrants work is ventilated and monitored. While the most commonly encountered hazards (oxygen deficiency, methane, or hydrogen sulfide) are highly predictable, at any moment (with the next flush, as it were) an unforeseeable hazard can suddenly appear. In this case, a more broadly responding detection technology may be more appropriate.

Readings from nonspecific measurement techniques may pose interpretive problems. The metal oxide semiconductor (MOS) sensor used in some survey instruments targeted towards sewer entry applications are so widely responsive that a positive reading may become impossible to interpret. On the other hand, technological advances have allowed the introduction of miniaturized versions of several detection technologies which in the past have been confined to bulky, dedicated survey monitors. For instance, increasing numbers of multi-sensor confined space gas detectors are now equipped with miniaturized photoionization detectors. While still broadly specific to a wide variety of volatile organic contaminants (VOCs), photoionization detectors frequently provide an excellent "yes / no" part-per-million range indication when a threshold

concentration for many types of solvent and or fuel vapors has been exceeded.

In many cases the atmospheric hazards associated with a particular confined space are easy to identify. The literature quickly reveals that fatal accidents in confined spaces that involve atmospheric hazards result from a limited number of atmospheric conditions. The most commonly encountered hazardous conditions involve oxygen (deficiency or enrichment), combustible gases and vapors, and toxic contaminants, most prominently, carbon monoxide, and hydrogen sulfide. While a multitude of other toxic contaminants can be present in the confined space atmosphere, CO and H₂S produce the preponderant majority of injuries and fatalities. On the other hand, exposure to other toxic contaminants, while not as frequently implicated in accidents which lead to the immediate loss of life, are certainly the cause of many serious injuries, and may produce serious or even life threatening long-term to unprotected workers.

The key to resolving this dilemma is to anticipate hazards that could be present, and then to develop a strategy for their assessment and measurement. In other words, when developing a monitoring program, it is critical to ensure that the initial hazard assessment and measurement procedures are broad enough to ascertain all the potential hazards which may be associated with the confined space.

The primary focus of this chapter will be detection techniques and methods used to measure the most commonly encountered hazards associated with confined space entry. The majority of portable atmospheric monitors manufactured for this application use similar technology and focus on the detection of these most commonly encountered hazards. The differences between one brand of instrument and another can be quite subtle. An understanding about the basic limitations of

these designs is essential when considering their use in a monitoring program. This chapter will explain some of the differences, as well as present the advantages and disadvantages of one monitoring technique over another. A secondary focus of the chapter is an examination of other detection techniques. These, while not widely used in confined space monitoring procedures, may have relevance against specific contaminants.

ATMOSPHERIC HAZARDS ASSOCIATED WITH CONFINED SPACES

General

The three basic categories of potential atmospheric hazard that can occur in or be associated with confined spaces include: oxygen level (deficiency or enrichment), ignitable gases, vapors or particulates, and toxic contaminants. The potential for the development of these hazardous conditions is affected by the following:

- physical nature of the space
- work being performed
- processes associated with the space
- products used or produced in conjunction with the space
- natural processes (such as decomposition, fermentation, ripening, etc.) which occur in or are associated with the space
- external sources of contamination

Hazard assessment should always consider conditions and activities in other areas and their potential impact on the atmosphere in the space.

In some situations, the source of the atmospheric hazard may be remote from the space. For example, at many refineries, pulp mills, and other industrial locations, the potential for a sudden catastrophic release

of toxic or explosive gas is always present. A sudden release in one area of the plant could quickly spread downwind to other areas. Development of an appropriate monitoring strategy depends on recognition of this potential.

AEROSOL HAZARDS

General

Aerosols are suspensions of fine solid particles or liquid droplets in air. Categories of aerosols include:

- Fumes: formed when metal or other materials vaporize by high heat (as in welding) and recondense to form ultra-fine particles.
- Mists and fogs: suspensions of tiny droplets of liquids.
- Dusts: particles produced by the breakdown of solid materials. Dusts include fibrous particles that have longitudinal geometry and particles that have regular or irregular compact geometry.

Ignitable dusts, mists and fogs are a special concern. Grain, coal, nitrated fertilizers, and other solid materials, as well as many liquids form ignitable mixtures when present in sufficient concentration in air.

OSHA provided a useful "rule of thumb" in the preamble to 29 CFR 1910.146, "Permit required confined spaces," for estimating hazardous conditions involving suspensions of dust. (OSHA 1993) OSHA indicated a hazardous condition exists when ignitable dust obscures vision at a distance of 1.5 m (5 ft).

Activities that disturb settled materials or that introduce materials into the air will have a profound influence on the amount of aerosol present in the air column of the space. Work activities associated with the generation of aerosols should include air

monitoring procedures for assessing potentially hazardous conditions. Additional monitoring equipment could be required for assessing build-up of vapors and oxygen levels. The equipment used under these conditions must be classified or approved for use in the types and severity of hazardous conditions which may be present in the space.

Measurement of aerosols

Aerosol measurement, in particular, solid particulates, most frequently involves the use of portable, battery-powered, sampling pumps. These pumps are designed to move a precisely maintained volume of air through a collecting mechanism such as a filter, cassette, or impactor over a specific interval of time. Depending on the collection technique, entrained or collected particles may be counted, weighed, or chemically analyzed to determine a concentration in workplace air.

Particulate survey techniques involving use of a sampling pump normally require laboratory analysis. This requirement normally eliminates their use in "real-time" measurement of particulate levels during work activity in confined spaces. Particulate monitors are available for assessing particulate burden in "real time." Direct-reading particulate monitors include clean room particle counters, fibrous aerosol counters, piezobalances and nephelometers. (The latter are used to measure the total or respirable fraction of particulate contaminants in the air.)

The nephelometer is the type of real-time dust monitor most commonly used during work activity in confined spaces. These devices utilize a calibrated light source (usually in the near infrared range) that radiates through a sensing chamber. Particulates in the sensing chamber reflect the incident light. The amount of back-scattering by the particulates is proportional to the mass of airborne material in the sensing chamber. Some nephelometers

contain a built-in mechanical pump. A pump enables active sampling of the atmosphere through the sensing chamber. Other instruments utilize natural air currents and simple diffusion to move dust through the sensing chamber. Hand-held units provide the ability to read particulate concentrations directly in units of mg/m³. One of the most widespread applications of these instruments is real-time dust monitoring in underground coal mines. Other potential applications involving confined spaces include bag-houses, grain elevators, remediation sites, pharmaceutical plants, and other locations containing toxic or explosive dusts.

The nature of the particulate hazard defines the measurement technique that is most appropriate. For example, due to the physical nature and high moisture content of wood smoke, assessment is usually made through the use of a real-time nephelometer. Asbestos sampling protocols, on the other hand, involve use of sampling pumps and after-the-fact laboratory analysis of fibers trapped on the surface of sampling filters, or use of a real-time fibrous aerosol monitor (FAM). Unless there is an urgent requirement to determine particulate concentrations on a real-time basis, the cost effective procedure is usually the after-the-fact laboratory analysis. As well, the fibrous aerosol monitor may require considerable time at low counting levels to obtain reliable data. Ignitable particulates present a special case where the assessment must occur on a real-time basis.

OXYGEN DEFICIENCY AND ENRICHMENT

The concentration of oxygen in confined spaces is a concern from two stand-points. Too little oxygen can cause asphyxiation. Excessively high (or "enriched") levels of oxygen above normal oxygen concentrations dramatically promote or accelerate combustion and other chemical processes. The concentration of oxygen in normal air is approximately 20.9%. The

balance (over 78%) consists primarily of nitrogen. The remaining fraction includes small amounts of water vapor, carbon dioxide, and argon as well as traces of other gases. The pressure of the atmosphere, and hence the number of molecules per unit of volume decreases with increasing altitude.

Most standards on confined spaces and regulatory agencies, such as OSHA, currently define oxygen deficiency by concentration. The usual benchmark is 19.5% by volume. This is also the default low oxygen alarm setpoint used by most instrument manufacturers. Some jurisdictions also define hazardous oxygen level on the basis of partial atmospheric pressure rather than concentration. (Workers' Compensation Board 1998) In this case, an oxygen pressure less than 16.3 kPa (kilopascals) or 122 mm Hg partial pressure is deemed to represent a hazardous condition. (A partial pressure of 16.3 kPa of oxygen is equivalent to a concentration of 16.3 % at sea level.) The reasoning behind this choice is that the body responds to atmospheric partial pressure of oxygen, rather than concentration.

The differences inherent in these approaches, as well as the effects of partial atmospheric pressure versus percent by volume concentration on the function of sensors used to measure oxygen will be discussed at length later in this chapter. Some instrument manufacturers round oxygen readings upward in a properly calibrated instrument to 21.0 %, while other manufacturers (the majority) round readings downward to 20.9 %.

The definition of oxygen enrichment varies in standards and regulatory documents. OSHA chose 23.5 % as the concentration for oxygen enrichment in the 1910.146 "Permit required confined spaces" Standard for general industry, while specifying 22 % in the 1915-Subpart B Standard for shipyard employment. (OSHA 1993, OSHA 1994) The latter value is consistent with nonmandatory

recommendations from groups such as the National Fire Protection Association (NFPA). (NFPA 1993) The most conservative standards specify 22 % as the concentration above which the atmosphere is deemed to be hazardous due to oxygen enrichment. For this reason, an increasing number of instrument designs which include a high oxygen alarm, use 22 % as the default high alarm setpoint.

An important consideration for use of monitoring instruments in environments containing high concentrations of oxygen is the testing used to classify or approve the instrument for use in hazardous locations. These protocols usually do not include testing for intrinsic safety at elevated concentrations of oxygen. For this reason labeling on the instrument will include a prohibition against use in oxygen concentrations that exceed testing or design parameters. A typical warning found in the owner's manual of a confined space monitoring instrument might state:

Intrinsic safety is based on tests conducted in explosive gas /air (21% oxygen) mixtures only. This instrument should not be used in atmospheres where oxygen concentrations exceed 23.5%.

The user should always consult the owner's manual or contact the manufacturer directly to verify design limitations before using any instrument in highly oxygen enriched atmospheres.

Any oxygen concentration other than 20.9 % (or 21 % in the case of instrument designs that round the reading upward) indicates an abnormal condition. A less than normal concentration of oxygen by definition indicates a greater than normal concentration of some other component or the presence of a contaminant in the atmosphere being sampled. Even when the oxygen concentration does not constitute a statutory hazardous condition, the user

should determine the cause of the abnormal reading prior to entering a confined space.

The safest approach is to initiate entry only when monitoring has determined that a "fresh air" oxygen concentration exists in the space. The only exceptions to this approach are circumstances where the cause of the abnormal oxygen concentration is known precisely, and where entry in these situations is explicitly permitted by written procedures.

Causes of oxygen deficiency

Confined spaces are particularly prone to the development or containment of oxygen deficient atmospheres. The reason that oxygen deficiency is common in confined spaces is that they develop by mechanisms that affect the contents of the space and boundary surfaces. Causes of oxygen deficiency include microbial action, displacement, combustion, oxidation, and absorption and adsorption. Work activity is also an important cause. Use of solvents, paints, degreasers, or hot work can affect oxygen levels.

Microbial action

The microbial decomposition of organic material proceeds by a number of metabolic pathways. Aerobic decomposition is one of the most efficient (or rapid) of these biochemical pathways. Aerobic microbes consume oxygen and produce carbon dioxide as their chief atmospheric metabolite. One of the first detectable changes in the atmosphere of a confined space due to microbial action is a reduction in the oxygen concentration and increase in carbon dioxide. Microbial action can rapidly consume the oxygen present in the atmosphere of a confined space. This process requires surprisingly little organic debris. In an example personally witnessed by the author, a small dry vault (approximately 2.2 m³ or 80 ft³) containing a potable water valve had no visible signs of rusting or corrosion. The oxygen

concentration was 5 % at the lowest point in the vault. The vault had been routinely sampled in the past, and had no prior documented history of oxygen deficiency. Investigation revealed that the only abnormal condition was the desiccated corpse of a small rodent in the bottom of the vault. We believe that microbial decomposition of this small amount of organic material was sufficient to produce this highly oxygen-deficient condition.

Displacement

The leading cause of oxygen deficiency in many industrial settings is displacement of the normal atmosphere by other gases and vapors. Gases and vapors tend to disperse quickly and spread evenly in a horizontal direction. On the other hand, gases and vapors tend to form very distinct density dependent layers in the vertical direction. Gases that are less dense than air tend to rise, while gases that are denser than air tend to sink. Denser than air gases tend to behave like invisible liquids. They can travel considerable distances along boundary surfaces, seeking the lowest level. This could be a pit, vault trench, excavation or other subgrade structure. Denser than air gases frequently implicated in the generation of oxygen deficiency include argon, nitrogen and propane. Denser than air vapors include gasoline, as well as many other solvent vapors.

Sometimes displacement is intentional, as when storage areas, curing ovens, or vessels are inerted or flooded with gases and vapors. This is a deliberate strategy to displace atmospheric oxygen. Although deliberate inerting with stack gas, carbon dioxide (dry ice vapor) or nitrogen is a common industrial procedure, most oxygen deficiencies are accidental.

Testing for oxygen or any other atmospheric hazard that may be present must occur at all vertical levels between the highest and lowest point in the confined space. Investigations of fatal accidents due

to oxygen deficiency frequently have documented nearly normal concentrations of oxygen near the entrance. At the same time, a lethal oxygen deficiency existed near the bottom of the space.

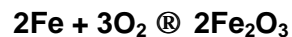
Table 1 illustrates this problem from a fatal accident investigation cited by NIOSH. (NIOSH 1994)

Table 1 Oxygen Concentration versus Depth Below Surface	
Depth (in feet) below surface	Oxygen concentration (%)
5	20.5
7	20.0
9	14.0
11	6.5
13	4.0

Testing by the investigators determined that the oxygen concentration dropped from 20.0 % to 4 % within a vertical distance of six feet (2 m). Sampling only at the point of entry -- had it occurred -- would not have identified the profound oxygen deficiency that existed near the bottom of the manhole. Evaluation of conditions in a confined space must always include testing at all vertical levels prior to entry.

Oxidation

Rusting is an oxidative process that both requires and consumes oxygen. In the presence of moisture, rusting consumes oxygen by means of the following reaction:



In confining environments such as ship compartments, empty water tanks and other containers with exposed metal surfaces, rusting alone may be sufficient to produce a lethal oxygen deficiency.

Combustion

Combustion requires and consumes oxygen. Deliberate introduction of an internal combustion engine into a confined space or hot work of any kind should be viewed with considerable caution. Not only do combustion processes consume oxygen, they also generate toxic products, including carbon, nitrogen and sulfur oxides.

Absorption / adsorption

Some substances are capable of directly absorbing or adsorbing oxygen from the atmosphere. Probably the most common adsorbent is activated carbon. Wet activated carbon filter beds will adsorb oxygen directly from the atmosphere until fully saturated. Similarly wet uncured concrete will absorb oxygen from the air.

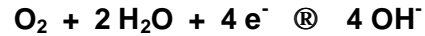
OXYGEN DETECTION

Fuel-cell type oxygen sensors

Most portable or survey instruments utilize fuel-cell type oxygen sensors. Fuel-cell oxygen sensors generally contain the following parts:

- Diffusion barrier
- Sensing electrode (cathode) made from a noble metal such as gold or platinum
- Working electrode (anode) made from a base metal, such as lead or zinc
- Basic electrolyte (such as a solution of potassium hydroxide or potassium acetate)
- Many designs additionally include an external moisture barrier or filter

Most currently available oxygen sensors used in portable instruments have working electrodes made from lead. Oxygen diffusing into the sensor is reduced to hydroxyl ions at the cathode:



Hydroxyl ions in turn oxidize the lead (or zinc) anode:



This yields an overall cell reaction of:



Fuel cell oxygen sensors generate electrical current. The amount is proportional to the amount of oxygen consumed. Oxygen detecting instruments simply monitor current output from the sensor. Of course, this is a simplification of the way oxygen sensing instruments are designed.

The electrolyte may be buffered, or consist of a solution (such as potassium acetate) which is less prone to poisoning or being ruined by gases such as carbon dioxide. The electrolyte also may be a semi-solid gel rather than a liquid. Use of a gel electrolyte improves low temperature performance as well as reducing the potential for leakage or drying out.

The working electrode seldom is a simple chunk of lead, since this surface must be available and accessible for contact with oxygen molecules before the electrochemical reaction can occur. The working electrode usually consists of lead wool or some other finely-divided form of the metal that provides a good surface area-to-volume ratio.

Other design features can include temperature compensating thermistor-resistors, internal membranes, and current collectors. The latter serve to convert the current output to a voltage. Of course, there are always tradeoffs in design choices. A design that improves cold temperature performance may at the same time slow the speed of response, current output, sensor life, or other performance parameters. Numerous variations on these general design options are used to optimize the

performance of an oxygen sensor for use in a specific product.

One of the most important design constraints is the build-up of lead oxide that develops in the capsule over the life of the sensor. As lead is converted into lead oxide, an increasing fraction of the volume of the sensor capsule is occupied by solid material. If the sensor design does not include a provision for this increase, it will eventually rupture. The latter could lead to leakage of electrolyte into the (usually) delicate and expensive electronics.

An important outcome from the above is that the working electrode in a fuel-cell oxygen sensor is consumed over time. In the cell reaction discussed above, when all available surface area of the lead (Pb) anode is converted to lead oxide (PbO), electrochemical activity ceases and current output falls to zero. At this point, the sensor must be rebuilt or replaced. Fuel-cell sensors are designed to last no more than one to two years.

In most instruments, even during inactivity, the sensor continues to generate current and is used up. Some instrument designs prevent the flow of electricity by breaking the circuit. This blocks the electrochemical reaction as long as the instrument is turned off and increases the effective life span of the sensor. The drawback to this design is the need for a lengthy restabilization period (sometimes several minutes) when the instrument is turned back on. During restabilization, current once again flows in the circuit. The reason for the lengthy stabilization period is that oxygen that diffused into the sensor over time accumulates in the electrolyte. The only means to remove the oxygen is the electrochemical reaction that converts it to lead oxide. The accumulated oxygen must be consumed before the sensor can provide accurate measurements. Effectively, this results in a "counting down" process when the instrument is turned on. Readings tend to start high, then slowly decrease to a stable

value. Instruments having this design must not be zeroed or calibrated until full stabilization has occurred.

The temperature of the atmosphere influences the output from fuel-cell oxygen sensors. The warmer the atmosphere, the faster the electrochemical reaction proceeds. For this reason, oxygen sensors usually include a temperature-compensating load resistor to hold current output steady. Microprocessor-based designs usually provide additional signal correction in software to improve accuracy further.

Cold temperatures are a major factor that limits performance. The freezing temperature of electrolyte mixtures commonly used in some oxygen sensors is as high as $-20\text{ }^{\circ}\text{C}$ ($-5\text{ }^{\circ}\text{F}$). Once the electrolyte freezes, electrical output falls to zero. The gelled electrolytes used in some oxygen sensors show much better cold temperature performance.

There are two fundamental variations in designs of fuel-cell oxygen sensor, "partial atmospheric pressure" and "capillary pore" type designs. These variations reflect the mechanism by which oxygen diffuses into the sensor. Dalton's Law states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of the constituents. The partial pressure of oxygen is that fraction of the total pressure due to oxygen.

Partial pressure oxygen sensors rely on the partial pressure (or $p\text{O}_2$) of oxygen to drive molecules through the diffusion barrier into the sensor. As long as $p\text{O}_2$ remains constant, current output is a reliable indicator of oxygen concentration. Shifts in barometric pressure, altitude, or other condition that affects atmospheric pressure will cause a systemic change in sensor output. To illustrate this problem, consider a sensor calibrated at sea level where atmospheric pressure is 760 mm Hg. Now consider the same sensor at an elevation of 3,000 m (10,000 ft).

Table 2				
Total and Partial Atmospheric Pressure for Oxygen as a Function of Elevation in Various U. S. Cities				
Example Location	Altitude (km)	Altitude (feet)	Total atmospheric pressure (mm Hg)	Partial atmospheric pressure O₂ (mm Hg)
San Francisco, CA	0	0	760	159
Atlanta, GA	0.3	1000	731	153
Spokane, WA	0.6	2000	703	147
Rapid City, SD	0.9	3000	676	141
Salt Lake City, UT	1.2	4000	650	136
Denver, CO	1.5	5000	625	131
Colorado Springs, CO	1.8	6000	601	126
Santa Fe, NM	2.1	7000	578	121
Alta, UT	2.4	8000	555	116
Winter Park, CO	2.7	9000	534	112
Keystone, CO	3.0	10000	514	107

Although at both elevations the air contains 20.9 % oxygen, at 10,000 feet the total atmospheric pressure is only 514 mm Hg, and the partial pressure for O₂ is only about 107 mm Hg. Since there is almost one-third less force driving oxygen molecules through the diffusion barrier into the sensor, current output is significantly lower. Table 2 lists the effects on total atmospheric pressure, together with the partial atmospheric pressure for oxygen, as a function of altitude, among several cities located in the United States.

Partial-pressure sensors offer a considerably greater area for passage of oxygen into the sensor than does the capillary pore design. As a result, partial-pressure sensors respond more quickly to changes in oxygen concentration at a given partial pressure.

It should be noted that several instrument designs which include partial atmospheric oxygen sensors include software to correct sensor readings for

barometric pressure fluctuation. In the case of these designs, oxygen readings will not be affected by changes in ambient pressure within design parameters.

Capillary-pore oxygen sensors utilize a narrow diameter tube through which oxygen diffuses into the sensor. Oxygen is drawn into the sensor by capillary action in much the same way that water or fluid is drawn up into the fibers of a paper towel. Capillary-pore sensors are much less influenced by changes in pressure than partial pressure oxygen sensor designs. Although rapidly changing pressure leads to a change in sensor output, as soon as the diffusion barrier capillary has stabilized at the new pressure, the output will return to the previous level. Because the volume of atmosphere contained in the diffusion barrier capillary is very small, stabilization at the new pressure is usually achieved within 10 to 30 seconds.

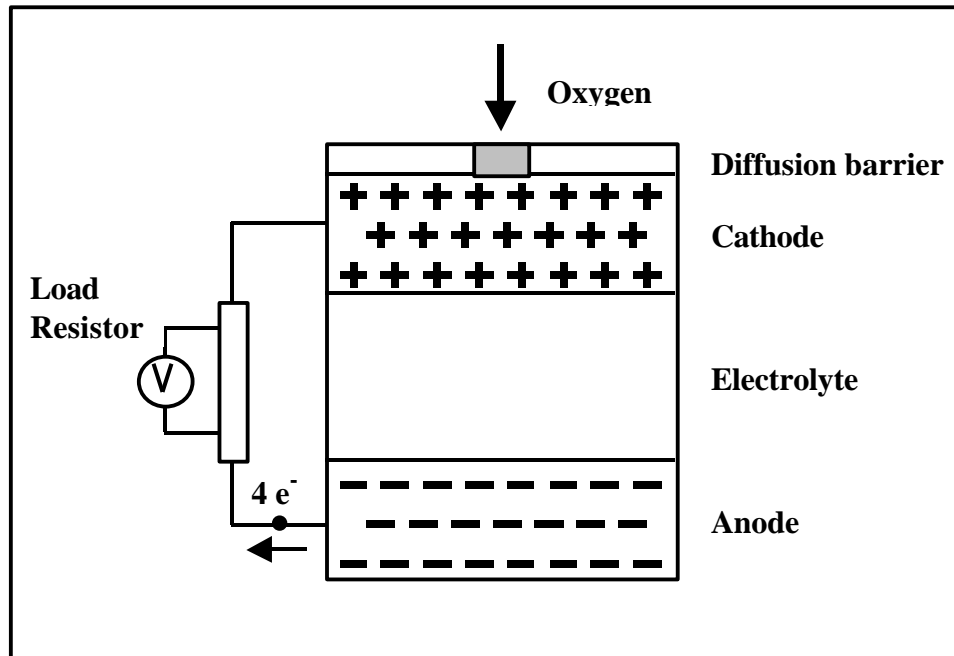


Figure 1. Simplified diagram of capillary pore type oxygen sensor.

This effect can be seen clearly when a properly calibrated capillary pore oxygen sensor is taken on board a commercial jet. Initially the sensor reads 20.9 %. As the jet takes off and begins to gain altitude the pO₂ drops causing a drop in oxygen sensor readings. When the jet reaches cruising altitude (actually, when cabin pressure is stabilized at normal operational levels) the readings return to 20.9 %. As the jet begins its descent prior to landing, pO₂ increases causing a rise in readings. As soon as the sensor is back at ground level (and the cabin once again depressurized) readings will return to 20.9 %.

Capillary pore designs are potentially vulnerable to blockage of the capillary. For this reason capillary-pore sensors include an external moisture barrier to prevent the pore from being blocked or plugged by solid materials, water, or other fluids.

Figure 1 provides a simplified diagram of a capillary-pore oxygen sensor. The amount of current produced by an oxygen sensor is proportional to the amount of oxygen that enters the sensor. Capillary-pore sensors include a narrow diameter tube through which oxygen diffuses into the sensor.

Most instruments designed for measuring oxygen in confined spaces display readings in units of percent by volume concentration, regardless of the type of sensor that is employed.

Readings are usually in increments of ± 0.1 % O₂., with a full instrument range on the order of 0 - 25 % oxygen. A few designs are capable of displaying readings in partial atmospheric pressure (kilopascals or millimeters mercury) rather than concentration.

Capillary-pore sensors are altitude and weather independent. Physiologically based oxygen deficiency or enrichment may not be obvious to users of this type of equipment because concentration would remain constant at all altitudes of normal use. Partial-pressure sensors are pressure (and therefore, altitude and weather) sensitive. Calibration of these instruments at sea level and use at higher altitude, or calibration at higher barometric pressure than present during actual use could cause underestimation of concentration. Even more likely, changes in pressure can easily lead to false high or low alarms. In some cases fluctuation in pressure due to forced air ventilation or maintenance of a pressure regime within an industrial site can be the cause of fluctuation significant enough to cause an alarm. As an example, a slight negative pressure is maintained in many nuclear power generating station containment buildings. In the case of one generating station known to the author, the partial atmospheric oxygen sensors installed at the facility went into low oxygen alarm every time the pressure system cycled. The operators eventually sought and received a variance to set the low oxygen alarms at 18 % rather than 19.5 % to reduce the number of false alarms. Conversely, calibration to 20.9 % at the surface of a mine could overestimate the concentration present at operating depth where total pressure is higher. An ambient condition easily could be falsely identified as oxygen-deficient or oxygen-enriched by oxygen-testing instruments containing sensors that are pressure-sensitive. On the other hand, instruments containing this type of sensor provide the best facility for estimating adverse conditions, since the body responds to partial pressure of oxygen and not concentration.

Mechanisms of sensor failure

Some oxygen sensors are affected by prolonged exposure to acid gases, such as carbon dioxide. Most oxygen sensors

should not be used continuously in atmospheres containing more than 25 % CO₂. In some cases, prolonged exposure to the acid gas damages the basic (alkaline) sensor electrolyte. In other situations, high concentrations of acid gas produce a current flux that alters the normal expected output of the sensor at a given concentration of oxygen.

Use in extreme conditions can affect data provided by the instrument. Extreme conditions are any which exceed published operating specifications for the instrument. Users should always consult the owner's manual or contact the manufacturer directly before using an instrument in any unusual or extreme environment. This includes operation in cold or excessively hot temperatures. Monitoring conditions that should trigger queries about appropriateness for use include:

- Inerted atmospheres
- Corrosive atmospheres
- Atmospheres containing high concentrations of combustible gas
- Atmospheres which contain high concentrations of other known contaminants
- Excessively hot or cold temperatures
- Excessively humid, wet, or dirty conditions

While the instrument may not pose an ignition or intrinsic safety hazard, the accuracy of readings may be adversely affected during use outside of design parameters.

As indicated previously, the working electrode in a fuel-cell sensor is consumed over time. When all available surface area of the lead (Pb) anode is converted to lead oxide (PbO₂), electrochemical activity ceases and current output falls to zero. This is the type of sensor failure most frequently experienced by users. This failure is fail-safe, since the oxygen deficiency alarm

activates whenever current output falls below a minimum level. At this point the instrument will alarm continuously until the sensor is replaced. Hence, no one is likely to attempt to use the instrument to obtain readings in this condition.

Causes of erroneously high output

Some conditions can lead to an erroneously higher, rather than lower electrical output from the sensor. This potentially is a very dangerous type of malfunction, since it is not easily detectable by the user. Erroneously high output can occur due to mechanical malfunction. If this occurs, the instrument could indicate a safe condition when the atmosphere is actually dangerously oxygen deficient!

Capillary-pore oxygen sensors include a narrow diameter tube through which oxygen diffuses into the sensor. Partial blockage of the pore would decrease the amount of oxygen drawn into the sensor. This would lead to a drop in current output. When used in a normal atmosphere, this would be interpreted by the instrument as an oxygen deficient condition, a false low. When used in an oxygen enriched atmosphere under this condition, the instrument could read a false acceptable. Damage to the sensor housing, such as a crack or opening that creates a new channel through which oxygen can diffuse can introduce more oxygen than would normally be able to enter. This can sometimes cause erroneously high readings.

Bubbles in the electrolyte also can cause erroneously high sensor output. When a sensor containing bubbles is rapidly taken from a warm area to a very cold area, the difference in temperature can cause sudden contraction in the bubbles. This decreases the pressure inside the sensor capsule and draws more oxygen into the capillary tube than normally would occur. The result is an

increase in current output and a false high reading. This type of situation can occur when an instrument stabilized to indoor conditions is taken outside and exposed to winter temperatures. This type of anomaly is not permanent. Once the bubbles stabilize to the new temperature, and the pressure inside the sensor capsule equalizes with that outside, output will decrease to normal levels.

Zero-adjusting or calibrating while the output is erroneously high creates a serious problem. Later on, when the sensor output has dropped back to normal levels, readings will no longer be accurate. Fortunately, the preventive actions that are needed are simple! Verify the accuracy of the instrument by exposing it to known concentration test gas before any daily period of use! This advice applies to all the sensors in the instrument, not just the oxygen sensor. This is by far the most prudent approach.

Most calibration gas mixtures used to verify the accuracy of the oxygen sensor in a confined space instrument use a concentration that is less than 20.9 %. The purpose for this is to activate the appropriate alarms when the sensor is exposed to the gas mixture. This means that if the sensor is working properly, readings should drop to the concentration indicated on the label of the calibration gas cylinder and the low O₂ alarm should activate. When calibration gas is not available in the field, ensure that the oxygen sensor reads 20.9 % in fresh air, then exhale onto the sensor. Readings should decrease, (in many cases to a low enough level to activate the low oxygen alarm), then recover. Readings which fail to decrease, or which require an abnormally long time to recover fully may indicate a problem with the sensor. Table 2 summarizes failure mechanisms in fuel-cell oxygen sensors.

Table 3 Failure Mechanisms in Fuel-Cell Oxygen Sensors	
Failure modes which lead to lower current output:	
All available surface area of Pb anode converted to PbO ₂	
Electrolyte poisoned by exposure to contaminants	
Electrolyte leakage	
Desiccation	
Blockage of capillary pore	
Failure modes which lead to higher current output:	
Cracking or damage to sensor housing or capillary pore	
Bubbles in electrolyte	

Figure 2 pictures a typical single-sensor oxygen monitor. (Courtesy of RAE Systems Inc. Sunnyvale, CA)

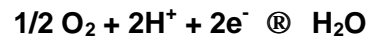
Solid polymer electrolyte (SPE) oxygen sensors

A recent development in oxygen sensor technology is the development of non-consuming, solid polymer electrolyte (SPE) sensors. Fuel-cell oxygen sensors generally contain the following parts:

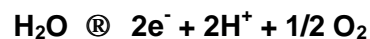
- Capillary diffusion barrier
- Sensing, counter and working electrodes made from porous platinum
- Solid polymer electrolyte (such as Nafion)
- External moisture barrier or filter
- Rigid housing

Solid-state electrochemical oxygen sensors include a solid-polymer-electrolyte such as Nafion, porous platinum sensing, counter and reference electrodes, a capillary barrier to limit oxygen diffusion, and a rigid

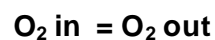
housing to avoid any leakage. Oxygen entering into the sensor diffuses into the solid polymer electrolyte, where it undergoes the following half-cell reaction:



Application of electrical current to the solid polymer electrolyte drives the electrolytic disassociation of water to produce oxygen according to the following half-cell reaction:



Thus, overall:



The amount of current necessary to pump oxygen molecules back out of the electrolyte is proportional to the concentration of oxygen molecules in the atmosphere being sampled. This principle of detection gives rise to the common name of “oxygen pump” for this type of sensor.

By applying a bias voltage on the reference electrode, the output current of the sensing electrode is proportional to the rate of oxygen consumption according to Faraday’s Law in case of purely limited diffusion. This current can be measured by connecting a resistor to produce a voltage signal. SPE sensors are suitable for measurement in the range of 0-25% oxygen by volume.

The chief advantages of this type of sensor derive from the fact that it is a non-consuming type design. Unlike fuel-cell oxygen sensors, SPE sensors do not consume lead in order to detect oxygen. In the case of SPE sensors the only thing consumed over time is the electrical energy required to pump the oxygen back out of the electrolyte. That means that SPE sensors are theoretically capable of operational lifespans of two to five years. In addition, again because of their non-consuming designs, SPE sensors are lightweight and particularly suited to miniaturization.



Figure 2. ToxiRAE Plus Single-Sensor Oxygen Monitor (Courtesy RAE Systems Inc., Sunnyvale California)

The chief limitation of SPE sensors is that when subjected to prolonged operation in extremely dry atmosphere, the SPE electrolyte may dry out, preventing the electrochemical detection reaction. Exposure to atmosphere which contains even a minimum amount of humidity is generally sufficient to rehydrate the electrolyte, and restore the function of the sensor.

IGNITABLE GASES AND VAPORS

The ignitable gases and vapors encountered in confined spaces arise from a number of sources. These can include microbial decomposition, displacement of the atmosphere originally contained in the space by ignitable gases and vapors, residuals from previous uses of the space or emissions from work activity. Sources from previous uses of the space include:

- Vaporization of residual contents (liquids and sludges)
- Products from chemical processes
- Desorption from structural materials

Desorption from vessel walls or other structural elements is a special concern. Desorbed vapors create a number of potential hazards ranging from oxygen displacement to toxic contamination far in excess of exposure limits. Desorption of substances that form ignitable mixtures from the inner walls of vessels is a particular concern. During storage, liquid

propane is absorbed into the porous walls of the tank in which it is being held. Following drainage, propane continues to desorb into the atmosphere of the tank.

Many work activities involve the use of organic solvents in a manner that creates highly concentrated mixtures in air. A prime example is spray-painting. Spray-painting creates a suspension of droplets of volatile liquid, as well as large wetted surfaces on structures. Both are sources of vapor.

A wide variety of ignitable gases and vapors may be encountered during initial evaluation of conditions in a confined space and work activity following initial entry. When present in sufficient concentration, gases and vapors of many substances become ignitable. Following contact with energy provided by suitable ignition sources ignition can occur. Ignition sources present in confined spaces can include hot work activity, sparking tools, lighting, power tools, electrical equipment, or even static electricity.

In order for an atmosphere to be ignitable (i.e. capable of the propagation of flame away from the source of ignition when ignited), four conditions must be met. The atmosphere must contain adequate oxygen, adequate fuel, a source of ignition, and sufficient molecular energy to sustain the fire chain reaction. These four conditions are frequently diagrammed as the "Fire Tetrahedron". If any side of the

tetrahedron is missing or incomplete or insubstantial, combustion will not occur.

Any gas or vapor capable of forming an ignitable mixture when mixed with air or oxygen will ignite at some inherent minimum concentration, provided that the other conditions in the fire tetrahedron are met. An ignitable mixture contains a flammable or combustible substance. The temperature at which there is sufficient vapor from a flammable substance is less than 38 °C (100 °F). The temperature at which there is sufficient vapor from a combustible substance is between 38 °C (100 °F) and 93 °C (200 °F). The minimum concentration at which a mixture ignitable is the Lower Flammable Limit or LFL. A mixture that will burn also can be made to explode. The term, Lower Explosive Limit or LEL, often is used interchangeably with LFL. While these terms are not equivalent in strictest terms, both will be used interchangeably here to avoid confusion. Below the LFL/LEL the ratio of gas/vapor to oxygen is too low for combustion to occur. Stated in other words, the mixture is "too lean" to burn.

Most (but not all) ignitable gases/vapors also have an upper limit of concentration beyond which ignition will not occur. The Upper Flammable Limit or UFL is the maximum concentration of gas/vapor in air that will support combustion. The term, Upper Explosive Limit or UEL, is often used synonymously with UFL. This convention will be used here. Above the UFL/UEL the ratio of gas/vapor to oxygen is too high for the fire reaction to propagate. Stated in other words, the mixture is "too rich" to burn. The difference in concentration between the LFL/LEL and UFL/UEL is the Flammable Range. Gas/vapor concentrations within the flammable range will burn or explode provided that the other conditions required in the fire tetrahedron are met.

The flammable range varies widely between individual gases and vapors. This

partly results from the convention of expressing LFL/LEL and UFL/UEL in percent units rather than in g/m³ (grams per cubic meter). When expressed in the latter units, the LFL/LEL for many substances are similar, averaging around 45 to 50 g/m³. Table 10.3 provides flammability limits for some commonly encountered substances.

Table 4		
Examples of Flammability Limits (NFPA Flammable Liquids, Gases, and Volatile Solids, 1977)		
Substance	LFL/LEL (% Vol.)	UFL/UEL (% Vol.)
acetone	2.6	12.8
acetylene	2.5	100
ammonia	16	25
carbon monoxide	12.5	74
ethylene oxide	3	100
hydrogen	4	75
hydrogen sulfide	4.3	46
methane	5	15
propane	2.2	9.5
From National Fire Protection Association, <i>Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids</i> , NFPA, Boston, 1977		

Flammability limits commonly listed in tables are determined at ambient temperatures and pressures, and at standard atmospheric concentrations of oxygen. Moderate oxygen enrichment exerts a profound effect on the flammability range by dramatically promoting and accelerating combustion.

Flammable/combustible gas and vapor detecting instruments usually read in "percent LEL" rather than "percent by volume". This distinction is extremely important! To illustrate, consider an environment in which

an instrument produces a reading of 3 % by volume. If the exact composition of the gas/vapor or mixture producing the reading is known, ignitability of the atmosphere can be determined. On the other hand, if the exact composition of the gas/vapor or mixture producing the reading is not known, ignitability of the atmosphere cannot be determined. If the reading is due to methane, (since the LEL for methane is 5 % by volume), the concentration is less than the LFL/LEL. If the reading is due to propane, (since the LEL for propane is 2.2 % by volume), the concentration is above the LEL, and a source of ignition could cause a fire or explosion.

Most instruments read from 0 to 100 % LEL. The reason for this is that consensus and regulatory standards use a percent value of the LFL/LEL to impose a margin of safety in hazard management. The most common limits are 5 or 10 % LFL/LEL. Ten percent of LFL/LEL is the default alarm setpoint on many instruments. Figure 3 illustrates the relationship between the "Percent LFL/LEL" scale for a flammable gas or vapor, and the flammability range for the same substance.

A fire hazard should always be deemed to exist whenever readings exceed 10 % LFL/LEL. This is the least conservative (or highest acceptable) alarm setpoint for instruments used for monitoring flammable/combustible gases and mixtures in confined spaces. An important consideration about the setpoint of 10% LFL/LEL is that many circumstances warrant a more conservative, lower alarm setpoint. The presence of any detectable concentration of flammable/combustible gas in the confined space indicates the existence of an abnormal condition. The only completely safe concentration of combustible gas in a confined space is 0% LFL/LEL.

Most evaluation for ignitable gases and vapors occurs with instruments

designed to detect the widest possible variety of mixtures. Evaluations should consider the size of the source, release or emission rate, the distance of the source to the point where ignition could occur and work activity.

Some types of instruments do read concentration in percent by volume flammable/combustible. The most notable example is the methanometer approved for use in MSHA-regulated mines. (MSHA is the Mine Safety and Health Administration.) Readings are always stated in units of percent by volume of methane. Monitoring activities related to "gassy" mines fall under the scope of MSHA regulations. These indicate explicitly the amount of methane that may be permissible. A reading of 5 % methane unambiguously indicates to the instrument operator that the atmosphere is 100 % explosive!

Instruments designed to measure high range flammable/combustible concentrations also read concentration in percent by volume. While the primary purpose of these instruments is to read concentrations higher than the LFL/LEL, when used in lower concentration ranges, concentrations are frequently still provided in percent by volume concentrations. For example, a typical flammable/combustible gas detector used to measure natural gas provides readings on a scale of 0 - 100 % by volume regardless of whether the concentration exceeds the LFL/LEL. At the other extreme, some instruments have a low range scale that reads in parts per million (ppm) of combustible gas. It should be noted that some designs include an auto-ranging feature which displays readings in increments which are appropriate to the concentration encountered. In the case of these designs the same instrument may display readings in ppm, percent LFL/LEL, or percent by volume.

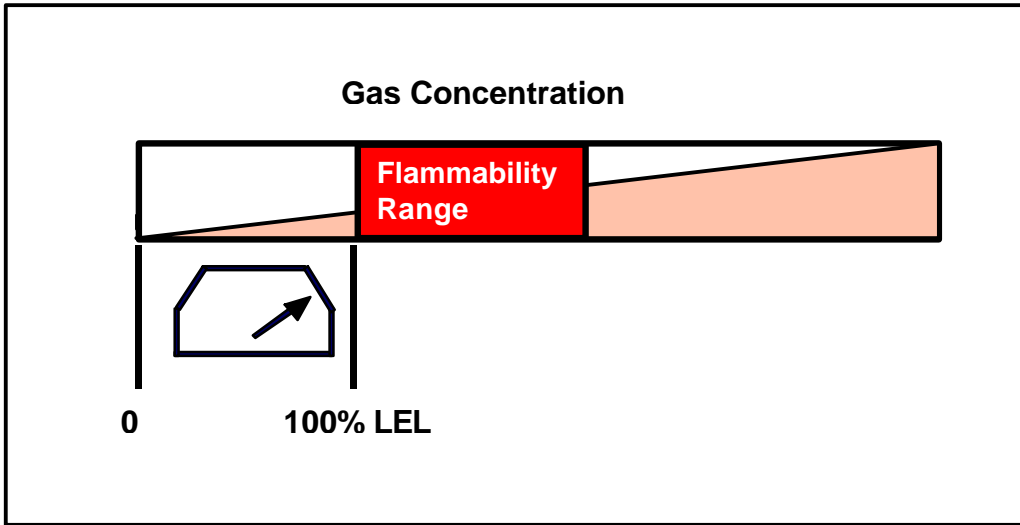


Figure 3 Flammable/combustible gas sensors read in percent LEL.
 (Reprinted courtesy Ergonomics Inc, "Corporate Health and Safety", 1996)

Role of flash point in monitoring of ignitable gases and vapors

Vapors are the gaseous state of substances that are either liquids or solids at room temperature. Vaporization or evaporation rate, the rate at which the change from liquid or solid to vapor occurs, is a key property in consideration of formation of ignitable mixtures. Vaporization is a function of temperature. Increasing the temperature of the liquid increases the rate and amount of vapor that is produced. Conversely, cooling the atmosphere decreases the amount of vapor produced and may condense vapors back to liquid.

In order for combustion to occur, the vapor of the substance must be present in the atmosphere. As a general rule, it's the vapor, not the liquid that burns. The temperature at which sufficient vapor is present for combustion is a key concept in fire protection. This applies especially to confined spaces where boundary surfaces reduce or eliminate the influence of air currents and the wind in vapor dispersion. Flash point is the

minimum temperature at which a liquid gives off enough vapor to form an ignitable concentration. The flash point is the temperature at which the LFL/LEL first occurs. The flash point is an inherent property of the substance.

Table 4 lists the flash point for a few common substances.

Table 5		
Examples of Flash Points		
Substance	Flash Point	
	°C	°F
Gasoline (aviation grade) ^a	- 46	- 50
Acetone	- 20	- 4
Methyl ethyl ketone	- 9	16
Ethanol (96%)	17	62
Diesel Oil (#1-D) ^a	38	100
^a Approximate minimum temperatures		
From National Fire Protection Association, <i>Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids</i> , NFPA, Boston, 1977		

The practitioner must consider the flash point of liquids which may be present in the workplace as part of the monitoring strategy.

Diesel oil or turpentine and other substances that have higher flash points may not be detectable at normal room temperature with a flammable/combustible gas indicator that reads in percent LEL. The detector cannot detect until the substance is present in the atmosphere as a vapor at some minimum level.

An extremely important caveat regarding the assessment process is temperature of the substance. Increasing the temperature of the liquid after the initial test can dramatically alter the amount of vapor in the atmosphere. This could occur in various ways:

- Solar heating on surfaces of the structure
- General work activity
- Spot heating during hot work, such as cutting, grinding, welding, gouging, drilling, and so on.

Increasing the temperature sufficiently could provide sufficient vapor for the composition of the atmosphere to enter the flammable range. Lack of attention to this situation has caused many fires and explosions during work activity in confined spaces and during work on the exterior of "empty" containers. Testing must occur under the conditions of work. Testing before work begins in the morning when a structure is cool may not predict the hazard that can arise later in the work shift.

At 10 °C (50 °F), ethanol does not produce a sufficient amount of vapor for ignition. At 21 °C (70 °F), vapor generation is sufficient to produce an ignitable mixture.

A common concern of individuals attempting to monitor vapor from high flash liquids, such as diesel fuel, is detection by nose but not by the instrument. The person

knows the substance is present because it is clearly nose detectable; yet the combustible gas monitor shows no response in the percent LEL range. Several factors might contribute to this situation. First, the instrument should be directly calibrated to the substance being measured. An instrument calibrated with methane may not be sensitive to vapor from diesel fuel. The fittings, hoses, or tubing used to convey the sample from the environment to the instrument may absorb the vapor. In this case, the vapor may never reach the sensor. Readings would be strongly depressed. There may also be a temperature-related effect. In winter, atmosphere in the space is often warmer than the external environment where the instrument and operator are located. While the atmosphere inside the space may be warm enough for the diesel fuel to exist as a vapor, the vapor may cool sufficiently while being ducted through the sample tubing to recondense into a liquid. The sensor detects only vapors.

Another important issue is the resolution of the instrument. An instrument that reads in percent LEL, with readings incremented in 1 % steps, cannot resolve changes in concentration smaller than ± 1 % of LFL/LEL. To illustrate, consider a combustible vapor which has an LFL/LEL of 0.7 % (7,000 ppm). (One percent is 10,000 ppm.) A properly calibrated instrument will only be able to resolve changes that are greater than 70 ppm. Although an individual might be able to smell the substance at 20 ppm, this would be below the detection minimum for the instrument. The instrument reading in this circumstance would probably be zero! It is very important to understand the resolution limits of the equipment being used when monitoring vapor from high flash liquids, such as turpentines, diesel fuel or jet fuel. In many cases percent LEL range instruments are simply not appropriate. Increasingly, many monitoring programs are turning to photoionization detectors, or use of combustible sensors operable in the low

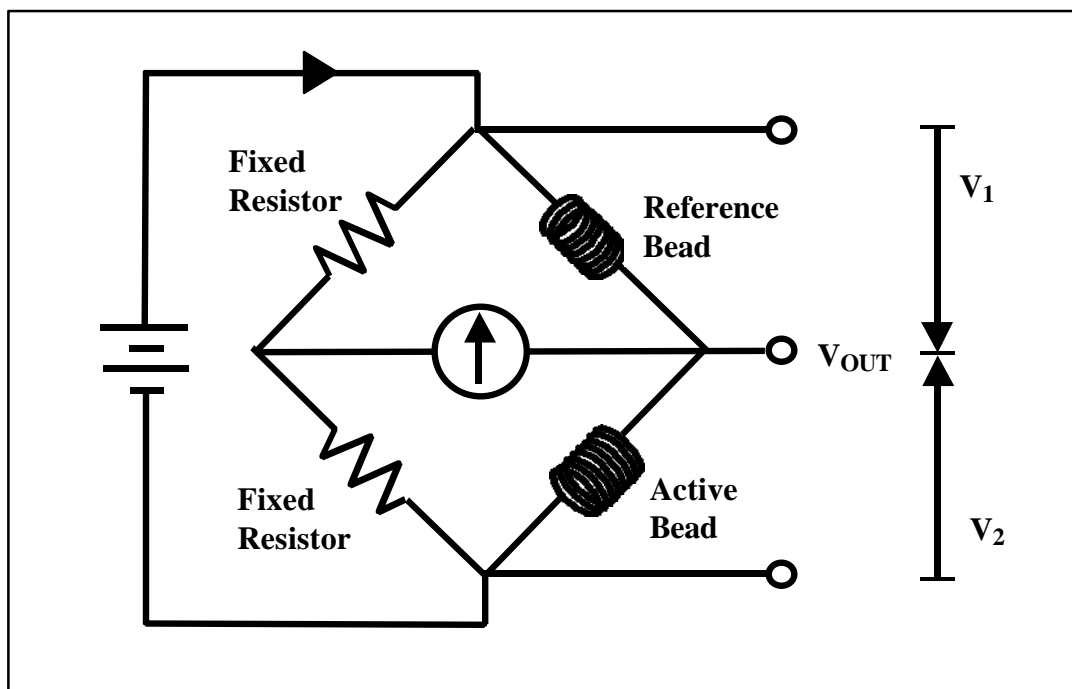


Figure 4 Wheatstone bridge electrical circuit. (Reprinted courtesy Ergonomics Inc, "Corporate Health and Safety", 1996)

parts-per-million range when monitoring for high flashpoint combustible liquid vapors.

An important point to stress in circumstances where the vapor cannot be detected with an instrument that reads in percent LEL is that this is not an indicator of lack of hazard. An instrument that is capable of resolving vapors into the ppm range may be more appropriate. On the other hand, if what is needed is a determination of ignitability, a properly configured and calibrated instrument that reads in percent LEL will provide that information.

Testing at all levels in a confined space during hazard assessment is critical. Gases and vapors that are less dense than air tend to rise to the top of a structure, while denser than air gases and vapors tend to sink. In confining environments this can lead to stratification of the gases into density dependent layers. Typical low density gases

that can form flammable mixtures include hydrogen, methane and ammonia. Typical denser-than-air contaminants that can form ignitable mixtures include propane, hydrogen sulfide and gasoline, and many commonly used organic solvents.

CATALYTIC (HOT BEAD) SENSORS

General discussion

Instruments for monitoring ignitable mixtures most frequently use catalytic (hot bead) sensors. Sensors of this type are frequently referred to as pellistors. While there are numerous variations, the underlying detection principle has not changed for the better part of a century. The hot bead sensor is a miniature calorimeter that contains two coils of fine platinum wire which are coated with a ceramic or porous alumina material to form refractory beads.

The beads are wired into opposing arms of a balanced Wheatstone Bridge electrical circuit. One bead is additionally treated with a platinum or palladium-based material that allows catalyzed combustion to occur on the treated surface of the "active" (or detector) bead. (Moseley, Solid State Gas Sensors, 1987) It should be noted that the porous or sintered nature of the bead means that the available surface is large compared to the diameter of the bead. The catalyst is not consumed during combustion. Combustion occurs at concentrations far below the LFL/LEL. Trace amounts of gas/vapor in the air surrounding the sensor will oxidize catalytically on the surface of the bead. The "reference" (or compensator) bead in the circuit lacks the catalytic outer coating, but in other respects exactly resembles the active bead. Figure 4 illustrates a simplified version of the Wheatstone Bridge electrical circuit utilized in most catalytic bead type combustible gas sensors. Figure 5 illustrates the structure of the pellistor bead, and Figure 6 illustrates the placement of the beads within the sensor housing and flame-proof stainless steel sinter (or fret).

A voltage applied across the active and reference beads causes them to heat. Heating is necessary for catalytic oxidation to occur. The temperature required may be as high as 500(C, or in some cases, even higher. (City Technology Product Data Handbook, 1997) In normal air the Wheatstone Bridge circuit is balanced; that is, $V_1 = V_2$ and the voltage output (V_{out}) is zero. If ignitable gas/vapor is present, oxidation will heat the active bead to a higher temperature. The temperature of the untreated reference bead is unaffected by the presence of gas. Because the two beads are strung on opposite arms of the circuit, the difference in temperature between the beads is registered by the instrument as a change in electrical resistance. Under these conditions, $V_2 > V_1$ and V_{out} is proportional to the amount of oxidation that occurred.

Heating the beads to normal operating temperature requires power from the instrument battery. The amount of power required is a serious constraint on the battery life of the instrument. Recent sensor designs have attempted to reduce the amount of power required by operating the sensor at a lower temperature. While this approach may result in longer battery life, it may also result in the sensor being easier to poison or inhibit, since contaminants which might have been volatilized at a higher temperature can more easily accumulate on the surface of the bead. It is particularly important to verify the calibration of low power combustible sensors by exposure to known concentration test gas on a regular basis.

Sensors used to measure combustible gas in the ppm range are usually operated at a higher temperature. Operation at the higher temperature can improve the ability of the sensor to oxidize volatile organic compounds and certain other classes of difficult to detect substances which may not be measurable by means of a low power sensor. For instance, low power sensors may not be used to measure halogenated hydrocarbons such as methylene chloride. Halogenated hydro-carbons are absorbed or form compounds which are absorbed by the catalyst, thus (at least temporarily) reducing or inhibiting the activity of the sensor. On the other hand, some high power combustible gas sensors are capable of being used to measure halogenated hydrocarbons such as methylene chloride or trichloroethylene. Consult the owner's manual or contact the manufacturer directly to verify which contaminants may be successfully measured by the sensor prior to use!

A variation on the two bead (active bead / reference bead) theme is the single bead pellistor design. This design utilizes a thermocouple rather than a second bead to provide temperature compensation.

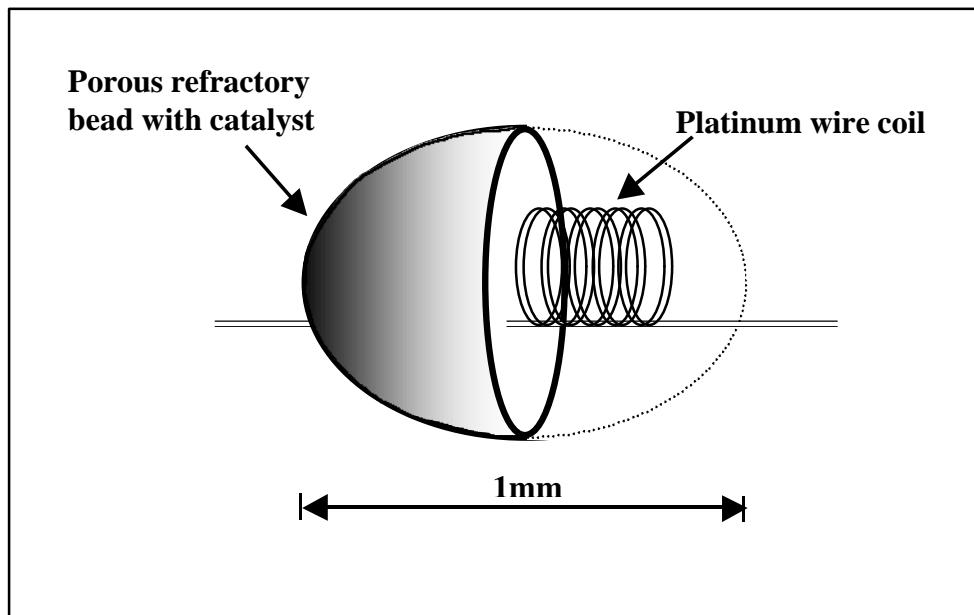


Figure 5 Schematic drawing of a catalytic bead. (Courtesy of City Technology, Ltd. Portsmouth, England)

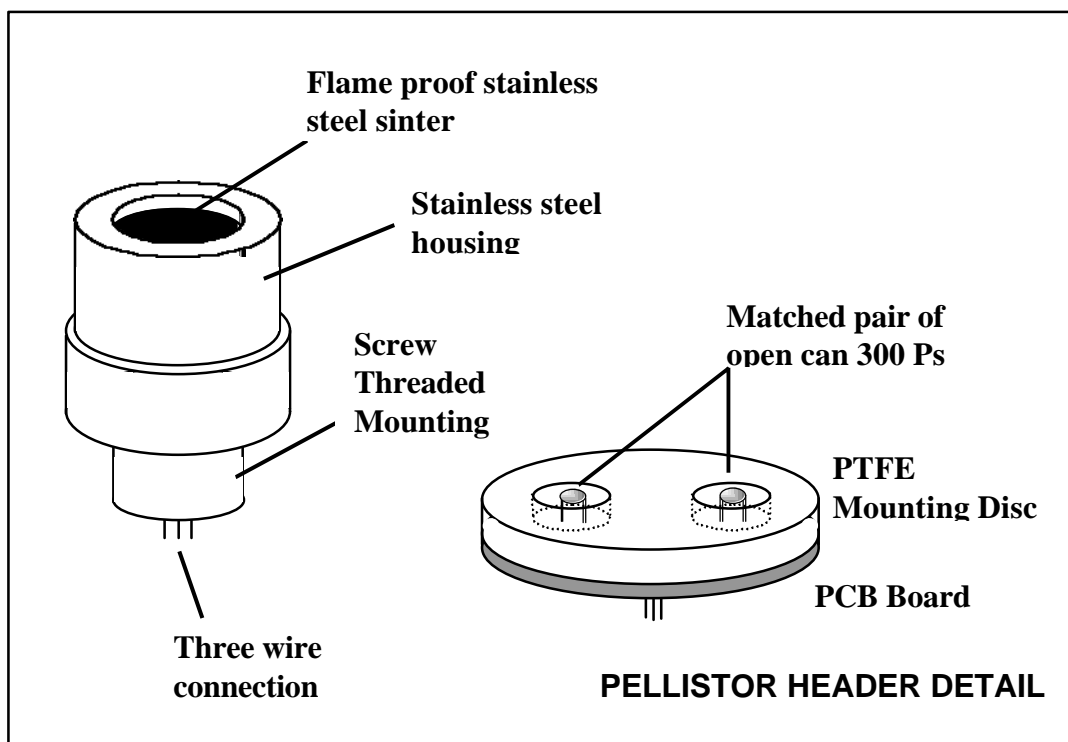


Figure 6 Schematic drawing of combustible sensor construction. (Courtesy of City Technology, Ltd. Portsmouth, England)

There are numerous other design difference between one brand or model of combustible sensor and another. Each design has been optimized for use in a specific instrument or application. Design differences may be found in the composition of the catalyst, coiling of the filament wire used in the beads, diameter of the filament wire, size and available surface area of the beads, power consumption, resistance to poisoning, and applicability for use in the ppm range. In other words, there may be significant differences in detection capability, power consumption, and general robustness of one design versus another.

An important consideration in use and interpretation of results from instruments equipped with a combustible gas sensor of this type is the concentration of oxygen in the environment being monitored. Catalytic (hot bead) sensors require at least 8 to 10 percent oxygen by volume to detect accurately. A combustible sensor in a 100 percent gas or vapor environment will produce a reading of zero percent LEL. This is the reason that testing protocols for evaluating confined spaces specify measuring oxygen first and then flammable/combustible gas/vapor. For this reason confined space instruments that contain hot bead sensors should also include a sensor for measuring oxygen. If the instrument being used does not include an oxygen sensor, be especially cautious when interpreting results. A rapid up-scale reading followed by a declining or erratic reading may indicate that the environment contains insufficient oxygen for the sensor to read accurately. (It may also indicate a gas concentration beyond the upper scale limit for the sensor, the presence of a contaminant which has caused a sudden inhibition or loss of sensitivity in the sensor, or other condition which prevents the sensor or instrument from obtaining proper readings.) The minimum amount of oxygen that must be present for the sensor to detect accurately is a function of design. Capabilities vary from one manufacturer to

another. Users who anticipate using their instruments in potentially oxygen deficient environments should contact the manufacturer for assistance.

Catalytic hot bead sensors respond to a wide range of ignitable gases and vapors. The amount of heat produced by the combustion of a particular gas/vapor on the active bead will reflect the heat of combustion for that substance. Heat of combustion varies from one substance to another. For this reason readings vary between equivalent concentrations of different combustible gases. Remember that the instrument reads electrical units that depend on change in resistance and not concentration units. The amount of heat provided by oxidation of the molecule on the active bead surface actually is inversely proportional to the heat of combustion for that gas. This occurs because of differences in molecular interaction with the catalytic surface. In general, the larger the size of the molecule the greater the heat of combustion. On the other hand, the smaller the molecule, the more readily it is able to penetrate the sintered surface of the bead, and interact with the catalyst in the oxidation reaction. Catalytic hot bead sensors, at least when operated in the percent LEL range, may not adequately detect "heavy" or long chain hydrocarbons, or the vapors from high flash liquids such as turpentines, diesel fuel or jet fuel. Once again, use of photoionization detectors, or use of combustible sensors operable in the low parts-per-million range may be a better approach. Consult the Operator's Manual, or contact the manufacturer directly to verify the capabilities of the instrument design when using a catalytic hot bead LEL sensor to monitor for the presence of these types of contaminants.

Calibration of these instruments is an important issue. A combustible gas sensor may be calibrated to any number of different gases or vapors. Where possible, the user should calibrate the instrument using the

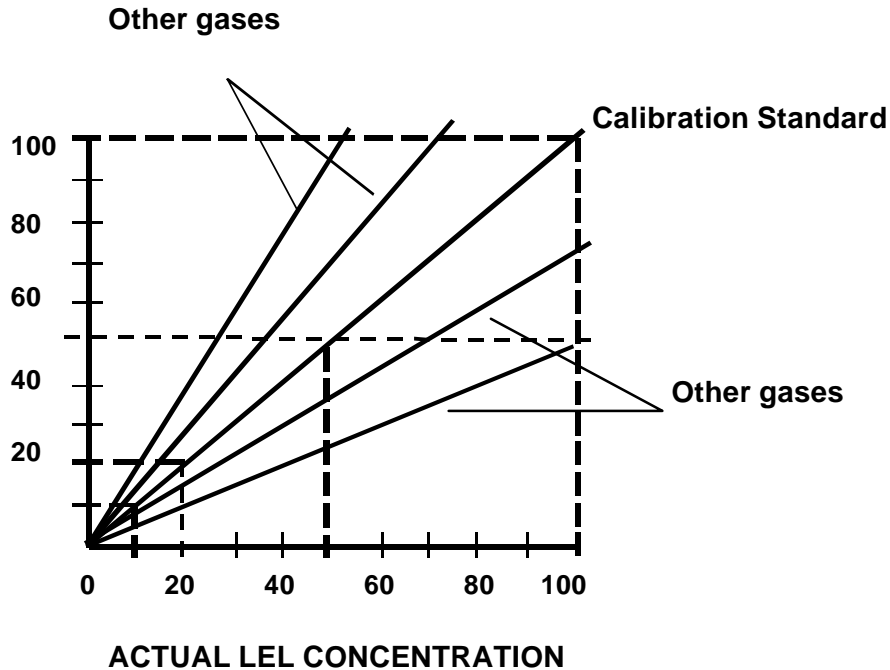


Figure 7 Relative response curves. (Reprinted courtesy Ergonomics Inc, "Corporate Health and Safety", 1996)

substance of interest. Calibration is a two-step procedure. In the first step the instrument is exposed to contaminant free "fresh" air (that is, air which contains 20.9 % oxygen and no combustible gas), turned on, and allowed to warm-up fully. The combustible sensor should read zero. If necessary, the combustible sensor is adjusted to read zero. Instrument manuals and other support materials usually refer to this step as the "fresh air zero." If the instrument cannot be taken to an area where the air is known to be fresh, "zero air" from a calibration gas cylinder should be used as an alternative source of contaminant-free air.

The second step is to expose the sensor to known concentration calibration gas, and (if necessary) adjust the readings to match the concentration. This is called making a "span adjustment". A "span adjustment" sets the sensitivity of the sensor to a specific gas. Always follow the manufacturer's instructions when calibrating or adjusting

the instrument. The type and concentration of calibration gas, the flow rate used to introduce gas to the sensors, and the adapters and fittings used during calibration all may affect the accuracy of the calibration procedure.

Never use methods or materials that differ from those described by the manufacturer. Use of incorrect flow rates, fittings, concentration of calibration gas or materials that are incompatible with the gas being used to calibrate the sensor can have a profound affect the accuracy of readings.

The response of a flammable-combustible sensor to an equivalent LEL concentration of gas varies from one substance to another. This is a natural outcome from calibration of these instruments in percent of LFL/LEL, rather than in units of g/m³. Hence, a 50 % LFL/LEL concentration of methane does not produce the same reading as a 50 % LFL/LEL concentration of propane. Instruments used only for a monitoring a

single substance should be calibrated with that substance. An instrument calibrated to a particular substance will be accurate within performance specifications of its design.

Figure 7 shows the response of a typical LEL/LFL reading instrument to several substances. Note that in the case of the gas which was used to calibrate the instrument (the calibration standard), a concentration of 50 percent LFL/LEL produces a meter response (reading) of 50 percent LEL in a properly calibrated instrument. Figure 7 also illustrates what occurs when an instrument is used to monitor substances other than the one to which it was calibrated. The diagram shows the relative response of the instrument to several different substances.

Note that the response to the substance to which the instrument was calibrated is still accurate. For the other substances the responses do not match. In the case of some substances the readings are always too high. The result from this is that the instrument overreacts to conditions and alarms prematurely. This type of error usually is not serious. The most likely result is that workers evacuate the affected area sooner than legally required.

Substances that produce lower relative readings than the calibration standard can create a potentially dangerous error. In Figure 7, the worst case only produces a meter reading of 50 percent LEL when the actual concentration is 100 percent LFL/LEL. If the instrument is set to alarm when the display reads 50 percent LFL/LEL, the alarm would sound simultaneously with a possible fire or explosion. The amount of relative error decreases the lower the alarm point is set. If the instrument is set to alarm when the display reads 20 percent LEL, a 50 percent LFL/LEL concentration of the same gas is enough to cause an alarm. If the alarm point is set to 10 percent LFL/LEL, the differences due to relative response of the sensor are minimized.

Most regulatory Standards such as OSHA 1910.146, and protocols such as ANSI Z117.1-1995, use 10 percent LFL/LEL as the threshold concentration above which a hazardous condition exists. (OSHA 1993, OSHA 1994, ANSI 1995) Many instruments use 10 percent LEL as the default combustible gas alarm setting. In fact, 10% LEL is the highest or least conservative alarm setpoint which may be used under most regulations and guidelines. This upper limit should not be used as an alarm setting without considerable thought. In its Compliance Directive (CPL 2.100) for Confined Space Entry, OSHA suggests that when entry is made according to the "Alternate entry procedures" specified in paragraph (c)(5)(ii) of 1910.146, a take action threshold of no higher than 5% LEL should be used to terminate entry and initiate evacuation procedures. (OSHA 1995)

Where alarm setpoints and action thresholds are concerned, the primary focus must be to enable work stoppage and safe exit. In some cases where continuous monitoring is occurring, 10% LEL might prove to be a reasonable action level. In other circumstances, the action level is the minimum detection threshold for the instrument being used to monitor for contaminant. Remember that the presence of any measurable ignitable gas/vapor indicates a potential problem.

The curves provided in the Figure 7 are simplified examples. The response of a flammable/combustible sensor is linear over a wide range, but flattens out near the top of its effective range. Standard catalytic (hot bead) sensors are not designed for use in concentrations that exceed the LFL/LEL for the substance being measured. Special techniques must be utilized in order to use catalytic type hot bead sensors in high-range applications.

Table 6			
Relative Response of a Flammable/Combustible Sensor			
Combustible gas / vapor	Relative response when sensor is calibrated on pentane	Relative response when sensor is calibrated on propane	Relative response when sensor is calibrated on methane
Hydrogen	2.2	1.7	1.1
Methane	2.0	1.5	1.0
Propane	1.3	1.0	0.65
n-Butane	1.2	0.9	0.6
n-Pentane	1.0	0.75	0.5
n-Hexane	0.9	0.7	0.45
n-Octane	0.8	0.6	0.4
Methanol	2.3	1.75	1.15
Ethanol	1.6	1.2	0.8
Isopropyl Alcohol	1.4	1.05	0.7
Acetone	1.4	1.05	0.7
Ammonia	2.6	2.0	1.3
Toluene	0.7	0.5	0.35
Gasoline (Unleaded)	1.2	0.9	0.6
Courtesy of Biosystems, Inc., Middletown, CT			

Relative calibration

The accuracy of combustible gas readings will be maximized when the instrument is calibrated using the same gas or vapor that will actually be monitored. When this is not possible or when the substance is an unknown, the user should select an alarm set point of 10 percent LEL or less.

Another approach utilizes the relative response of the sensor when calibrated with one substance and exposed to another. This involves multiplying the actual instrument reading by a correction factor or by using a chart containing the response curve of the sensor to several different substances. Prediction of concentration based on theoretical relative response deserves caution, since the relative response varies from sensor to sensor. In addition, response ratios can change over the life of a sensor. If the substance measured is identified incorrectly, or the wrong correction factor is used, significant inaccuracy in the

calculation could occur. This approach is not suitable for mixtures.

Table 6 lists the relative response of a typical flammable/combustible sensor when calibrated to one gas/vapor then exposed to another. Note the difference in the relative responses when the instrument is calibrated to propane or pentane, rather than methane.

It is important to note that the values included in Table 5 are provided as a general example of how this information is typically conveyed, and should not be used as the basis for actual calculations. The sensors used in a particular instrument may or may not have values similar to those shown in Table 5. Even later generations of the same model sensor may exhibit different relative response ratios if the manufacturer has made modifications to the design. Users should consult the owner's manual or contact the manufacturer of the instrument they will be using to verify the correct values to use when making calculations based on relative response.

As an illustration, consider a detector calibrated on methane that is then used to monitor ethanol. From Table 5 it can be seen that when calibrated on methane, the sensor shows a relative response to ethanol of 0.8. In other words, the readings will be 20% lower than actual.

Some manufacturers provide a table of correction factors rather than relative response ratios for the gas being measured. The correction factor is the reciprocal of the relative response. In the case of our example, the correction factor would be calculated as: $1 / 0.8 = 1.25$. Multiplying the instrument reading by the correction factor for ethanol (as determined above) provides the true concentration. Given a correction factor for ethanol of 1.25, and an instrument reading of 40 percent LEL, the true concentration would be calculated as:

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

Note that the correction factor for ethanol is different when the instrument is calibrated on propane. In the case of a propane calibrated instrument, instrument readings for ethanol will be higher than actual. Given that the correction factor for ethanol in this case is $1 / 1.2 = 0.83$, when the instrument reads 40 percent LEL, the true concentration for ethanol is 33 percent LFL/LEL.

40 % LFL/LEL x 0.82 = 33 % LFL/LEL		
Instrument Reading	Correction Factor	True Concentration

The closer the relative response to 1.0, the more accurate the reading becomes. To illustrate, consider a sensor that is calibrated to propane and then exposed to acetone. The response ratio (1.05) is so close to unity that for all intents and purposes any error is trivial.

Follow the manufacturer's instructions when selecting the substance to which the instrument will be calibrated. When not sure what substances might be encountered, the best course usually is to use a calibration mixture that provides a broad sensor response. Calibration using other substances should occur in situations where these are predominantly present, or where the relative response closely approximates that of the substance to be measured.

The data in Table 5 indicate that, when an instrument containing this sensor is calibrated with methane, readings for most other substances on the list are dangerously low. On the other hand, when calibrated with pentane, readings for other substances are excessively high. When calibrated with propane, most of the substances on the list produce readings that are close to or slightly higher than actual. For many applications, propane (or a mixture which provides a similar level of sensitivity) is the substance that is most appropriate for calibrating this sensor. Remember that manufacturers that use sensors with different characteristics may offer substantially different advice. Always follow the manufacturer's instructions when deciding which gas to use for calibration.

Prediction of concentration based on theoretical relative response or correction factors deserves caution, since the relative response varies from sensor to sensor. In addition, response ratios can change over the life of a sensor. If the substance measured is identified incorrectly, or the wrong correction factor is used, significant inaccuracy in the calculation could occur. Also, this approach is not suitable for mixtures. It is also very important to understand the method used by a manufacturer to communicate this information. Some manufacturers communicate this information in the form of tables or graphs of relative response. Others provide this information in the form of tables of correction factors. A number of manufacturers include a built-in library of

correction factors in the instrument's on-board memory. This is by far the most "user friendly" method of conveying this information, since readings are automatically converted into corrected equivalent readings for the substance being measured. Still, all the concerns and limitations discussed in the preceding paragraph remain applicable. It is critical to understand which method is used by the manufacturer before attempting to calculate true concentration based on relative response!

Sensor poisons and inhibitors

The atmosphere in which an instrument is used can have an effect on the sensors. Poisoning or degraded performance can occur when sensors are exposed to certain substances. Some commonly encountered substances which degrade LEL/LFL sensor performance are listed in Table 7.

Table 7
Combustible sensor poisons and inhibitors
Combustible sensor poisons:
<ul style="list-style-type: none"> • Lead containing compounds (especially tetraethyl lead) • Sulfur containing compounds • Silicones • Phosphates and phosphorus containing substances
Combustible sensor inhibitors:
<ul style="list-style-type: none"> • Hydrogen sulfide • Halogenated hydrocarbons (Freons, trichloroethylene, methylene chloride, etc.)

In the case of some substances, the compounds decompose on the catalyst and form a solid barrier over the catalyst surface. Exposure to substances of this type leads to irreversible loss of sensitivity. A

single exposure to a high concentration of a silicone-containing substance can destroy the sensor almost immediately. Other substances are absorbed or form compounds which are temporarily absorbed by the catalyst, inhibiting normal reaction. In the case of these substances the inhibition is usually temporary, and the sensor may substantially recover after a period of operation in fresh air. (City Technology Product Data Handbook, 1997; Moseley, Solid State Gas Sensors, 1987) Exposure to high concentrations of halogenated hydrocarbons can inhibit sensor performance in this way. Exposure to halogenated solvents causes accumulation of halogen molecules on the surface of the catalyst. Running the instrument while the sensor is located in fresh air tends to "cook off" much of the accumulated contamination. Nevertheless, recovery seldom is complete. Usually some permanent loss of sensitivity is a consequence from any exposure to any sensor poison or inhibitor.

Some substances (such as hydrogen sulfide) may function in both ways to degrade performance. Loss of sensitivity usually is dose dependent. A single very high exposure to hydrogen sulfide may produce an immediate irreversible loss in sensitivity. On the other hand, chronic exposure to low levels of hydrogen sulfide may require years to cause a significant loss of sensitivity.

The accuracy of flammable/combustible sensors can also be affected by exposure to high concentrations of ignitable mixtures. Excessive heating of the active bead can volatilize the catalyst coating. This could cause a partial or total loss of sensitivity. Excessive heating also can cause a break to develop in the filament or circuit wire of the sensor. Exposure to a very high concentration of ignitable gas or vapor (with concurrently low concentrations of oxygen) can lead to deposition of carbon black within the sintered surface of the active bead. Accumulation of carbon black

within the bead can cause splitting to occur. This causes a mechanical break in the circuit or significantly alters the sensitivity and stability of the sensor.

To minimize the potential for damage or loss of sensitivity to the sensor, some instruments "alarm latch" whenever the concentration exceeds 100 percent LEL. (This concentration usually is not high enough to damage the sensor permanently.) Under these conditions the instrument will indicate an over-limit condition, and audible and visual alarms will sound continuously. In addition, power to the sensor is cut to prevent damage. Until the over-limit alarms are cleared by manually resetting the instrument, the combustible sensor remains unpowered.

This logic is utilized by a number of manufacturers that have met requirements for classification for intrinsic safety by the Canadian Standards Association (CSA) under their standard for combustible gas detection instruments. (CSA C-22.2 No. 152-M1984) This testing protocol includes a "methane flood" test which evaluates performance of the instrument when exposed to a high concentration of methane. The instrument is turned on, calibrated, and placed for eight hours in a test chamber containing 80 % by volume of methane. This exposure is followed immediately by a test to verify accuracy when the instrument is exposed to 50% LEL of methane. Without the logic discussed above, most flammable/combustible sensors would be quickly destroyed by exposure to 80% by volume of methane.

Loss of sensitivity to methane

Age and usage affect sensitivity of flammable/combustible sensors. Chronic exposure to low levels of poisons or inhibitors acts cumulatively. This usually means that the sensitivity must be increased when calibration occurs. In the extreme, the sensor may require replacement. This again demonstrates that regular calibration is

essential to the safe use of these instruments.

For most combustible (hot bead) sensors, if sensitivity is lost due to poisoning, it tends to be lost first with regards to methane. This means that a partially poisoned sensor might still respond accurately to propane while showing a significantly reduced response to methane. This introduces a significant concern when choosing the substance to calibrate a flammable/combustible sensor. While sensitivity to propane or pentane may be all that is needed, use of propane or pentane as the only calibrant may lead the user to overlook a loss of sensitivity to methane. This could potentially be very dangerous, since methane is by far the most commonly encountered of all flammable/combustible gases associated with confined space entry.

Four methods exist for determining a loss of sensitivity to methane. The first is to calibrate the instrument using the calibrant which provides the best level of sensitivity (for instance pentane or propane) and then expose the sensor to a known concentration of methane. The relative response factor for methane can then be used to verify whether there has been loss of sensitivity. This approach increases the time needed to calibrate the instrument and complicates the logistics. Another problem is what to do if there has been a loss of sensitivity to methane.

The second approach is to calibrate the instrument directly to methane. An instrument "spanned" to methane will continue to detect methane accurately even when loss of sensitivity develops. Spanning the instrument during calibration simply makes up for any loss in sensitivity. As discussed, when the sensor is calibrated with methane, readings for most other substances tend to be dangerously low.

The third approach is to calibrate using methane at a concentration that produces a level of sensitivity equivalent to that provided by another calibrant (for

instance, propane, pentane, or hexane). Several manufacturers have begun to make use of these "equivalent" or "simulant" calibration mixtures. For the sensor described in Table 5, consider the methane mixture needed to calibrate to a propane level of sensitivity. The LFL/LEL of propane is 2.2 % by volume. In a properly calibrated instrument, a concentration of 1.1 % propane would produce a reading of 50 % LEL. A concentration of 1.62 % methane produces the same response. This is exactly the reading that should be shown in an instrument which has been calibrated for a propane level of sensitivity. Other concentrations of methane may be used to simulate other calibration gases such as pentane, hexane, or even substances (such as jet fuel vapor) which are not easily packaged in field portable cylinders. Since the calibration is based on methane, any loss of sensitivity to methane will result in over-spanning the sensor. Readings for substances other than methane will be a little higher than actual.

The fourth method is applicable only to instrument designs which include a built-in library of correction factors. In this case the instrument is calibrated by using methane, then the user chooses a correction factor (such as propane or pentane) from the instrument's library to provide a level of sensitivity roughly or exactly equivalent to the substances being measured. The benefit of this method, once again, is that since methane is used as the calibration gas, incremental loss of sensitivity to methane simply results in the instrument being "over-spanned", or producing higher than actual readings for the gas selected from the library of correction factors.

Calibration verifies that sensors remain accurate. If exposure to test gas indicates a loss of sensitivity, the instrument needs adjustment. If the sensors cannot be properly adjusted they must be replaced before any further use of the instrument. This is an essential part of ownership.

Low range hydrocarbon detectors

Although the primary hazard of most flammable/combustible gases and vapors is fire and explosion, they can pose other hazards. Denser than air gases and vapors can displace oxygen in confining environments. In many circumstances, even when the concentration is less than 10% LFL/LEL, a toxic hazard exists. To illustrate, ethanol (or grain alcohol) has an LEL of 3.3 % or 33,000 ppm. At 10% LFL/LEL, the concentration is 3,300 PPM, a significant toxic hazard exists, since the Threshold Limit Value--Time-Weighted Average is only 1 000 ppm. (ACGIH 1997)

Flammable/combustible gas and vapor instruments that read in the percent LEL range are designed to monitor contamination in the flammable range. In some instruments output from the Wheatstone bridge is electronically multiplied and corrected to produce a reading in various ppm ranges. Typical ranges are:

- 0 to 10,000 ppm (closely equivalent for many substances to the flammable range)
- 0 to 1000 ppm
- 0 to 100 ppm

Obtaining a stable signal from a flammable/combustible sensor that is operated in the ppm range is not a trivial engineering challenge. The combustible sensors used in these designs have large beads that require considerable power. The sensors operate at higher temperatures in the ppm range than in the percent LEL range. These instruments also have integral sample draw pumps to improve stability.

High range flammable/combustible instruments

Standard catalytic (hot bead) sensors require at least 8 to 10 percent by volume of oxygen to detect accurately. In addition, extremely high concentrations of gas can heat the bead so hot that it becomes cracked or damaged,



Figure 8. 1-5 Sensor VRAE Gas Detector equipped with dual-mode combustible sensor capable of both catalytic oxidation (0 – 100% LEL) and thermal conductivity (0 – 100% volume) detection. (Courtesy RAE Systems Inc., Sunnyvale, CA)

or suffers a loss of sensitivity due to vaporization of the catalyst. Different approaches are required to measure concentrations that exceed the LFL/LEL.

Thermal conductivity sensors

A thermal conductivity sensor measures flammable/combustible mixtures in the 0 to 100 % by volume range. The sensor contains two coils of fine wire that are coated with a ceramic material to form beads. The beads are strung onto the opposite arms of a balanced Wheatstone bridge circuit. Neither bead receives a catalyst coating. Instead, the reference bead is isolated from the air being monitored in a sealed chamber. The active bead is exposed

to the air which containing the gas/vapor mixture. Power is provided to the sensor to heat the beads to operating temperature. Detection depends on the "air-conditioning" effect of high concentrations of gas on the active bead. If a flammable/combustible mixture is present, the active bead will dissipate heat more efficiently than the reference bead. Once again, the difference in temperature between the two beads is proportional to the amount of flammable/combustible present. Since the two beads are strung on the opposite arms of a Wheatstone bridge, the difference in temperature between the beads is perceived by the instrument as a change in electrical resistance.

A recent innovation is the availability of hot bead sensors which are capable of operation in both catalytic oxidation and thermal conductivity modes. In this type of combustible sensor the catalyst coated active bead is constructed and positioned in the normal way within the sensor, but the compensating reference bead is housed in a semi-sealed chamber which is penetrated by a capillary pore to limit diffusion. During percent LEL range detection readings are obtained in the usual way by catalytic oxidation on the active bead. When operated in thermal conductivity mode, power is cut to the active bead to guard against damage to the bead, while the compensating bead continues to be maintained under power. Once again, the "air-conditioning" effect of the combustible gas on the bead is used to provide a reading. Figure 8 shows a Multi-sensor survey monitor equipped with a dual-mode combustible sensor capable of both catalytic oxidation (0 – 100% LEL) and thermal conductivity (0 – 100% volume) detection.

Oxygen displacement

Several brands of flammable/combustible instruments include a high range mode which allows calculation of combustible gas based on the amount of oxygen which has been displaced by the combustible gas. As combustible gas is introduced into an environment being monitored, more and more of the oxygen is displaced by combustible gas. Readings from an oxygen sensor are used to calculate the combustible gas concentration. Readings are generally given in percent-by-volume concentration with a range of 0 to 100 % combustible gas. Again, it is critical to reiterate the difference between readings displayed in percent LEL versus those displayed as percent by volume. Methane has an LFL/LEL of 5 % by volume. A reading of 5 % by volume is equivalent to a reading of 100 % LEL. In either case, the mixture would be fully explosive.

For maximum accuracy the sensor should be calibrated to the specific combustible gas that will be monitored. In fact, the displacement algorithm may be highly specific to a particular flammable/combustible gas/vapor. For instance, some manufacturers explicitly limit use of this type of high range mode to testing for methane or natural gas. Users should check with the manufacturer before using the instrument to monitor for any flammable/combustible gas/vapor other than those explicitly identified by the manufacturer.

Dilution fittings

As discussed, the accuracy of standard hot bead sensors is affected when used in highly oxygen deficient atmospheres. Below 8 to 10 % by volume (depending on the specific design), the sensor does not have sufficient oxygen to function properly.

A dilution fitting is a sample draw adapter that allows use of a standard hot bead sensor to obtain direct readings from oxygen deficient atmospheres. The adapter includes a dilution orifice designed to mix the gas sample with an equal volume of fresh air. Since fresh air contains 20.9 percent oxygen, the sample would contain at least 10 % oxygen. At this level, the sensor will read accurately.

An important consequence of diluting the sample with fresh air is that the amount of flammable/combustible gas/vapor in the sample also is diluted. Since the adapter provides a 50:50 dilution, the combustible and toxic gas readings must be doubled to obtain the true concentrations.

The adapter should be removed as soon as dilution sampling is completed. Leaving the dilution adapter in place during normal operation can lead to potentially dangerous misinterpretation of test results.

Make sure to locate the instrument in fresh air at all times while the dilution orifice is being used. Only fresh air

containing 20.9 % oxygen should be used to dilute the sample. If the dilution adapter is located in an oxygen deficient or otherwise contaminated atmosphere, proper sample dilution will not occur, and accurate readings will not be obtained.

The amount of air drawn into the dilution orifice is affected by the length and inner diameter of the sample draw hose. It is also affected by altitude and the flow rate of the mechanical pump contained in the instrument. Each adapter should be individually calibrated while attached to the monitor and sample probe assembly that will be used during sampling.

Dilution orifices make possible sampling for flammable/combustible gas/vapor from environments which could not be monitored otherwise. Improper use of dilution orifices can lead to inaccurate readings. These have the potential for being the basis of flawed decisions, a major cause of accidents. Manufacturers are very concerned about the potential for misuse of dilution adapters. Users must clearly understand the limitations before making use of this accessory.

METAL OXIDE SEMICONDUCTOR SENSORS

A type of sensor occasionally used for measurement of combustible gases and vapors in the percent LFL/LEL range is the metal oxide semiconductor (or MOS) sensor. MOS sensors are also used for monitoring at toxic levels. The MOS sensing element consists of a metal oxide semiconductor such as tin dioxide (SnO₂) on a sintered alumina ceramic bead contained within a flame arrestor. In clean air electrical conductivity is low. Contact with reducing gases such as carbon monoxide or flammable/combustible gases increases conductivity. Sensitivity of the sensing element to a particular gas/vapor is alterable by changing the temperature. MOS sensors are designed to respond to the widest possible range of toxic and

flammable/combustible gases/vapors. The most frequent usage of MOS sensors is ppm range hydrocarbon or toxic gas detection. A more detailed discussion of the MOS principle of detection, as well as specific advantages and disadvantages of this type of sensor is given in a later section of this chapter.

TOXIC GASES AND VAPORS

General discussion

Many toxic substances are commonly encountered during preparation of confined spaces for entry. Exposures to entirely unrelated substances can occur as a result of work activity. These exposures often are short-term and can occur because of sudden releases of material.

Airborne toxic substances typically are classified on the basis of their ability to produce physiological effects on exposed workers. Toxic substances tend to produce symptoms in two time frames: acute and chronic. Standards for workplace exposure provide a benchmark for protecting individuals against these effects. Confined spaces and the nature of work activity that occurs in them create the potential for accidental exposures above recognized standards. These overexposures can be fatal.

Hydrogen sulfide (H₂S) is a good example of an acutely toxic substance which is immediately lethal at relatively low concentrations. Exposure to 1,000 ppm produces rapid paralysis of the respiratory system, cardiac arrest, and death within minutes. Carbon monoxide (CO) also can act rapidly at high concentrations (1,000 ppm) although not as rapidly as hydrogen sulfide. Similarly, oxygen deficient atmospheres (< 10 %) also can cause death in the same time-frame. As discussed in the introduction, manufacturers responded to the needs of industry by producing portable instruments capable of providing rapid warning about these conditions.

Another need for instrumentation and monitoring equipment is the lower levels of exposure that occur during normal work activity. Work activity often is short in duration. Determining exposures rapidly is extremely important, since results from these studies form the basis for corrective actions. The atmosphere in a confined space during work activity can be highly complex and difficult to assess. The nature of the toxic contaminants present will also affect the choice of instruments used to monitor the confined space atmosphere.

Another influence on selection of equipment for monitoring is the type of limit applicable to the exposure. Many Standards and permissible exposure protocols define exposure limits in the following ways:

- An 8-hour time-weighted average (TWA)
- A short term exposure limit (STEL) calculated as a 15-minute time-weighted average
- A ceiling (CEILING) not to be exceeded

Exposure limits for gases and vapors are usually given in units of parts per million (ppm) and mg/m³. Exposure limits for liquid and solid aerosols are given in units of mg/m³.

The TWA concept is based on a simple average of worker exposure during an 8-hour day. The TWA concept permits excursions above the TWA limit only as long as they do not exceed the STEL or ceiling, and are compensated by equivalent excursions below the limit.

The regulatory TWA is a calculation using sampling results projected to a full eight hours. Time not measured is projected as zero exposure in many jurisdictions.

The method used by an instrument manufacturer to calculate and display TWA values can be a source of real confusion to

users. Some instruments include a TWA calculation that is simply the average of the measured concentration over the monitoring interval, and not projected to an 8-hour time-frame. Other manufacturers project the accumulated exposure over an 8-hour period. How to calculate the TWA when the work shift or monitoring interval exceeds 8-hours is another source of potential confusion. Some jurisdictions specify that when the work shift or exposure interval exceeds eight hours the summed exposure over time continues to be divided by 8 to calculate the TWA. Others specify that the monitoring interval used to calculate the TWA must not exceed eight hours. Manufacturers are equally divided! Some instrument designs calculate TWA for shifts which exceed 8-hours by dividing by 8. Other designs calculate TWA only on the basis the most recently completed 8-hours. Once again, the user must understand the method used by the instrument manufacturer to calculate the TWA value. If the Owner's Manual is vague on this point, call the manufacturer to establish the method used. Then call the regulatory authority to determine how they require this information to be interpreted.

Many instruments include the capability of displaying a "peak" or "ceiling" concentration which represents the highest (or in the case of oxygen, highest and lowest) concentration noted by the instrument during the monitoring interval. The specific nature of the values used by the instrument for this purpose varies between designs.

Sensors respond continuously to changes in the atmosphere being monitored. This information is constantly sampled by the instrument, and used to update the readings on the instrument display. Most instruments integrate sensor output over some period of time (for instance 1 second) before using it to update the displayed readings. Instrument designs may also use filtering algorithms or further integrate readings to reduce or remove anomalous

short term spikes or "glitches" which might otherwise lead to false positive or negative (downscale) alarms. This information is used to calculate "running" time-history calculations such as ceiling, STEL, and TWA. The amplitude of the "Peak" value displayed by the instrument will be a function of the exposure concentration, the speed of sensor response, and how frequently readings are updated. Instrument designs which update information more frequently may display higher readings when challenged by a brief high level exposure, than designs which integrate readings over a slightly longer time frame.

The best means for keeping track of TWA, STEL and CEILING calculations on a real-time basis is a microprocessor-based instrument. Microprocessor-based instruments are capable of solving these complex time-history equations, and updating the instrument memory many times per minute. In addition, most include independent alarm points for TWA, STEL and CEILING, and are capable of determining automatically when an alarm condition exists by the most conservative method of calculation.

Measurement of toxic gases and vapors

Of all the areas of atmospheric assessment, toxic gas measurement has available the most numerous detection technologies. While this may seem like an embarrassment of riches, it is not. Atmospheres in confined spaces, especially during work activity can be highly complex. No individual technology may be able to resolve a contaminant unambiguously from the others, at high speed and at reasonable cost. The method of choice could be a compromise.

BADGE-TYPE DOSIMETERS

One of the most useful technologies, the badge-type passive dosimeter is also one of the simplest to use. The most common varieties are small devices designed to clip

onto the shirt collar or lapel as close as possible to the breathing zone. The badges contain one or more layers of a material capable of absorbing the substance of interest. Badges designed to measure a specific contaminant frequently contain external filters or sorbent media that remove interferences. Badges used as organic vapor detectors usually contain one or more layers of an activated carbon material capable of absorbing a wide variety of organic substances.

Gases and vapors in the atmosphere move by passive diffusion into the badge where they are absorbed into or adsorbed onto the sorbent media. The badge is worn for a specific interval of time, then sealed in a container and sent to a laboratory for analysis. Breakthrough is characterized by the presence of contaminant in the secondary layer. Breakthrough indicates that the primary layer may have been saturated or exposed to such a high concentration of contaminant that the primary sorbent layer was incapable of absorbing all of it. Under these circumstances, prudence would dictate use of dosimeters run concurrently or consecutively. (The most accurate results will be obtained from an interval of exposure just slightly shorter than the time at which breakthrough occurs.)

This technology offers good discrimination between closely related molecular species such as benzene, toluene and xylene. The precision of rigorous laboratory analysis coupled with the fact that several hours of exposure can be integrated to produce the final time-weighted average exposure makes for highly accurate detection. The chief limitations of passive dosimeter badges are that readings are not obtainable in real-time, and the lack of laboratory analytical protocols. Protocols are available only for a limited range of contaminants.

For a number of important applications dosimeter badges represent the most practical and cost-effective approach

for assessing conditions. This is especially true for contaminants for which no other practical direct reading measurement technique is available. Work activity in confined spaces can occur in highly confined conditions. Workers could experience extreme discomfort and difficulty during the wearing of bulky and heavy sampling equipment. As well, this could pose a snagging or other safety hazard. Dosimeter badges are small, lightweight and unobtrusive.

SORBENT TUBE SAMPLING

Sorbent tube sampling utilizes the same concepts as dosimeter badges: absorption or adsorption of contaminants into or onto a sorbent medium. Sorbent tube sampling offers a number of additional refinements. The sorbent is loaded into sealed glass tubes that resemble short straws. A number of sorbent media, each with different properties, are available. (The medium is selected to optimize absorbance or adsorbance for a specific contaminant.) To sample, the ends are broken off and the tube is inserted into a manifold. Instead of relying on passive diffusion, this methodology utilizes a precision low flow sampling pump to pull a calibrated volume of air through the tube over a specific interval of time. Some manifolds can accommodate several tubes simultaneously, each with an independently adjusted flow rates for concurrent sampling. On completion of sampling, the tubes are removed from the manifold, capped and sent to a laboratory for analysis.

Sorbent tube sampling is a powerful tool for assessing conditions. As with passive dosimeters, the chief limitation is that readings are not obtainable in real-time. Laboratory analytical protocols are available only for a select group of contaminants. Sorbent tube sampling requires a pump and tubing. For personal samples, this equipment must be worn/carried somewhere in the clothing of the subject.

This equipment could become quite bothersome during work in tight quarters.

COLORIMETRIC MEASUREMENT TECHNIQUES

Colorimetric measurement techniques utilize reagents that undergo a color change when exposed to the specific contaminants they are designed to detect. Colorimetric detection is a real-time measurement technique. It can be used both for broad range screening, as well as for analysis of specific contaminants.

Colorimetric detector tubes¹

Colorimetric detector tubes resemble short glass straws packed with fine grain silica gel, activated alumina, or other medium. The tube contents are impregnated with the reagents that undergo a color change reaction when exposed to specific contaminants. To use, the ends are broken off and the tube is inserted into a hand pump designed to pull a calibrated volume of air. (Figure 9) Contaminants in the air that can react with the reagent, produce a color change progressively along the tube as the air passes through. The length of the color change is proportional to the amount of contaminant present. (Figure 10) The outside of the tube usually includes a measurement scale for estimating concentration, as well as other information such as the sample volume and number of pump strokes required to obtain a reading, the direction of flow when the tube is properly installed in the pump, and measurement units in which the reading is expressed.. The reading is taken as the furthest distance along the tube that the color change just becomes visible. If the leading edge is diagonal instead of perpendicular to

¹ The Author is indebted to Dr. Werner Haag of RAE Systems Inc., Sunnyvale, CA for his collaboration in the writing as well as preparation of the charts and figures reproduced in the "Colorimetric Detector Tubes" section of this Chapter.



Figure 9 Colorimetric gas sampling tube installed in piston type pump. (Courtesy RAE Systems Inc., Sunnyvale, California)

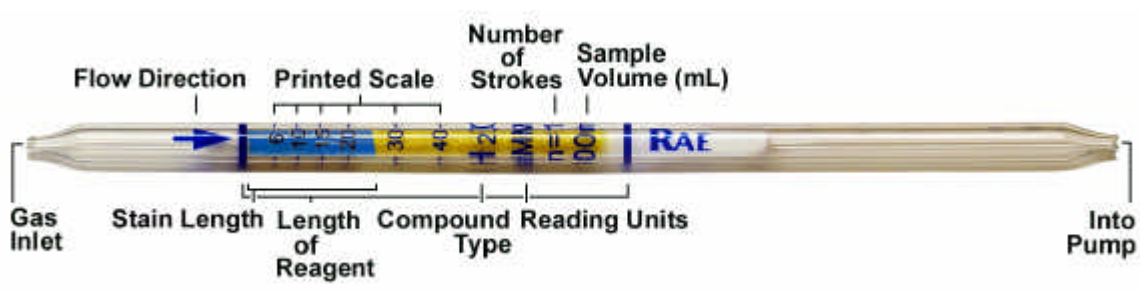


Figure 10 Colorimetric gas sampling tube for ammonia. (Courtesy RAE Systems Inc., Sunnyvale, California)

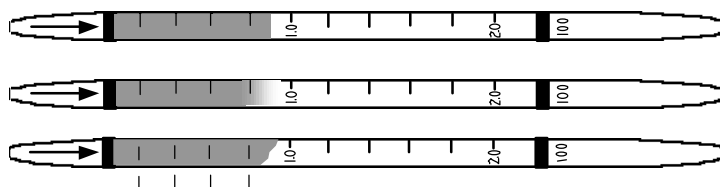


Figure 11 Reading of various types of endpoints after sampling: all register 0.9. (Courtesy RAE Systems Inc., Sunnyvale, California)

the axis of the tube, use the average of the minimum and maximum values. The three tubes shown in Figure 11 are all read as 0.9.

Gas detection tubes operate on a chemical reaction between the vapor phase compound and a liquid or solid detecting reagent, which is supported on an inert matrix. The colorimetric reaction used for the detection of carbon monoxide provides

a good example of this type of chemistry. In this reaction carbon monoxide reduces iodine pentoxide to liberate iodine, which is brown in color:



Read the tube immediately after gas sampling, as colors may change, fade, or disperse with time.

The most common types of gas detector tube reactions are the following:

- **Acid-base reactions**

These include reactions of acidic gases like HCl and HF with bases, and reaction of alkaline vapors such as ammonia with an acid in the tube. A dye present in the tube changes color as the pH changes on exposure to the vapors.

- **Reduction-oxidation (Redox) reactions**

These generate an oxidized or reduced compound, which has a different color. The chlorine tube uses oxidative coupling of colorless o-toluidine to form an orange azo-dye. White di-iodine pentoxide is reduced by CO and many organic vapors to form deep brown colored iodine. Orange chromium (VI) is reduced by many organic compounds to form brown or green colored Cr(III) compounds.

- **Ligand-exchange reactions**

These generate new complexes that are more colored than the starting reagents. The most notable is the conversion of white lead acetate to brown-black lead sulfide in the detection of H₂S. In the case of phosphine, the exchange of PH₃ for the chlorine ligand of mercuric chloride releases HCl, which in turn causes a pH-dependent dye color change.

The chief advantages of colorimetric tubes are their ability to provide real-time test results for a wide range of contaminants. All that is necessary to test for a new contaminant is to change the tube. In addition, identifying an unknown contaminant is often possible by using a specific sequence of "yes/no" indicator tubes. Various types of pumps are used to pull the sample through the tube. Types of pumps include hand-operated bellows, syringe-type piston pumps and mechanically assisted versions.

The chief limitations of colorimetric detector tubes are cross-sensitivity to contaminants other than the ones being

measured, and inability to provide dynamic results for concentrations that vary with time. Another potential problem is measurement of contaminants which are discontinuously present. Each sample is a "snap-shot" of concentration within a movie containing hundreds of frames. This limits the utility of colorimetric tube measurement when concentrations are potentially subject to rapid change. In addition, interpretation of test results can be strongly affected by the "crispness" of the leading edge of the stain, ambient humidity and age of the tube.

Humidity has little effect on most tubes either because the reaction is insensitive to moisture or because drying agents are added to absorb the moisture in a pre-layer (Figure 12). Humidity tends to have the greatest effect on compounds that are highly water-soluble, such as acids and bases. HF is a notable example that requires humidity corrections; water-adsorbing prelayers cannot be used because they tend to be reactive with HF.

The humidity effect tends to be greater the lower the concentration range of the tube. Any necessary correction factors are listed in the manufacturer's individual tube data sheets. When correcting for humidity, the correction factor (CF) is multiplied by the reading in addition to multiplying by any temperature correction. Note that it is the relative humidity at the measurement temperature that defines the correction, rather than the absolute humidity.

Temperature can affect tube readings in at least three ways. (Figure 13) First, as the temperature increases, the gas density decreases, causing a tendency for the reading to decrease (see pressure effects described below). Second, as the temperature increases, the reaction rate increases, causing the reading to be sharper and shorter. A third, balancing effect is that adsorption is often a prerequisite

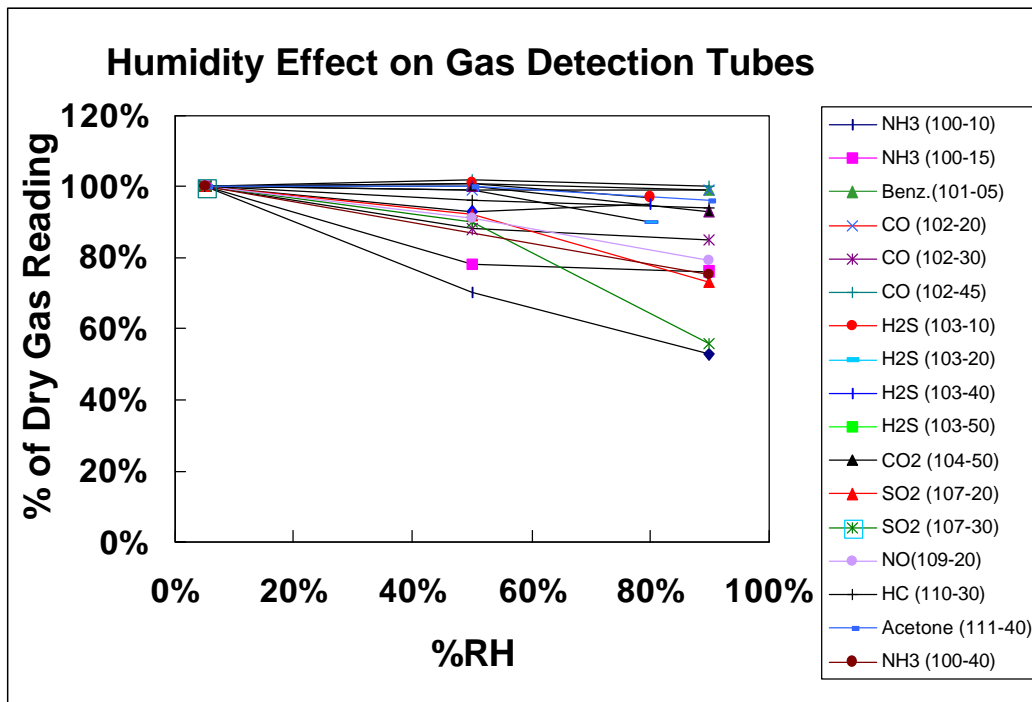


Figure 12. Effect of humidity on gas detection tube readings. (Courtesy RAE Systems Inc., Sunnyvale, California)

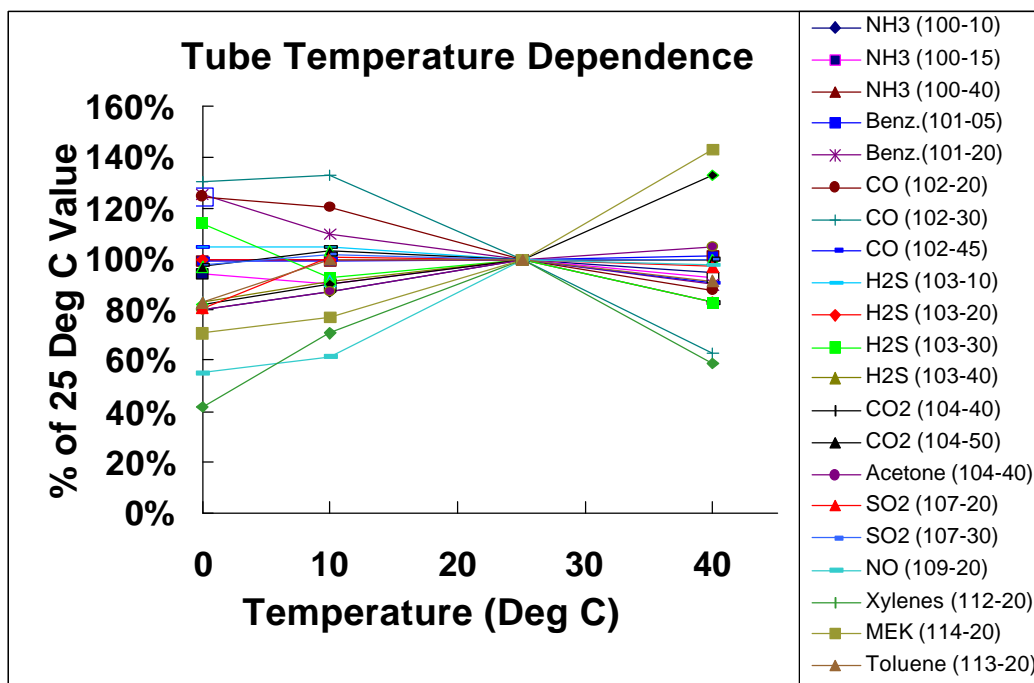


Figure 13. Effect of temperature on gas detection tube readings. (Courtesy RAE Systems Inc., Sunnyvale, California)

for reaction. Adsorption is weaker as temperature increases, and thus the reading can become longer.

The interplay of these competing effects results in some stains that are longer with increasing temperature, and others that are shorter.

Additional factors occur in special cases. For example, pretube or prelayer reactions are sometimes more complete at higher temperatures, causing higher readings in the measurement layer. In some cases, the color of the stain can change. In the water vapor 120-20 tube, the color stain is green at room temperature and a more purple color below room temperature.

Tubes change color in proportion to the mass of the compounds reaching the reagent, i.e., the absolute concentration. Therefore, as the pressure decreases at higher altitudes, the apparent response is reduced because there are fewer molecules per unit volume sampled. The conventional desired reading is in ppmv, which is a relative concentration, i.e., a mole or volume fraction (% of molecules of compound per molecules of total gas [air]) rather than an absolute concentration.

Most detector tubes which are routinely sold for industrial use are factory calibrated at 1 atmosphere (760 mm Hg) pressure at sea level. Some manufacturers offer specially calibrated tubes for use in high altitude or other unusual pressure environments (such as submarines).

For tubes calibrated in absolute concentrations such as lbs./MMCF or mg/m³, no pressure corrections are needed. For tubes calibrated in relative concentrations (e.g., ppm), correct for pressure using one of the following equations:

$$\text{Corrected reading} = \frac{\text{Observed Reading} \times 760 \text{ mm Hg}}{\text{Pressure (mm Hg)}}$$

$$\text{Corrected reading} = \frac{\text{Observed Reading} \times 101.3 \text{ kPa}}{\text{Pressure (kPa)}}$$

$$\text{Corrected reading} = \frac{\text{Observed Reading} \times 14.7 \text{ psia}}{\text{Pressure (psia)}}$$

For altitudes less than 2 km above sea level, the pressure in mm Hg can be estimated as a function of altitude using the following equation:

$$P \text{ (mm Hg)} = 760 \exp(-0.1286[\text{alt}(\text{km})])$$

Example correction factors are listed in the table below as a function of altitude. Weather changes may also affect the atmospheric pressure, but the necessary corrections are usually <10%.

Automated colorimetric measurement systems

An interesting recent development in colorimetric measurement technology are products that integrate colorimetric reagent technology with electronic and photoanalyzer technology. This integrated system recognizes the substance that the colorimetric "chip" is designed to measure and draws the appropriate volume of air through the sensing capillary by means of a calibrated automatic pump. It then automatically provides a digital reading by means of an integral photoanalyzer. This sampling system increases the sensitivity and accuracy of the colorimetric measurement technique. In some cases this unit can accurately register concentrations of vapor in 0.01 ppm increments.



**Figure 14. SampleRAE Motorized, Precision, Tube-Sampling Pump.
(Courtesy RAE System Inc., Sunnyvale CA)**

While interfering contaminants and other environmental conditions still affect the accuracy of readings, the improvement in precision and accuracy provides a significant improvement in many applications.

Another recent innovation is the use of motorized, precision sampling-pumps which are programmed to automatically draw a precise volume of atmosphere through the colorimetric tube. (Figure 14) Use of programmable, motorized sampling-pumps of this type is particularly useful when dealing with tubes which require a large volume of atmosphere, or a large number of sampling “strokes” to obtain a reading.

Colorimetric badges and dosimeter tubes

The same kind of colorimetric chemistry is also used in passive badge and tube-type dosimeters. These products are worn in the

same manner as other types of dosimeters. Contaminants are absorbed into media containing the same reagents as used in colorimetric tubes. As the contaminant is absorbed into the badge, the color becomes more and more intense or darker. Colorimetric badges generally include a chart for comparing color intensity to estimate concentration.

In another variation, contaminants passively diffuse into a dosimeter tube. Dosimeter tubes closely resemble standard colorimetric detector tubes. The length of stain once again is proportional to the concentration of contaminant. The main difference between dosimeter tubes and standard colorimetric detector tubes is the use of diffusion rather than a pump to pull contaminants through the tube. Another important difference is that dosimeter tubes provide a time-weighted average rather than

instantaneous concentration for the contaminant being measured.

PAPER TAPE AND METAL FOIL DEVICES

A variation on the colorimetric badge is the paper tape. Colorimetric reagents are impregnated into a substrate that is wound into a roll. The tape slowly unwinds and passes through a sensing chamber where it is exposed to the atmosphere being sampled. The instrument includes a precision analyzer that detects and quantifies the color change. Depending on the contaminant, paper tape analyzers can detect accurately into the part-per-billion range.

Paper tape monitors most commonly are used in permanently installed systems. The most common application for field portable instruments is detection of isocyanates and other contaminants that have extremely low exposure limits.

A conceptually similar device uses a gold-film coil. Resistance changes in the presence of mercury or hydrogen sulfide. The increase in resistance provides a highly accurate reading on a digital meter.

The chief drawbacks of paper tape and other cassette-type monitors is the comparative delicacy of the electronics, large size, and overall expensiveness of the systems. For these reasons they have limited utility in evaluating hazardous conditions in confined spaces. On the other hand, they provide an option where a specific contaminant is present and no other detection technique is available.

ELECTROCHEMICAL SENSORS

Electrochemical sensors are one of the most widely used types of sensors incorporated in portable gas detectors. Substance-specific electrochemical sensors are available for a limited number of contaminants (less than 20). Ideally they show little or no response

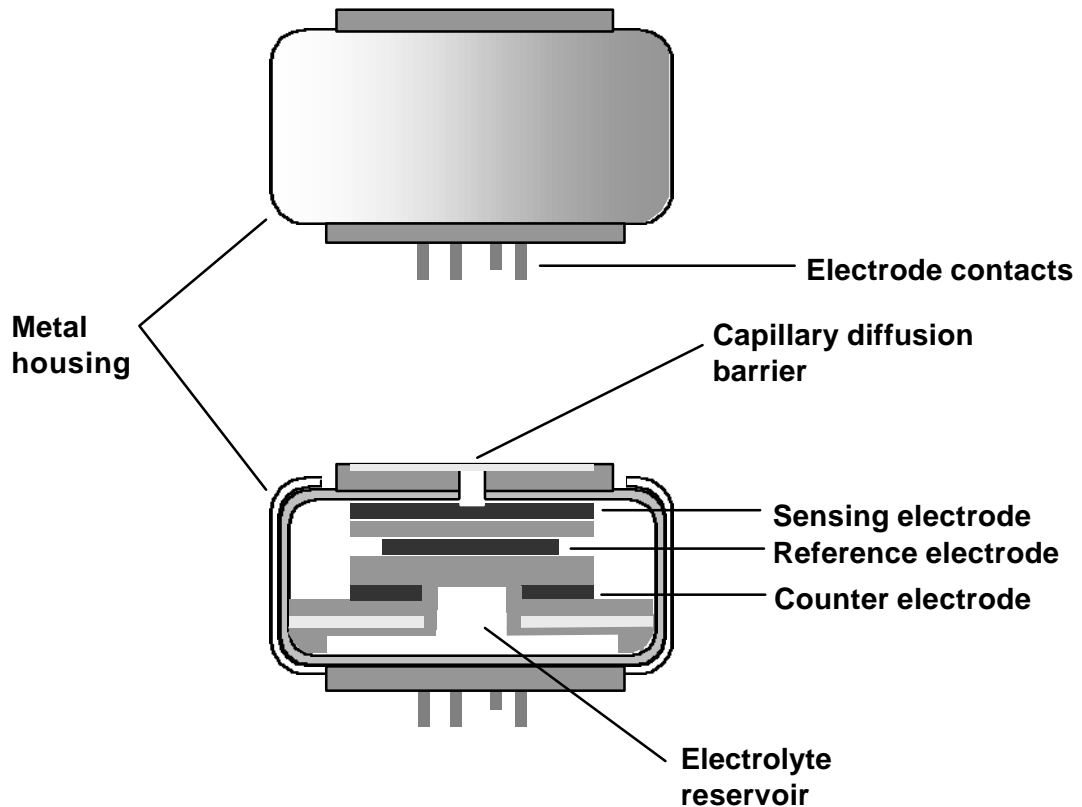
to interferents. Broad-range electrochemical sensors are designed to provide a measurable response to a wide array of contaminants. Most electrochemical sensors fall somewhere between the two extremes in terms of specificity. Electrochemical sensors are compact, require little power, exhibit excellent linearity and repeatability, and generally have long life span.

Multi-sensor confined space monitors generally contain an oxygen sensor, a flammable/combustible sensor and one to three additional electrochemical sensors. Single sensor instruments equipped with electrochemical toxic sensors are also available for use in situations where a single toxic hazard is present.

Substance-specific electrochemical sensors contain the following parts:

- A diffusion barrier that is porous to gas but nonporous to liquid
- Reservoir of acid electrolyte (usually sulfuric or phosphoric acid)
- Sensing electrode
- Counter electrode
- Reference electrode (in three electrode designs)
- Some sensors additionally include filters designed to remove interferents which would otherwise react with the sensor. Filters may be inboard (integral) components of the sensor, or may be external to the sensor proper.

The sensing electrode catalyzes a specific reaction. Depending on the sensor, the substance being measured is either oxidized or reduced at the surface of the sensing electrode. This reaction causes the potential of the sensing electrode to rise or fall relative to that of the counter electrode.



**Figure 15 City Technology 4 Series carbon monoxide sensor.
(Courtesy City Technology, Ltd.)**

The two electrode detection principle presupposes that the potential of the counter electrode remains constant. In reality, reactions at the surface of each electrode cause them to polarize. This significantly limits the concentration of contaminant they can measure. (Moseley et al. 1991)

In three electrode designs, what actually is measured is the difference between the sensing electrode and reference electrode. (Figure 15) Since the reference electrode is shielded from any reaction, it maintains a constant potential. This provides a true point of comparison. In this design, the change in potential of the sensing electrode is due solely to the concentration of the reactant gas or vapor. (City Technology 1997)

The current generated by the sensor is proportional to the amount of reactant present. The amount of current generated per ppm of reactant is constant over a wide concentration range. This consistency in output over a wide concentration range provides the exceptional linearity of electrochemical sensors. To illustrate, a City Technology 4 Series carbon monoxide sensor produces an output signal of $0.07 \pm 0.015 \mu\text{A/ppm}$ over a nominal range of 0 to 500 ppm. Anywhere within this range the output will be highly linear. The sensor is actually capable of discontinuous usage to concentrations as high as 1500 ppm with only minor loss of linearity.

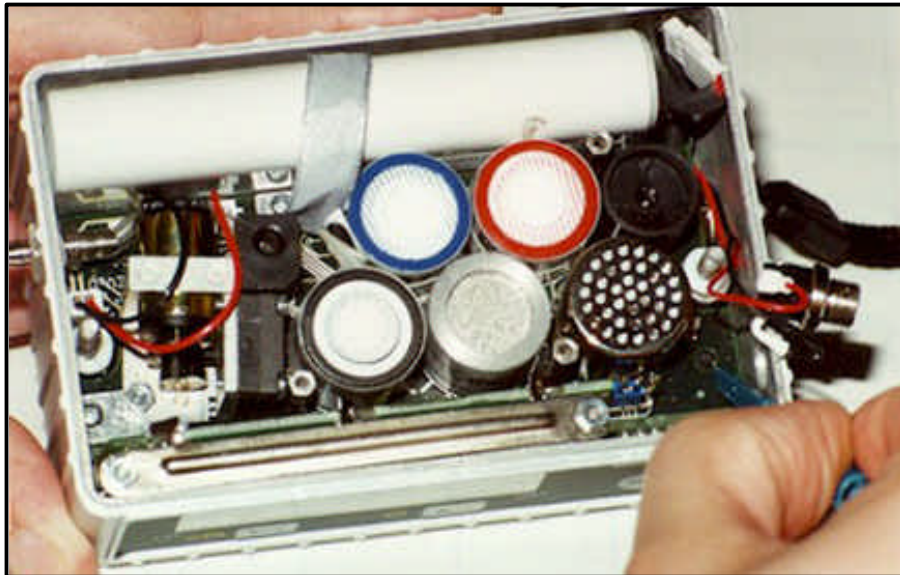


Figure 16 Portable direct reading instrument with sensor compartment cover removed showing compact PID, oxygen, electrochemical toxic, and catalytic bead (pellistor) type sensors installed. (Courtesy RAE Systems Inc., Sunnyvale, CA)

The oxidation of carbon monoxide in an electrochemical sensor provides a good example of the detection mechanism used in a non-consuming electrochemical sensor design:

Carbon monoxide is oxidized at the sensing electrode:



The counter electrode balances out the reaction at the sensing electrode by reducing oxygen from the air to water:



The only materials consumed during the detection reaction are the molecule of carbon monoxide, power from the battery of the instrument and oxygen. This is the reason that non-consuming electrochemical sensors have such long lifespans. The lifespan of the sensor is not affected by exposure to the contaminant that it measures. The sensor is a catalyst for the

reaction. No part of the sensor is consumed during the detection reaction. As long as the sensor is located in an atmosphere containing even trace amounts of oxygen and moisture, the sensor will be able to replenish itself directly from the atmosphere.

Similar non-consuming reactions are utilized in the electrochemical detection of a variety of reactant gases including chlorine, chlorine dioxide, ethylene oxide, hydrogen, hydrogen sulfide, nitrogen dioxide, ozone, phosphine, and sulfur dioxide.

Some operating environments render electrochemical sensors of this design impossible to use. For instance, a non-consuming electrochemical hydrogen sulfide sensor would not normally be usable for monitoring for H₂S in a natural gas pipeline containing no oxygen. Once all of the oxygen available in the electrolyte was consumed, the sensor would then fail to

respond to hydrogen sulfide. When re-exposed to an oxygen-containing atmosphere, the sensor would regain its ability to detect H₂S.

The fact that the electrolyte provides a supply of oxygen means that for short periods, non-consuming sensors can detect the contaminant they are designed to measure even in the absence of oxygen. This is fortuitous since many reactive gases (such as chlorine) have very short shelf-lives when packaged in calibration mixtures that include oxygen. Gas mixtures used to calibrate sensors for highly reactive gases, such as chlorine, usually contain no oxygen. For example, a typical calibration gas mixture used to calibrate a chlorine sensor contains 5 ppm of chlorine in nitrogen.

A bias voltage is sometimes applied to the counter electrode. This helps drive the detection reaction for a specific contaminant. Biased sensor designs enable detection of less electrochemically active gases such as hydrogen chloride and nitric oxide.

Several other contaminants (such as ammonia and hydrogen cyanide) are detectable by less straight-forward reactions that consume parts of the sensor. For example, the gold sensing electrode of the hydrogen cyanide sensor is consumed during the reaction.



In the case of the ammonia sensor, the electrolyte is consumed. The lifespan of the ammonia sensor is directly related to its exposure to NH₃. A City Technology 7AM ammonia sensor has a lifespan of one year when continuously exposed to 2 ppm of ammonia. (This is sometimes expressed as a "2 ppm-year" lifespan.) While the sensor will last a full year in 2 PPM ammonia, it will last only six months when exposed to 4 PPM or three months at 8 ppm. This type of sensor should be used only when the normal ambient background concentration of ammonia is sufficiently low to allow a

reasonable operational life. For example, this type of sensor should not be used at a poultry farm or nitrate fertilizer plant where ambient concentrations of ammonia may be as high as 20 to 30 ppm.

Electrochemical sensors are stable, long-lasting, require very little power and are capable of resolution (depending on the sensor and contaminant) to ± 0.1 PPM. Electrochemical sensors are normally usable over a wide range of temperature (in some cases from - 40 to 50 °C (- 40 to 120 °F)). However, the uncorrected sensor output may be strongly influenced by changes in temperature. For this reason these instruments generally include temperature compensating software and/or hardware.

The chief limitation of electrochemical sensors is the effect of interferences. Substance-specific sensors are designed to respond only to the gases they are supposed to measure. The higher the specificity of the sensor, the less likely the sensor will be affected by other gases. For example, a substance-specific carbon monoxide sensor is deliberately designed not to respond to other gases, such as hydrogen sulfide or methane. Electrochemical sensors frequently include an external filter. The size and composition of the filter are determined by the type and expected concentration of the interferences to be removed.

While inclusion of a filter is frequently able to increase specificity, removal of a filter may be used to broaden response to a wider variety of gases. To illustrate, the primary difference between a substance-specific carbon monoxide sensor and one capable of detecting both carbon monoxide and hydrogen sulfide is the external filter. The external filter removes hydrogen sulfide from the atmosphere that diffuses into the sensor. Carbon monoxide sensors that do not include an external filter are frequently marketed as "dual purpose" sensors for the simultaneous detection of both CO and H₂S.

Dual purpose CO/H₂S sensors can be calibrated for either gas. A properly calibrated sensor will be exactly accurate (within the design specification of the instrument) for the gas to which it is calibrated. If the sensor is calibrated to carbon monoxide and then exposed to 35 ppm of carbon monoxide, the reading will be 35 ppm. The sensor will show a relative response to other gases. When calibrated on carbon monoxide the relative response of the sensor to hydrogen sulfide is about 3.5:1.0. This means a concentration of about 10 ppm of hydrogen sulfide would produce a reading of 10 x 3.5 or 35 ppm. This is a very convenient relative response, since many jurisdictions use 10 ppm as a TWA for hydrogen sulfide and 35 PPM for carbon monoxide. This means that the instrument will alarm any time the concentration of either carbon monoxide or hydrogen sulfide exceeds this threshold.

Since the sensor responds to both gases simultaneously, the user cannot determine which is producing the reading. That is, the user cannot determine which hazard is present or at what specific concentrations. The instrument will provide an immediate indication whenever concentrations exceed the alarm setpoint. These sensors also respond to a variety of other toxic contaminants including gasoline, alcohols, hydrogen, acetylene, ethylene, toluene, nitric oxide and sulfur dioxide. Where the atmosphere contains a complex mixture of contaminants, this type of sensor could lead to constant alarms that have no meaning for a low set point. These sensors cannot discriminate between hazards or tell them apart when more than one contaminant is present at the same time.

A recently introduced variant on the dual purpose carbon monoxide/hydrogen sulfide electrochemical sensor is the 4-electrode "COSH" design. These sensors contain two separate sensing electrodes, one for CO and one for H₂S. Each sensing electrode provides an independent, substance-specific signal, and can be

individually calibrated. In order to increase specificity, the sensor is internally configured so that incoming gas passes by the hydrogen sulfide electrode first. Hydrogen sulfide, which would otherwise have an interfering effect on the CO electrode, is removed via the electrochemical detection reaction at the H₂S electrode, and is not present in the gas sample which finally reaches the CO sensing electrode. Thus, the sensor is able to differentiate between CO and H₂S, with minimal interference between the two contaminants on the sensor outputs.

When a specific contaminant is suspected or known to be present, the best approach is to use an instrument containing a substance-specific sensor. Regulations generally support this concept. The OSHA Standard for general industry explicitly requires the use of a direct-reading instrument containing substance-specific sensors whenever a particular toxic hazard is known to be present. (OSHA 1993) For instance, when chlorine is known or suspected, one of the toxic sensors selected should be chlorine-specific and calibrated directly with this gas. A broad range sensor unable to discriminate between chlorine and other contaminants should not be used for this purpose.

Even though care has been taken to reduce cross-sensitivity in substance-specific designs, interferences still exist. In some cases the interfering effect is positive; this results in readings that are higher than actual. In other cases the interference is negative; this produces readings that are lower than actual. Reducing gases, such as hydrogen sulfide and carbon monoxide, are oxidized at the sensing electrode. Oxidizing gases, such as chlorine, chlorine dioxide, nitrogen dioxide, and ozone, are reduced at the sensing electrode. The effect of the interfering gas (increase or decrease in output signal) depends on the gas to be measured (reducing or oxidizing) and the interferent (reducing or oxidizing).

Table 9
Interferent Effect on Electrochemical Sensor Output

INTERFERING GAS	SENSOR TYPE				
	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

Courtesy City Technology, Ltd., Portsmouth, England

Table 8 summarizes these relationships.

Table 8 Interferent Effect on Sensor Output		
Interfering Gas	Effect on the output of a reducing gas sensor (e.g. effect on a hydrogen sulfide sensor)	Effect on the output of an oxidizing gas sensor (e.g. effect on a chlorine sensor)
Reducing Gas	Increase output	Decrease output
Oxidizing Gas	Decrease output	Increase output

Table 9 lists the interferences of electrochemical toxic sensors used in a typical instrument. Depending on the nature of the reaction with the sensor, the interferent either increases (positive cross sensitivity) or decreases the signal (negative

cross sensitivity). Each entry represents the response of the sensor to 100 ppm of interferent, thus providing a percentage sensitivity.

The user must understand clearly the effects of potential interferents on the output from sensors used to monitor the atmosphere during pre-entry preparation and work activities involving confined spaces. To illustrate, the chlorine sensor listed in Table 8 will show a reading of approximately - 0.3 ppm when exposed to 10 ppm of H₂S. A 10 ppm concentration of H₂S could "cancel out" a 0.3 ppm concentration of chlorine. This situation could occur at pulp and paper mills.

Once again, it is important to note that the values included in Table 9 are provided as a general example of how this information is typically conveyed, and should not be used as the basis for actual calculations or decisions. The sensors used in a particular instrument may or may not have values similar to those shown in Table 9. Even later generations of the same model

sensor may exhibit different interferences if the

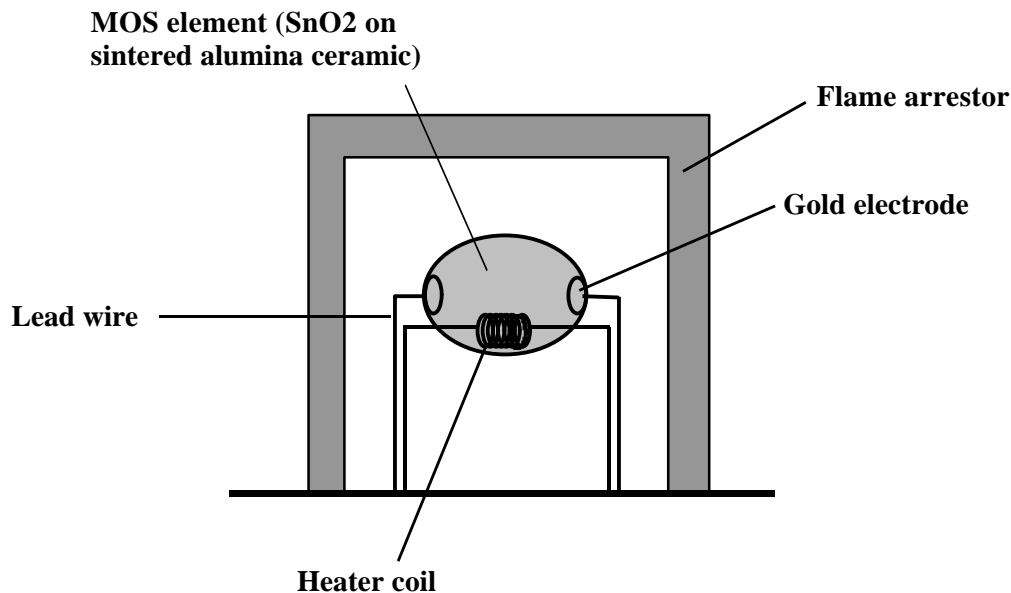


Figure 17 Metal oxide semiconductor (MOS) sensor. (Reprinted courtesy of Ergonomics, Inc. "Corporate Health and Safety", 1996.)

manufacturer has made modifications to the design. Users should consult the owner's manual or contact the manufacturer of the instrument they will be using to verify the correct values to use when making decisions based on interfering contaminants.

METAL OXIDE SEMICONDUCTOR SENSORS

Metal oxide semiconductor (or MOS) sensors may be used for monitoring at toxic levels in the ppm range, as well as flammable/combustibles in the percent range. As discussed previously, MOS sensing elements consist of a metal oxide semiconductor, such as tin dioxide (SnO_2) on a sintered alumina ceramic bead contained within a flame arrestor. (Figure 17) In clean air the electrical conductivity is low. Contact with reducing gases, such as carbon monoxide or combustible gases, increases conductivity. Sensitivity to a

particular gas is alterable by changing the temperature of the sensing element.

They are designed to respond to the widest possible range of toxic and flammable/combustible gases and vapors. These include vapors from halogenated solvents and other contaminants that are difficult to detect by other means. This nonspecificity can be advantageous in situations where unknown toxic gases may be present, and a simple go/no go determination is sufficient.

Sensitivity of the sensing element to a particular gas is mathematically predictable. A commonly used strategy is to preprogram the instrument with a number of theoretical specific response curves. If the exact nature of the contaminant is known, readings of the sensor can be adjusted to reflect the expected sensitivity of the sensor to the contaminant being measured. MOS sensors offer the ability to detect low (0 to 100 ppm)

concentrations of toxic gases over a wide

MOS sensors are broad range devices. The chief limitations of this kind of sensor are the difficulty in interpreting readings, the potential for false alarms and the effects of humidity on the sensor. As humidity increases, sensor output increases. As humidity decreases to very low levels, sensor output may fall to zero even in the presence of a contaminant. In addition, the user must exercise caution in assumptions about contaminants presumed to be present. The user may erroneously use the response curve for a contaminant that is highly detectable by the sensor, yet is not present. The instrument may have low sensitivity to the contaminant that is actually present. The result would be erroneously low readings. Another issue affecting the use of MOS sensors is the relatively narrow linear response to many common contaminants. As long as the concentration of the contaminant lies within the linear range of the sensor, the output is sufficiently accurate to allow for quantifiable readings. If the concentration lies outside the linear range of the sensor, the effective usage of the sensor is limited to a "yes/no" indication about the presence of the contaminant. That is, the instrument would be unable to provide a quantifiable measurement of the actual concentration present. Some instruments limit the type of information provided by the MOS sensor to a bar graph or other semi-quantified output. The MOS sensor in these instruments usually is included as a fourth or fifth channel of detection.

IONIZATION DETECTORS

General discussion

The aim of initial hazard assessment should be determination of overall or total contaminant levels. Further monitoring with more sophisticated or narrowly focused analyzers then refines initial testing results. One of the most useful real-time survey techniques for surveying volatile organic contaminants (VOCs) utilizes detection

temperature range.

using ionization. A source of energy removes an electron from neutrally charged target molecules. The electrically charged fragments are called ions. Ionization detectors collect the charged particles on charged plates. This produces a flow of electrical current proportional to the concentration of contaminant. The ionization process may be written as:



The amount of energy needed to remove an electron from a particular molecule is the ionization potential (or IP). Ionization potentials are usually expressed in units of electron Volts (eV).

Photoionization detectors (or PIDs) use ultraviolet light as the source of energy for ionization. Flame ionization detectors (or FIDs) use a hydrogen flame. Regardless of the source, the energy must be greater than the IP in order for an ionization detector to be able to detect a particular substance. Ionization detectors are nonspecific and therefore, should always be used in concert with other methods of detection. This is especially important when contaminants not detected by these units are potentially present. Table 9 lists the ionization potentials for a few selected chemical substances.

Table 9
Ionization Potentials for
Selected Chemical Substances

Substance	Ionization Potential (eV)
carbon monoxide	14.01
carbon dioxide	13.77
hydrogen cyanide	13.60
methane	12.98
hydrogen chloride	12.74
water	12.59
oxygen	12.08
chlorine	11.48
propane	11.07
hydrogen sulfide	10.46
n-hexane	10.18

ammonia	10.18
acetone	9.69
benzene	9.24

The fact that water, oxygen, carbon dioxide and other gases naturally present in the atmosphere can be ionized puts an upper limit on the useful energetics of the source of energy. The source therefore must not ionize substances in the normal atmosphere as well as the contaminants under investigation.

Instruments containing PID and FID detectors are complementary, rather than competitive. The type of detector chosen should reflect the contaminant(s) being measured. Since neither technique is equally good at detecting all ionizable contaminants, prudence would stress the use of both types of instruments. Several manufacturers now offer dual PID/FID analyzers in the same instrument.

Ionization detectors are non-specific, that is, they provide a "broad range" indication of all detectable molecules present in the atmosphere being monitored. In addition, the response is relative to the gas that was used during calibration. Except when the instrument is used to measure the same gas used during calibration (in clean air at similar temperature and humidity), or when a correction factor or curve is used to correct the readings to reflect the true concentration, readings may be higher or lower than the true concentration. This can be especially confusing when monitoring to establish a "Total VOC" concentration when several differentially detectable molecular species are simultaneously present. Also, ionization detectors are not linear over their entire detection ranges. Simple numerical correction factors used to correct readings are only accurate over the linear detection range. More sophisticated ionization detector designs frequently store correction factors as curves, allowing the instrument to be used to obtain accurate readings outside of the linear range. Although ionization detectors are capable of detection in the low part-per-million or even part-per-billion range, results indicating the positive presence of contaminants should be treated as qualitative not quantitative, until the

specific nature of the contaminants being measured are elucidated further through the use of more precise analytical techniques.

Ionization detectors can only detect certain gases and vapors. Neither type of detector used alone or together is capable of detecting all potential contaminants. Nonvolatile liquids and solids, particulates, and many toxic gases and vapors cannot be detected at all. Because of the limitations of ionization detectors, a reading of zero should not be interpreted as a guarantee about the absence of contamination.

PHOTOIONIZATION DETECTORS (PID)

Photoionization detectors use high energy ultraviolet (UV) light from a lamp housed within the detector to provide the energy for ionization. The energy provided by the lamp is determined by the wavelength of the UV light being produced, and is measured in electron Volts (eV). Several different lamps are available for use. The choice of a lamp governs the types of compounds that can be detected. Absorption of a photon of ultraviolet radiation energetic enough to ionize a molecule (RH) initiates the process of photoionization.



The quantity, hu , represents a photon having an energy greater than or equal to the ionization potential of species RH. In general, the smaller the molecule, the tighter the electrons are bound and the higher the ionization potential. The larger the molecule and the more double or triple bonds, the lower the IP. The ions are collected in an ionization chamber that is adjacent to the lamp. The ion chamber contains an accelerating electrode (biased positively) and a collecting electrode where the current is measured. The current measured (after amplification) is proportional to concentration.

The energy of the photons produced by the UV lamp determines whether a

specific chemical is detectable. The energy must be higher than the ionization potential of the contaminant in order for detection to occur. Lamps are available in a number of output energies including 9.5, 9.8, 10.0, 10.2, 10.6, 11.7 and 11.8 eV (depending on manufacturer). Most manufacturers allow for the use of several lamps in the same detector. The lower the energy of the UV light produced by the lamp, the lower the number of chemicals the PID will be able to detect. The higher the energy of the light produced by the lamp, the wider the range of detectable contaminants.

Higher energy lamps are subject to more physical limitations. In general, the higher the lamp energy, the shorter will be the service life. PID lamps generally consist of a glass body filled with an elemental gas or mixture of gases (oxygen, nitrogen, hydrogen, argon or krypton) at low pressure. Electric current or radio waves are used to excite the gas to produce the UV light. The UV light is focused in a tight beam directed through a small window in the body of the lamp. The highest energy lamps (11.7 and 11.8 eV) contain a window made from lithium fluoride. Lithium fluoride is easily degraded by the absorption of water vapor as well as exposure to UV light produced by the lamp. Hence, these high energy lamps tend to have very short operational lifespans, and may only last one or two months in normal operation. In addition, although the energy of the UV light produced by high energy lamps allows the ionization of a wider range of substances, the amount of light produced is less than that produced by lower energy lamps. This means that higher energy lamps tend to produce both a weaker ionization current and have an increased tendency towards drift.

It may be possible to increase specificity by selecting lamps of a particular energy. For instance, 9.8eV lamps have an energy output sufficient for the detection of benzene (IP = 9.24eV), but provide insufficient energy to drive the ionization of

many other contaminants. On the other hand, the windows of 9.8 eV lamps (calcium fluoride or a sandwich of layers which include calcium fluoride) tend to have relatively short operational lifespans, lasting only about six months in normal operation.

The windows of 10.6 eV lamps (magnesium fluoride) do not tend to absorb water and are not as easily degraded by exposure to UV. As a result, 10.6 eV lamps generally have much longer service lives, and frequently last one to two years in normal operation. At the same time, 10.6eV lamps have an energy output sufficient to detect a wide range of VOCs. As a consequence, 10.6 eV lamps tend to be the most widely used.

PID instruments are nonspecific. The reading produced by the instrument is the sum of the signals of all the detectable substances present in the atmosphere being monitored. Also, as a function of their varying ionization potentials and other physical properties, equivalent concentrations of gases other than the one used to calibrate the instrument may not produce equivalent readings. Thus, PID readings are always relative to the gas that was used to calibrate the detector. Calibration is based on ion current sensed at the detector in response to a known concentration of a known gas or vapor. Instrument response to gases other than the one used for calibration are relative in nature. A reading of 10 ppm only indicates that the ion current experienced by the detector is equivalent to that produced by a 10 ppm concentration of calibrant. The amount of a different contaminant needed to produce this current may be larger or smaller than the concentration of the gas used to calibrate the instrument.

Since PID readings are always relative to the calibrant, they should be recorded as ppm-calibration gas equivalent units, or PID units, never as true concentrations *unless* (1) the contaminant being monitored is the

same as the one used to calibrate the instrument, or (2) the reading is corrected to account for any difference in relative response. Most manufacturers furnish tables, or include a built-in library of correction factors to correct or normalize readings when the contaminant being measured is known. The most advanced designs allow users to store the calibration curves for several different calibration gases, then pick from the built-in library of correction factors to provide real-time readings for the contaminant being measured. Thus, the user might pick 100 ppm isobutylene from the list of calibration curves stored in the instrument's memory, then choose acetone as the contaminant being measured. In this case the instrument is able to express readings in true parts per million acetone equivalent concentrations.

It is important to remember that normalized or not, ionization detector readings are still subject to all the limitations discussed above. It is very important to treat gas concentration calculations based on theoretical relative response ratios cautiously. In actual practice, the relative response may be affected by environmental conditions such as temperature and humidity. Also, if an error is made in determining the specific kind of gas present, and the wrong correction factor is used, the accuracy of the calculation may be significantly affected.

Photoionization detectors can be affected by a number of environmental factors. The most serious is humidity. Although water vapor (IP = 12.59 eV) is not ionized by PID detector lamps, water vapor does serve to deflect, scatter and absorb UV light in the ionization chamber. Although high concentrations of measurable contaminants will usually produce a reading even in the presence of significantly high humidity, high concentrations of water vapor may reduce or even effectively block the ability of the instrument to register low concentrations of contaminant. Nonionizing gases and vapors (contaminants with IPs

higher than the energy of the detector lamp) may also scatter or block UV light in much the same manner as water vapor. Nonionizing contaminants such as methane can profoundly reduce the sensitivity of the detector. One study reported that 0.5 % by volume (or 10% LEL) of methane reduced the sensitivity of the PID detector to toluene by 30 %. High concentrations of oxygen have also been found to "quench" sensitivity in some PID designs. Basically, the shorter the pathlength between the ionization chamber and the current collector, the less opportunity for scattering or quenching to occur. A useful analogy is the way an automobile's headlight beams are scattered back at the driver on a foggy night. The amount of scattering is a function of both the concentration of water droplets in the air, as well as the distance between the observer and the headlight. The shorter the distance, the less the amount of scattering that will be seen. The pathlength between the ionization chamber and the current collector, as well as the severity of the effects of environmental conditions on readings, varies widely between different photoionization detector designs. The effect of humidity on readings should be an important point to explore when evaluating competing PID designs.

Dust and particulates in the atmosphere being sampled also reduce sensitivity of the detector via back-scattering and absorbance of the UV light. In addition, deposition of particulate contaminants on the lamp window can reduce energy transmitted to the sample. Condensation of water vapor or other hot gases and vapors on the window can have a similar effect. For these reasons some manufacturers recommend cleaning the lamp before every use. Once again, however, the need to clean PID lamp and detector assemblies varies widely between different PID designs. A primary factor in determining how frequently the lamp requires cleaning is the direction of the flow



Figure 18 Compact, multi-sensor confined space gas detector with LEL, O₂, CO, H₂S and PID equipped with 10.6 eV lamp. (Courtesy of RAE Systems Inc. Sunnyvale, CA)

of atmosphere through the ionization chamber. In “axial” flow designs the flow is directed at the face of the lamp. This tends to increase the likelihood of deposition of contaminants on the face of the lamp as well as to increase the pathlength between the point of ionization and current collector, thus increasing the effects of environmental conditions on readings. In “laminar” flow designs the flow is directed parallel to the face of the lamp, reducing the deposition of contaminants on the face of the lamp. This design also tends to reduce the pathlength between the point of ionization and the current collector. A further refinement is to orient the direction of the ion current flow at right angles to both the direction of the UV light, and flow of the sample across the face of the lamp. This “3D” design further reduces the chance of deposition of materials on the surface of the lamp window, thus sharply reducing the need to clean the lamp on a frequent basis.

Whatever the design, photoionization detectors and lamps should be cleaned whenever they exhibit symptoms which are consistent with a lamp which requires cleaning. Typical symptoms which would indicate the need to clean or replace the lamp include inability to hold a steady zero in clean air, or notable loss of sensitivity of

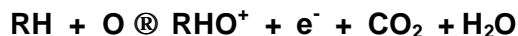
the sensor. Periodic cleaning of the lamp window will remove film deposits and restore lamp sensitivity. Be very careful when cleaning or replacing the PID Lamp not to damage or scratch the window of the lamp. If the window is damaged it will be necessary to replace the lamp before the PID can be returned to service.

In the past, photoionization detectors have tended to be bulky, temperamental and expensive. This has significantly limited their use during work involving confined space. This has changed dramatically over the last few years. Today compact, multi-sensor designs which include LEL, O₂, and electrochemical toxic sensors as well as a miniaturized photoionization detector have allowed this very useful detection technique to be included in many confined space monitoring programs. (Figure 18) In some applications, such as military and commercial aviation wing-tank and fuel-cell entry, PID equipped confined space gas detectors have become the industry norm.

FLAME IONIZATION DETECTORS (FID)

Flame ionization detectors use a hydrogen flame as the source of ionization energy. These instruments are able to detect nearly all organic compounds. In clean air, the

hydrogen flame is free from ions and nonconducting. Organic contaminants containing either a carbon-hydrogen or carbon-carbon bond break down according to the following reaction when exposed to the hydrogen flame in the ionization chamber.



Positively charged carbon containing ions are collected on a negatively charged plate. The ion current is proportional to the hydrocarbon concentration.

A major difference between FID and PID detection is the amount of variance in sensitivity from one organic substance to another. The amount of energy (or ionization potential) necessary to dislodge an electron to create a charged fragment determine the sensitivity of a PID detector to a specific molecule. The shape, size and specific chemical bonds present within the molecule determine the IP. IP varies widely from one substance to the next. For these reasons the sensitivity of a PID detector also varies widely from one substance to the next.

FID sensitivity does not vary as significantly from one organic substance to another because the amount of energy necessary to break specific carbon-carbon or carbon-hydrogen bonds is relatively constant. For this reason FID sensitivity is more generalized, and varies much less significantly between one hydrocarbon and another. Another very important difference between the two detection techniques is that FIDs can detect methane, while PIDs cannot. FIDs have traditionally been the preferred instrument for detection of methane and other saturated alkanes as well as unsaturated hydrocarbons and alkenes at part-per-million levels. Hydroxyl (OH-) or chloride (Cl-) functional groups tends to reduce sensitivity, while inorganic contaminants such as chlorine, ammonia or hydrogen cyanide are not detected.

One of the most important considerations concerning use of an FID is the high pressure (16 MPa or 2300 lb/in²) cylinder of hydrogen required by the instrument. Both refilling and storage may represent a significant issue to the user. An additional consequence of the use of a live hydrogen flame is that some currently available FID detectors are not classified as to intrinsic safety. They cannot be operated in a hazardous location that may be subject to accumulation of flammable/combustible gas and vapor. Ensure that any FID that is to be operated in a potentially hazardous location has been classified as to intrinsic safety! Other issues which limit performance are carbon buildup in the detector which can lead to "flame outs", and the position sensitivity of the detector due to the use of a live flame to drive ionization.

In the past, FIDs have tended to be bulky, temperamental, and expensive. This has changed somewhat over the last few years. However, while today's FIDs are by comparison substantially more dependable and easier to operate, they are still rarely used in confined space applications. On the other hand, in fugitive emissions testing and many other non-confined space monitoring applications, they continue to provide valuable service.

INFRARED DETECTORS

In the past, infrared based instruments tended to bulky and expensive spectrophotometers. They required a very high level of operator expertise to obtain accurate readings. Incorporation of modern electronics and signal processing capabilities into infrared based equipment has significantly altered the reality behind these perceptions. Fixed-pathlength, substance-specific instruments are becoming available for an ever widening variety of contaminants. Instruments are available for carbon dioxide, Freons®, ammonia, and methane, as well as for low range hydrocarbon detection in the ppm range.

Molecules may be conceptualized as balls (atoms) held together by flexible springs (bonds) that can vibrate (stretch, bend or rotate) in three dimensions. Each molecule has certain fixed modes in which this vibratory motion can occur. Vibrational modes are dictated by the nature of the specific bonds that hold the molecule together. The larger the molecule, the greater the number of modes of movement. Each mode represents vibrational motion at a specific frequency. The modes are always the same for a specific molecule. Chemical bonds absorb infrared radiation. The bond continues to vibrate at the same frequency but with greater amplitude after the transfer of energy. 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.

Specific molecules absorb infrared radiation at precise frequencies. When infrared 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. Since most chemical compounds absorb at a number of different frequencies, IR absorbance can provide a "fingerprint" for use in identification of unknown contaminants.

There are two methods of presenting the data: transmittance or absorbance. The two terms are related by the following equation:

$$\text{Absorbance} = \log \left(\frac{1}{\text{Transmittance}} \right)$$

The thermopile detector in a traditional IR spectrophotometer actually measures transmittance. This data is usually substituted into the above equation for presentation as absorbance. (Any error in the transmittance values substituted into this equation is magnified in the calculation of absorbance.)

Infrared absorbance spectra can provide both qualitative and quantitative information. The position (frequencies) and relative strengths of the absorbance maxima provide a qualitative indication about the nature of the contaminants. Peak areas and peak height of the absorbance maxima are proportional to the concentration of the absorbing molecules. When the analyzer is calibrated to a known concentration of the contaminant to be measured, these quantities provide the basis for determining concentration.

Interpretation of infrared absorbance spectra can be complex when multiple contaminants are present. Spectral bands may overlap or obscure each other. Water and carbon dioxide molecules in ambient air also absorb infrared radiation. This absorption can obscure what otherwise might be useful absorbance maxima for a given compound. Only polar molecules are able to absorb infrared radiation. This is a function of the net change in electric dipole moment during vibrational motion.) Monatomic (single-atom) gases such as helium (He), argon (Ar) and mercury vapor, as well as nonpolar diatomic (two-atom) gases such as oxygen (O₂), nitrogen (N₂), and chlorine (Cl₂) do not absorb infrared light and are not detectable by this means.

Infrared Absorbance Spectrum of Halothane

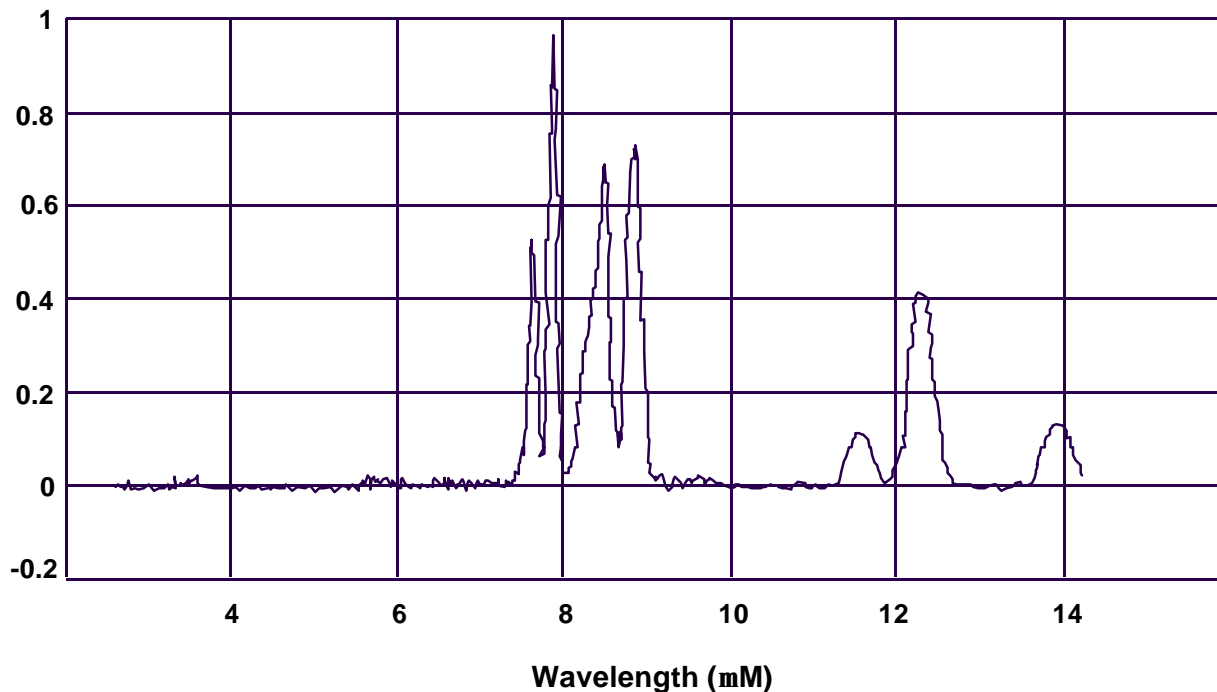


Figure 19 Infrared absorbance of halothane. Halothane is 2-bromo-2-chloro-1,1,1-trifluoroethane, a common anesthetic. (Courtesy Foxboro, Inc. Foxboro, MA.)

Typical applications include monitoring for the presence of chlorofluorocarbons, fumigants such as ethylene dibromide and Vikane(r), anesthetic gases such as nitrous oxide (N₂O) and halothane, sterilants such as ethylene oxide, formaldehyde, hydrogen peroxide, halogenated solvents such as methylene chloride, organic solvents such as toluene, carbon dioxide, carbon monoxide, as well as many other organic compounds.

IR spectrophotometers

Field IR spectrophotometers contain a broad range (2.5 to 14.5 μ m) IR source and a variable pathlength gas cell. The longer the optical pathlength the more sensitive the response. Varying the pathlength provides a dynamic monitoring range from sub part-

per-million to percent concentrations. The air sample is drawn into the sensing chamber by a pump, where it is exposed to the infrared radiation. A solid-state (thermopile) detector measures absorbance. Depending on the model, absorbance data are printed by an internal printer or downloaded to an external printer, datalogger or personal computer.

IR spectrophotometers can scan the sample. This exposes the sample to the full range of infrared source to determine where absorbances occur. If the contaminant is known, the absorbance frequency is used. A number of models facilitate qualitative identification by providing a library of absorbance spectra in the instrument memory. The software compares these to field results to provide "best fit"

identification of unknown contaminants. Field IR spectrophotometers are most useful where the contaminant is suspected or known to be present.



Figure 20 Compact, multi-sensor confined gas detector with LEL, O₂, CO₂, CO and PID. (Courtesy of RAE Systems Inc. Sunnyvale, CA)

The less that is known about contaminant that may be present, the more challenging the interpretation of results becomes.

Substance-specific infrared instruments

Substance-specific instruments filter the IR source to provide a narrow range of frequencies. Dedicated substance-specific detectors exist for carbon dioxide, halogenated hydrocarbons such as Freons®, methane, and other gases with good absorbance characteristics. (Figure 20) Substance specific IR detectors cannot be used as a "broad range" survey device. The greatest strength of these instruments is their ability to monitor relatively nonreactive contaminants, such as carbon dioxide. IR-based carbon dioxide detectors have been particularly useful for investigating building-related problems. They also are useful for evaluating conditions in confined spaces. This is potentially very important, given the emerging role of CO₂ in fatal accidents. IR-based instruments also are also proving to be very useful for the monitoring of methane in hostile environments. IR-based detectors are not

affected by high concentrations of sulfides, silicones or other substances that would quickly destroy a hot bead catalytic sensor.

Photoacoustic analyzers

The increase in vibration due to absorbance of IR energy by a molecule is a very short-lived effect. The molecule quickly transfers the energy in the form of heat to adjacent molecules. (The effect is similar to the way a microwave oven heats food. Water molecules in the food absorb microwave radiation, then quickly transfer the absorbed energy to nearby molecules, thus heating the food.) The transfer of absorbed energy has the effect of heating the atmosphere and, when the sensing chamber is sealed, increasing the pressure as well.

The photoacoustic analyzer measures fluctuating pressure changes due to the absorbance and transfer of IR energy using high-precision condenser microphones. The photoacoustic analyzer is accurate to the part-per-billion range. The photoacoustic analyzer measures absorbance directly, as opposed to calculation from percent transmittance. As a result, this instrument is very precise. Increasingly sophisticated

software allows photoacoustic analyzers to monitor simultaneously up to 15 contaminants, and through cross-compensation analysis of interferences, to provide specific concentrations for each.

Fourier transform infrared (FTIR) analyzers

Field-portable Fourier transform infrared (or FTIR) analyzers represent some of the most exciting new direct reading instruments to emerge over the last few years. FTIR analyzers compare IR absorbance in reference (fresh) air to absorbance in contaminated air using a Michelson interferometer. Light from the IR source is split into two beams. One passes through clean reference air. The other passes through the atmosphere containing contaminants. In "monostatic" systems a remotely located reflector returns the beam to the detector. In "bistatic" systems both the IR source and source optics are remote from the detector. A parabolic mirror (up to 20 inches in diameter) is used to gather the returning light. The Michelson interferometer produce an "interferogram" which (by means of Fourier transform analysis) mathematically generates the IR absorbance chart.

Unlike classic IR spectrophotometers which use an internal pump to draw a sample from a highly localized point source through the sensing chamber, FTIR systems are capable of analysis over very long optical paths. In some cases the reflector or IR source can be located 0.4 km (0.25 miles) or more from the detector. This makes FTIR systems ideal for assessing plumes and fugitive emissions.

GAS CHROMATOGRAPHY

Gas chromatography describes a number of techniques used to separate mixtures of gases and vapors into specific components. All exploit the differential movement of the mixture of gases through a solid or viscous

liquid material. The sample is injected into a carrier gas (the mobile phase) which "pulls" the sample through the stationary phase where separation occurs. The stationary phase is frequently called the separation column. Different molecules in a mixture have differing affinities for the substances in the column and the carrier.

Contaminant molecules having low affinity for the stationary phase and high affinity for the carrier move through the column at the same rate as the carrier. The higher the affinity for the column material, the slower the contaminants move through it. Because contaminants move through the column at different rates, they eventually separate into discrete bands. A suitable detector positioned downstream from the column senses the emergent bands of molecules.

Columns are available in a variety of lengths and can be strung together. A variety of materials are used in the stationary phase. "Packed" columns are solidly filled with material. The columns are usually coiled and may be encapsulated for use in isothermal ovens. "Capillary" columns (0.32 or 0.53 mm ID) have a hollow core. The stationary phase is coated onto the inside wall. The type and length of column selected should be a function of the characteristics of the molecules to be separated.

Once separated, a variety of detection techniques are used to characterize and/or quantify individual components. These include PID, FID, thermal conductivity, electron capture (ECD) and argon ionization, as well as a number of others. Use of separation columns precludes use of the detector as a real-time monitor. Columns provide snap-shots of concentrations in a discrete sample rather than dynamic real-time measurement. The sample must be obtained either automatically by the analyzer, or as a grab sample that is then injected into the GC. Time is required for

contaminants to move through the length of the column to the detector.

The carrier gas is a function of manufacturer preference and the nature of the detector. Common carrier gases include "ultra zero air" which contains less than \pm 0.1 ppm total hydrocarbon (used with PID), argon (used with argon ionization detectors), as well as nitrogen and helium. Common types of stationary phase media include liquid paraffin, silicone oils, squalene, and apiezon greases for the separation of nonpolar molecules; alkylaryl sulphonate and dinonyl phthalate for separation of intermediate polar molecules; and dimethylsulfolane and polyethylene glycols for the separation of strongly polar molecules. The manufacturer of the detector will supply or specify the appropriate columns, media and carrier to be used with the analyzer.

FIXED DETECTION SYSTEMS

Proper assessment of existing or potential atmospheric hazards is essential for management of air quality in confined spaces. There are two basic approaches to atmospheric monitoring: portable gas detectors assigned to workers who enter the affected area, or fixed detection systems. Fixed detection systems are permanently installed in the affected area and function 24 hours per day. An approach for addressing on-going atmospheric hazards in frequently entered confined spaces is a continuously operational fixed point detection system. Alarms activate whenever conditions become unsafe.

Fixed systems can activate ventilation fans, security notification equipment, such as auto-dialers, as well as external alarm lights and sirens. Fixed detection systems also activate or deactivate specific processes through process control. Presence of a hazardous substance in an area which would indicate a breakdown.

Another important function provided by fixed systems is demonstrating

compliance with regulatory requirements. Records from fixed systems can show compliance with OSHA or EPA limits, for example. Although some detection techniques are more commonly used than others, systems are available with virtually every detection technology discussed in this chapter. The hazard to be measured determines the type of detector.

In many circumstances, a permanently operational or fixed gas detection system in the confined space can provide better protection than portable instruments used on an infrequent basis to determine whether atmospheric conditions are safe for entry.

HAZARD MANAGEMENT

Once a specific hazard has been identified and quantified, the most prudent management stratagem is to eliminate it. Regulatory limits, such as OSHA Permissible Exposure Levels, are maximum concentrations to which an unprotected worker may be exposed while on the job. Likewise, Threshold Limit Values (TLVs) provided by the American Conference of Governmental Industrial Hygienists (ACGIH) are recommendations for maximum worker exposure. Above these concentrations the air is deemed to be hazardous. Unprotected workers should not be allowed to remain in those conditions for any reason.

Sometimes the best approach involves the combined use of both fixed and portable monitors. Deciding which approach to use is not always a trivial exercise. The following questions provide a guide for making this decision.

- **What kind of atmospheric hazard is potentially present?**

The kind of hazard profoundly influences the type of warning that is needed. The urgency to warn against rapidly acting hazards, such as hydrogen sulfide or oxygen deficiency, is much greater than that needed for slower acting agents, such as carbon

monoxide. Understanding the hazards posed by specific contaminants, and conditions that can occur is critical to structuring an appropriate monitoring program.

- **What is the source of the hazard?**

This question brings more questions for which answers are needed. Is the source of the hazard readily identifiable? Is the hazard associated with the work performed in the confined space or near it? Is microbial action involved? What chemical products are used in or near the space? What industrial processes are occurring? Can sources of contaminants that are remote from the confined space present an additional risk under emergency circumstances?

- **Are the hazards potentially present all of the time, or only when procedures, activities and/or products associated with the confined space entry are in use?**

Some confined spaces are entered on a very frequent basis. For example, some pits in a commercial garage are routinely entered and occupied by mechanics. Hazards known to be chronically present in areas where workers routinely enter without special precautions should be monitored on a continuous basis. This environment would benefit from the installation of a permanently operational fixed gas detection system.

- **What is the physical nature of the area affected?**

Again, this question prompts more questions. Is the entire facility affected, or only the confined space? Are the areas in which the confined space is located out-of-doors and subject to good ventilation? Is the confined space located indoors or localized in confining areas that prevent rapid dispersal of contaminants? Fixed detection systems are ideal for 24-hour-a-day "sentry" applications.

- **How much time is required for workers to leave the affected area safely?**

Are the areas immediately outside the confined space congested with equipment, machinery or other obstacles to safe evacuation? Monitoring programs should provide workers adequate time to "self rescue" from the confined space, as well as areas outside the space also potentially affected in an emergency. Workers require adequate warning before hazardous conditions become life threatening so that they have sufficient time to evacuate the affected area in safety. Fixed detection systems are frequently used to provide the alarm for evacuation of an affected area.

- **Must the affected area be maintained safe for continuous worker occupancy?**

Is the confined space permanently secured against unauthorized entry, or is the area one which is routinely entered by workers without special precautions being taken? Atmospheric hazards in areas routinely entered on an uncontrolled basis should be monitored on a continuous basis.

- **What is the level of control over worker activities in the affected area?**

Is entry into the confined space strictly controlled and limited to specially trained personnel? (It should be!) The lower the level of control over worker activities, the more desirable a continuously operational fixed detection system becomes.

- **What is the level of training of potentially affected workers?**

One of the advantages of fixed detection systems is that workers entering the monitored area usually are not involved in the day-to-day operation of the system. Addition of a fixed detection system coupled with other engineering controls, such as permanently installed ventilation, may actually allow the reclassification of the confined space as an environment outside the scope of regulatory requirements for an

entry. What workers entering the area must do is to follow company procedures in the event an alarm sounds.

- **What are the trade-offs in cost?**

Equipping workers individually with gas/vapor detectors can become expensive. On the other hand, a permanently installed system that provides general monitoring in an area and equivalent protection can be by far the most cost-effective approach to ensuring worker safety.

WIRELESSLY INTEGRATED PORTABLE AND FIXED INSTRUMENT SYSTEMS

It is likely that over the next few years a wide variety of products – including atmospheric monitors – are going to be equipped with wireless RF (radio frequency) modems which allow real-time transfer of information from a remotely-located measurement device to a base station located anywhere from immediately adjacent, to miles away from the location of the detectors. The base station or “Host Controller” might be located in a mobile HAZMAT response truck, (Figure 20), the personal computer in the safety office of a facility where contractors are engaged in confined space entry activities, or anywhere else there is a need for real-time monitoring, safety or security information to be displayed. This instantaneous data transfer has the potential for totally redefining the type, timeliness and quality of the information used to make many types of on-the-spot decisions. It is also critical that as this new method for transmitting data becomes more widely available, it is used in ways which conform to the letter as well as spirit of confined space entry and other safety regulations.

The way the new technology works

Real-time communication by means of radio, intercom, or other hard-wired connection has been a part of many confined space entry programs for many

years. After all, maintaining communications between entrants, attendants, and other personnel associated with entry is a mandatory requirement under permit-required confined space entry procedures. The big changes on the horizon have to do with the inclusion of direct, real-time transmission of monitoring data between the gas detector and a remotely located base station (or stations).

There are two basic approaches being utilized at the moment. The first is interfacing the instrument with an add-on radio communication module. The second is including an integral RF (radio frequency) modem inside the instrument. Several related technological trends and advances have made using real-time RF data transmission increasingly attractive. One factor is the availability of “ISM” (industrial / scientific / medical) radio transmission frequencies that (at least in the United States) do not require a user license for transmission. Other factors are found in the increasingly sophisticated methods used for radio transmission and signal processing that make it possible to maintain a solid communication link between the instrument and the remotely located base controller. The spread-spectrum, frequency-hopping methods used to protect the real-time digital RF data stream signal from interference from other RF sources makes the communication link secure and robust enough to use it dependably in safety monitoring programs.

There are two basic approaches to the configuration of the base controller as well. In some cases the base controller is a dedicated “black box”, with displays, controls and alarms designed to provide alarm state information primarily on a local basis. In the other case the base controller is actually a laptop or personal computer that has been equipped with a radio receiver designed to allow real-time communication with the remotely located instruments. Sometimes the system includes both types of base controller capabilities.

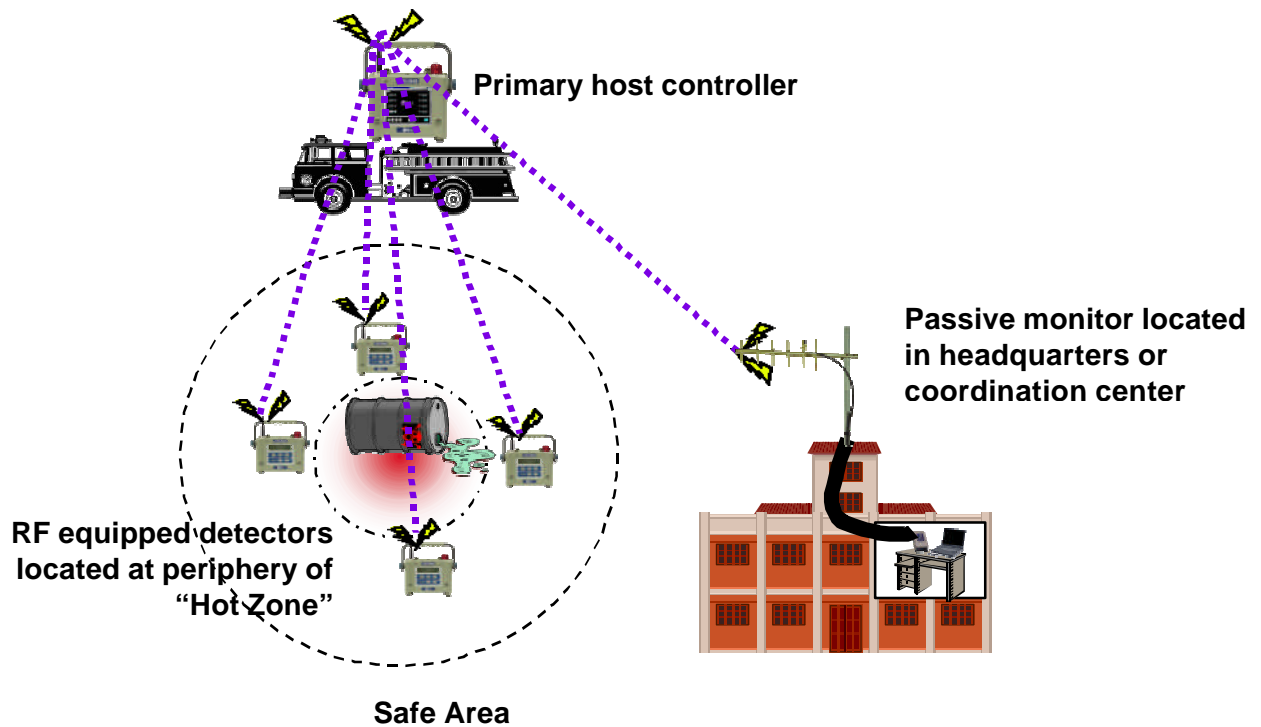


Figure 21 RF equipped portable monitors used to establish used to establish a monitoring perimeter during a hazardous material response²

Sometimes the base controller is located immediately outside the confined space, where it can be used to help maintain better communication between the attendants and entrants. Sometimes the information is transmitted to a more remote location, for instance, the office of the Safety Manager, or to a third-party rescue provider. Sometimes the information is transmitted redundantly to several remote locations. The emerging technology effectively allows real-time communication literally on a world-wide basis. Once the monitoring results exist as a digital information stream in a computer, it can easily be sent onward within seconds via cellular telephone, hard-wired land-line, or over the Internet, literally anywhere in the world.

Most systems are scalable, and capable of handling anywhere from one or two detectors, to (in some cases) handling and displaying readings for up to 128 detectors simultaneously. An important architectural issue is whether or not multiple systems can be blended “on the fly” into larger systems or information arrays. For instance, a single confined space entry team might consist of three entrants, each of whom is equipped with a monitor, and an attendant equipped with a portable base station located at the point of entry. The real-time monitoring information might also be redundantly displayed on a monitor located in the office of the plant Safety Director. Along with the real-time monitoring information from this first team, the Safety Director might also choose to

² Figure 21 diagram courtesy of Chris Wrenn, RAE Systems Inc., Sunnyvale, CA

display monitoring and entry status information from other confined space entry teams simultaneously working in other areas of the plant. Finally, in the event of an emergency, it might be very important for additional monitors to be added very quickly to the smaller systems used during routine operations. The important thing is for the system to be capable of the flexibility required by the nature of the confined space entry procedures being undertaken.

Using real-time information to improve worker safety

No new technology comes without some new concerns. One concern which has been raised relates to the temptation to use the technology in order to replace or reduce the obligation for the presence of a standby attendant during permit required confined space entry procedures. The availability of the new technology has not changed the wording of OSHA 1910.146, "*Permit required confined spaces*". For confined space entries made pursuant to paragraph (d), "*permit required confined space program*", the regulation clearly stipulates the mandatory presence of at least one attendant outside the permit space into which entry is authorized for the duration of the entry operations. 1910.146 paragraph (i) defines the duties of the attendant. While ensuring that the atmosphere within the space continues to be safe for authorized entrants is a primary responsibility, the duties of the attendant go far beyond this single specific duty. Simply replacing the attendant with a telemetered stream of atmospheric monitoring information sent to a remote location would obviously satisfy neither the letter, nor the intent of the regulation. On the other hand, 1910.146 paragraph (d), section (6) goes on to note that attendants may be assigned to monitor more than one permit space provided the duties described in paragraph (i) can be effectively performed for each space that is monitored. Likewise, attendants may be stationed at any location outside the permit

space to be monitored as long as the duties described in paragraph (i) can be effectively performed for each permit space that is monitored. The bottom line is that in many cases the availability of real-time monitoring data can substantially enhance the ability of the attendant to verify that the atmosphere remains within safe entry limits, to alert entrants to the need to evacuate the space, or to coordinate rescue activities.

Another potential use of real-time data transmission technology is in confined space entries which are made pursuant to 1910.146 (c) (5) (ii). The "alternate entry procedures" explained in this section are restricted to permit spaces which are characterized by certain specific conditions. The most basic requirement is that the employer must demonstrate that the only hazard posed by the permit space is an actual or potential hazardous atmosphere. The requirements for permit entry under 1910.146 (c) (5) (ii) require that the atmosphere within the space shall be tested as necessary to ensure that the continuous forced air ventilation (another requirement) is preventing the accumulation of a hazardous atmosphere. What 1910.146 (c) (5) (ii) does not include is a mandatory provision for the presence of an attendant outside the permit space into which the entry – pursuant to this section – has been authorized. It goes beyond the scope of this chapter to debate the prudence of entry procedures which do not include the presence of an attendant. The fact is that a great many entries are permissibly made on a regular basis under the provisions contained in this section *without* the presence of an on-hand safety attendant. In this case, the inclusion of real-time monitoring data transmitted to a central location is a clear enhancement for the safety of entrants.

Another clear case for the inclusion of real-time monitoring data transmission is in cases where, in the event of an emergency, rescue services are to be provided by a



Figure 22 RF equipped multi-sensor gas detector, and wirelessly integrated AreaRAE gas detection system. (Courtesy RAE Systems Inc., Sunnyvale, CA)

“third-party” provider. The non-mandatory Appendix F to 1910.146, “*Rescue Team or Rescue Service Evaluation Criteria*”, goes to great lengths to explain the specific circumstances under which it may be acceptable to rely on a third-party rescue provider rather than a rescue team already on-site at the confined space.

Once again, it goes beyond the scope of this chapter to debate the circumstances under which it is prudent to rely on rescuers who are not physically present at the space until after an emergency has occurred. Once again, the fact remains that many programs rely on exactly this approach to conducting a rescue. One thing is very clear, if this is the approach to conducting a rescue, the timeliness of sounding the alarm, or activating the response team is crucial to the ability of the team to successfully respond to the incident. Having the atmospheric monitoring data, and alarm-state information, displayed in real-time on a monitor located in the rescue service provider’s office is clearly a step towards

improving the ability of the rescue provider to rapidly respond in an emergency.

Future developments

Real-time transmission of monitoring data is only the first step in the wireless safety revolution. Telemetered worker safety data will certainly not be restricted to atmospheric monitoring results. Real-time health status data, such as body temperature, pulse-rate, and other physiological information will also be available on a real-time basis. Not to mention integrated two-way voice and video communication, thermal imaging, and a host of other advanced technological capabilities.

CRITERIA FOR INSTRUMENT SELECTION

General discussion

Atmospheric testing is used to assess conditions in a confined spaces by determining potential hazards and establishing potential exposure levels. Atmospheric monitoring is used to ensure



Atmosphere reaches sensors by diffusing through slots or vents in sensor compartment cover

Figure 23 Diffusion LEL / O₂ personal monitor. (Courtesy RAE Systems Inc., Sunnyvale, CA)

that conditions remain safe (nonhazardous) for all potentially affected workers. The instrument that will provide best service and value in a particular situation reflects consideration about many factors:

- Atmospheric hazards
- Monitoring environment
- Sampling strategy
- Level of user sophistication
- Requirements for record keeping
- Other performance criteria which define the characteristics of the requirements

One thing is certain, is that the purchaser will face a very large number of options and choices. While the most widely used instruments used in assessing conditions in confined spaces share many

similarities, there are still many important differences between designs. The purchaser should consider the requirements of entire program before buying an instrument, not after.

Most confined space instruments currently in service include a fuel-cell type oxygen sensor, a catalytic (hot bead) flammable/combustible sensor, and one or two electrochemical sensors for detecting specific toxic gases. A minority of detectors additionally include either an MOS sensor or a photoionization detector for broad range monitoring purposes. Some instruments also incorporate an infrared sensor for carbon dioxide or methane. This section will explore some of the advantages and disadvantages associated with choices, configurations, and options available for these instruments.

SAMPLE-DRAW VERSUS DIFFUSION

In normal operation, most confined space instruments are worn on the belt, used with a shoulder strap or chest harness, or held by hand. Once turned on, these devices operate continuously until the battery is exhausted. Diffusion instruments utilize natural air currents to bring the atmosphere being sampled to the instrument. Gases then pass to the sensors by diffusion through holes, vents, or apertures in the instrument housing or cover of the sensor compartment. (Figure 23) Normal air movements are sufficiently energetic to bring the sample to the sensors. Most sensors react rapidly to changes in the concentration. This type of operation monitors only the atmosphere that immediately surrounds the detector.

Sample-draw kits enable diffusion-type instruments to sample from remote locations. Two types of sample-drawing kit are available. In each case the sample is drawn in through a probe assembly, and ducted through a length of hose to the instrument. One type uses a hand-operated squeeze-bulb to draw the sample through the hose. The other uses a battery-operated continuous mechanical pump. In some designs the pump attaches to the instrument, and pulls the sample from the probe assembly back to the sensors. In other designs a "pistol"-type pump located at the end of the sample hose pushes the air to the location of the sensors. Still other designs contain an integral pump that operates continuously whenever the is turned on. Since the pump operates continuously, this type of instrument operates only in the sample-draw mode. Each configuration has both advantages and disadvantages.

Drawbacks of diffusion operation

The chief drawback associated with diffusion operation is the inability to sample at locations remote from the instrument. Short of lowering the instrument on a string, there is no way to test the lowest point in a manhole while standing outside

the space. A particularly dangerous misuse of diffusion-type instruments occurs when users test only at the point of entry because that is the only point that can be reached. They then base the initial decision about entry on this dangerously incomplete information. They then enter the space while wearing or carrying the instrument and expose themselves and it to conditions further into the space. This puts the entrant in danger where conditions are life-threatening, since the individual then must escape from the space after the instrument alarms. Further, conditions below the level of the instrument may go unmeasured, unless the entrant remembers to lower it. Sampling at all levels in a vertical space is critically important because of potential stratification of gases. This is the information needed before making a determination to proceed.

Fortunately, every leading manufacturer of diffusion-type instruments offers a sample-draw kit for use with their product. Availability of such a kit should be an important consideration when purchasing an instrument. Another is the type of sample-draw unit: squeeze bulb or motorized pump. Potential buyers of squeeze-bulb products should consider usage. Fatigue could become a serious issue. As well, the number of compressions must be calculated to ensure that the sensors sample an atmosphere that is representative of conditions in the space.

Generally, pre-entry sampling will involve use of the remote sampling kit, while monitoring after entry will utilize diffusion operation.

Drawbacks of sample-draw operation

Several cautions apply to the use of sample-draw kits or other modes of sample-draw operation. The most important is leakage. Components in the sample-draw system upstream from the pump are under negative pressure. In-leakage would dilute the sample with the atmosphere entrained at the

point of the leak. Under some circumstances, the atmosphere reaching the sensors is not merely diluted, but entirely replaced by leakage into the system.

Diaphragms in mechanical pumps are notorious for stiffening, deteriorating, or abrading over time or with use. A leak in a pump diaphragm can result in a unit that appears to be performing normally based on visual observation, yet is incapable of drawing at the correct flow-rate. The best way to guard against the potential for leakage is to test the sample draw system prior to every use.

To test the integrity of manually aspirated, squeeze-bulb type sample draw kits, attach the instrument to the sample draw assembly, squeeze the bulb, block the sample probe inlet and note whether the bulb remains deflated. If there are no leaks in the system, the bulb remains deflated until the blockage is removed.

Most mechanical or motorized pumps utilized in monitoring instruments contain a low flow alarm. To test these systems, attach the pump and sample draw assembly to the instrument and block the end of the probe with a finger. If there are no leaks in the system, the low flow alarm should activate. This method also applies to the sample draw system of instruments containing built-in sample-draw pumps.

Important safeguards in sample-draw systems are the probe assembly and filters attached to the sample line. Probe assemblies usually include filters or traps. These prevent entry of particulate and/or liquid contaminants into the system. Clean air prolongs the life of the sensors by preventing build-up of particulates on membranes. Damage to the pump can occur from particulate abrasion. Damage to the sensors or instrument electronics can result from fluids sucked into the sample draw system.

A concern about operation of sample-draw systems is time lag. This is the time

taken by the pump to move the air from the inlet of the probe to the sensors. This adds to the time required by the sensor to respond to the contaminant. Remember, response can only begin only after the sample reaches the sensors. If the t_{90} (or time required for the sensor to reach 90 % of final response) is 45 seconds, and the time taken for the sample to reach the sensor also is 45 seconds, the amount of time needed to reach t_{90} output will be 90 seconds. The longer the sample-draw hose, the greater the amount of time needed for the sample to reach the sensors. Time lag due to line length highlights another concern about sample-draw operation: absorptive and adsorptive losses. These result from interaction with the material of construction of the sample hose. Absorptive and adsorptive losses reflect the amount of time the sample spends in the sample hose. Highly reactive gases, such as chlorine, are nearly impossible to measure quantitatively without significant losses due to interaction with components in the sample-draw system. Although detection of gross concentrations is possible, measuring chlorine in the 0.1 ppm increments needed to assess exposure is very difficult when the sample is obtained through a sample-draw system. Diffusion sampling (when feasible) is usually the better approach for measurement of highly reactive gases. Fuel mixtures such as diesel oil, or "JP-8" also have an affinity for certain types of sample-draw tubing.

Another issue is sample temperature. Confined spaces are frequently warmer than the area where the instrument is likely to be located. In the case of high flash combustible liquids, the difference in temperature is sometimes sufficient to cause condensation of vapor into liquid in the sample hose. Since the sensors are designed to detect gases and vapors, and not liquid concentrations, condensation can sharply depress the reading.

SENSOR SELECTION

Confined space monitors are available with space for two, three, four, five, or even six sensors. Make sure the instrument chosen for a specific application can accommodate the needed number and type of sensors. While the unit need not be equipped with all the sensors in order to function, the critical issue in the purchasing decision is future need. An instrument that lacks the capability of changing or adding additional sensors if this need is likely in the future would represent a mistake. Field configurability also is highly desirable. Adding an additional sensor should not be difficult. Most leading designs allow the user simply to plug in the new sensor, and make the setup choices necessary to let the instrument know that a change has been made. A number of instrument designs include automatic sensor recognition. This makes the process of adding or changing sensors even easier to accomplish.

One of the major issues facing the gas detector purchaser is the choice of toxic sensors. If the confined space to be monitored is characterized by the known or potential presence of a specific toxic contaminant, the best and safest approach is a substance-specific sensor. The sensor, of course, requires direct calibration by a known concentration of that substance. If the level of knowledge about hazards likely to be encountered in the space is low, a broadly responding sensor may be the better approach.

OSHA wrestled extensively with this issue in the Standard on confined spaces in general industry. (OSHA 1993) According to Appendix E (Sewer System Entry), broad range sensors are best suited for initial use where actual or potential contaminants have not been identified. Appendix E further discusses the fact that such sensors only indicate exceedence of a hazard threshold of a class of chemicals. Therefore, substance-specific sensors are best suited for use where actual and potential contaminants have been identified. However, Appendix E

concludes that the atmosphere in sewers can change unpredictably and that substance-specific devices may not detect new potentially lethal hazards. The employer must decide, based on knowledge and experience, the best type of testing instrument for a specific entry operation. The bottom line is that if hydrogen sulfide or carbon monoxide are known to be present, the monitoring instrument should contain sensors that allow for the direct and quantifiable measurement of these contaminants. In many cases the most prudent approach is to include substance-specific electrochemical sensors for identified contaminants, as well as a broad range toxic gas sensor (such as PID or MOS) for other contaminants which may be potentially present. Several manufacturers offer four or five channel compact multi-sensor confined space instruments with exactly these capabilities.

CLASSIFICATION FOR INTRINSIC SAFETY

Instruments purchased for use in a confined space, hazardous location, or other environment characterized by the potential presence of flammable or explosive gases, should carry a Classification for Intrinsic Safety. A Classification for Intrinsic Safety usually is not an obligatory requirement on instruments purchased or sold for these applications. It ought to be!

Devices classified as "Intrinsically Safe" prevent explosions in hazardous locations by employing electrical designs that eliminate the possibility of ignition. This generally involves adding protective components in series with energy storage devices. The purpose for the protective components is to reduce the 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.

The Classification for Intrinsic Safety received by the instrument references the severity of the explosive hazard of the flammable atmosphere in which the testing occurred. (NEC, 1995) For example, many confined space instruments are Classified for use in Class I, Division 1, Groups A, B, C, and D Hazardous Locations. This means that the testing was conducted in a "Group A" atmosphere (an atmosphere containing an explosive mixture of acetylene). An instrument capable of passing tests in a Group A atmosphere, by definition is Intrinsically Safe for use in Groups B, C, and D atmospheres.

Group B atmospheres contain hydrogen, fuel and combustible process gases containing more than 30 percent hydrogen by volume, or gases or vapors of equivalent hazard, such as butadiene, ethylene oxide, propylene oxide, and acrolein. Group C atmospheres contain gases or vapors, such as ethyl ether, ethylene, or gases or vapors of equivalent hazard. Group D atmospheres contain gases or vapors such as acetone, ammonia, benzene, butane, cyclopropane, ethanol, gasoline, hexane, methanol, methane, natural gas, naphtha, propane, or gases or vapors of equivalent hazard. Many confined space instruments also carry a Classification for use in Class II, Groups E, F, and G Hazardous Locations. These Groups refer to combustible or explosible dusts. Group E atmospheres contain combustible metal dusts, including aluminum, magnesium, and their commercial alloys, or other combustible dusts whose particle size, abrasiveness, and conductivity present similar hazards in the use of electrical equipment. Group F atmospheres contain combustible carbonaceous dusts, including carbon black, charcoal, coal, or dusts that have been sensitized by other materials so that they present an explosion hazard. Group G atmospheres contain combustible

dusts not included in Group E or F, including flour, grain, wood, plastic, and chemicals.

Any instrument purchased for use as a confined space gas detector should carry the logo of the testing laboratory that conducted the evaluation, as well as the specific Hazardous Location Groups for which the Classification applies. For instance, the label might read:

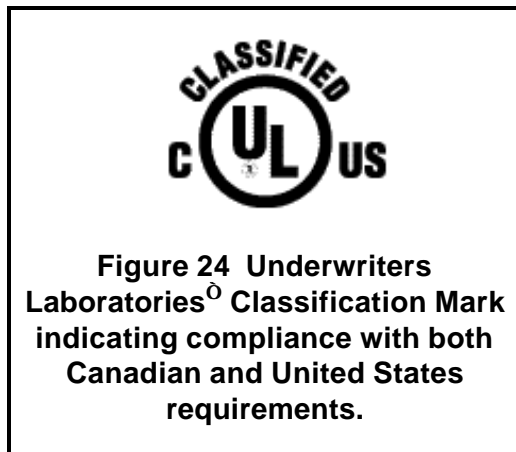
**Classified by Underwriters
Laboratories, Inc.® and Canadian
Standards Association as to Intrinsic
Safety for use in Hazardous
Locations Class I, Division 1, Groups
A, B, C, and D**

Users should beware of statements on the label or literature accompanying the gas detector that indicate the instrument is "intrinsically safe by design". If the logo of a Nationally Recognized Testing Laboratory (such as Underwriters Laboratories, Canadian Standards Association, Factory Mutual, Intertek Testing Services, etc.) is not prominently displayed on the instrument label, the instrument probably has not been submitted for third-party evaluation.

Evaluation methods used to determine Intrinsic Safety may differ from one testing laboratory to another. To illustrate, the Canadian Standards Association (CSA) tests for the Intrinsic Safety of the design of the instrument. CSA also evaluates the accuracy and stability of flammable/combustible sensor readings. Testing conducted by other testing laboratories may or may not include this additional performance evaluation. An increasingly common trend is for manufacturers to use a single testing laboratory to establish compliance with multiple performance standards. For instance, Underwriters Laboratories® is capable of providing testing to determine compliance both with its own domestic United States standards, as well as Canadian Standards Association, and European Community requirements. The "C" and the

“US” in the UL® Classification Mark shown in Figure 24 indicate compliance with both Canadian and United States requirements.

Instruments that have been additionally tested for Intrinsic Safety with regards to European Community standards will also carry this information on the label. For instance, **EEx ia d IIC T4** would indicate compliance with the latest edition of the European Community “ATEX” standard for intrinsic safety. The “T4” in the approval indicates the Temperature Code and the specific categories of combustible gas for which the instrument is rated.



ISO REGISTRATION

Manufacturers are increasingly promote themselves on having attained registration for one or another of the ISO (International Standards Organization) Quality Standards. Attaining ISO registration is no easy feat. ISO-registered companies have submitted their Quality Systems to a rigorous third party evaluation, and have met the exacting performance criteria contained in the ISO standard to which they are registered. Being an ISO-registered company, however, does not automatically guarantee the excellence of the products that the company sells. An ISO-registered company is free to produce mediocre products, as long as they produce them in a highly consistent manner. Fortunately, this is seldom the case. The ISO registration process ensures that

manufacturers take a careful look at the quality of the products they design, make, or market, and that they do their utmost to increase customer satisfaction. The bottom line is that ISO registration is an excellent indicator about the way that a company does business.

BATTERIES

Batteries, while not the heart of a portable instrument, are close to it. Batteries determine the size and weight of an instrument. They also determine service life. The flexibility provided by the instrument manufacturer determines whether the user can buy emergency replacements in a small town that will keep the instrument running.

Confined space instruments may be equipped with either disposable alkaline, or rechargeable batteries, or both. The primary advantage of rechargeable batteries is overall cost effectiveness. Frequent (or daily) replacement of disposable batteries can be very expensive. While alkaline batteries may not be the most cost effective approach, having the ability to use them "in a pinch" is a strong design advantage. Several instrument designs offer interchangeable rechargeable and alkaline battery packs.

Types of rechargeable batteries used in these instruments include lead-acid, NiCd (nickel-cadmium), NiMH (nickel-metal-hydride), and Li-ion (lithium-ion) designs. The primary advantage of lead-acid batteries is their ability to be left continuously on the battery charger whenever the instrument is out of service. Lead-acid batteries are highly resistant to damage due to overcharging. The primary disadvantage of lead-acid batteries is damage sustained when allowed to drain or discharge completely. NiCd (nickel cadmium) batteries are the most widely used rechargeable battery. Although NiCd batteries usually are not damaged by deep-discharging, they lose capacity when not "exercised" by being allowed to discharge fully before being put back on the charger. Many users refer to this loss of

capacity as "developing a memory". Conversely, allowing the battery to completely discharge itself may also cause irreversible damage.

In most cases the NiCd memory effect is attributable not to lack of "exercise", but the damage due to heating of the battery cells during prolonged overcharging. The charger continues to pump current into the battery even after charging is complete. This heating causes structural changes in the battery that result in sharply reduced capacity. The battery pack then may be able to provide only a few minutes of power to the instrument instead of the normal 8 or 10 hours of continuous operation. Sometimes "cycling" (charging then draining the battery a number of times) may partially restore the lost capacity. Usually, once damage has occurred, the only way to restore the full operational capability of the instrument is to replace the battery.

Over the last few years, battery manufacturers, as well as manufacturers of battery charging systems have made major improvements in design. Today's "smart" battery chargers contain electronics for assessing the condition of the NiCd battery pack during charging, and to drop from a "fast" charge rate to a "trickle" the moment charging is complete. The "trickle" charging rate is too low to produce damage from heating. As result, instruments containing NiCd batteries can be recharged in a very short period of time, and left on the charger for long periods of time without damage. Batteries in these instruments do not require discharging or exercising before being placed back on the charger. Similarly, many NiCd battery packs now also contain protective electronic components that prevent the batteries from deep discharging to the point of damage.

Rechargeable lithium-ion batteries

Although advances in battery charger design have reduced problems associated with the use of NiCd batteries, manufacturers are tending to choose other types of batteries, such as nickel metal hydride, or lithium-ion when designing new instruments. In particular, lithium ion batteries seem to be becoming the rechargeable battery of choice in most recently introduced designs.

The reasons behind the emergence of lithium-ion as the battery of choice are impressive (Figure 25):

- **Highest energy density**

Lithium-ion batteries have the highest energy density per unit volume of any currently available battery type. That means they store substantially more power in the same available space. In addition, lithium-ion batteries can be manufactured in "prismatic" or rectangular shapes, allowing the battery pack to more efficiently fill the available space than cylindrical NiCd cells. (Figure 26) These attributes allow manufacturers to design instruments that are smaller in size, yet operate substantially longer per charge than earlier versions.

- **Lightest weight**

Because lithium-ion batteries are constructed out of thin polymer layers rather than heavy metal electrodes immersed in an acid bath, they are extremely lightweight, making them by far the lightest rechargeable battery available.

- **Do not develop memories**

Perhaps most importantly, lithium-ion batteries are not prone to loss of capacity due to overcharging or developing "memories". Unlike lead acid and NiCd batteries, lithium-ion batteries do not self-discharge while on the shelf or out of use, and lose very little capacity over a very long operating lifetime.

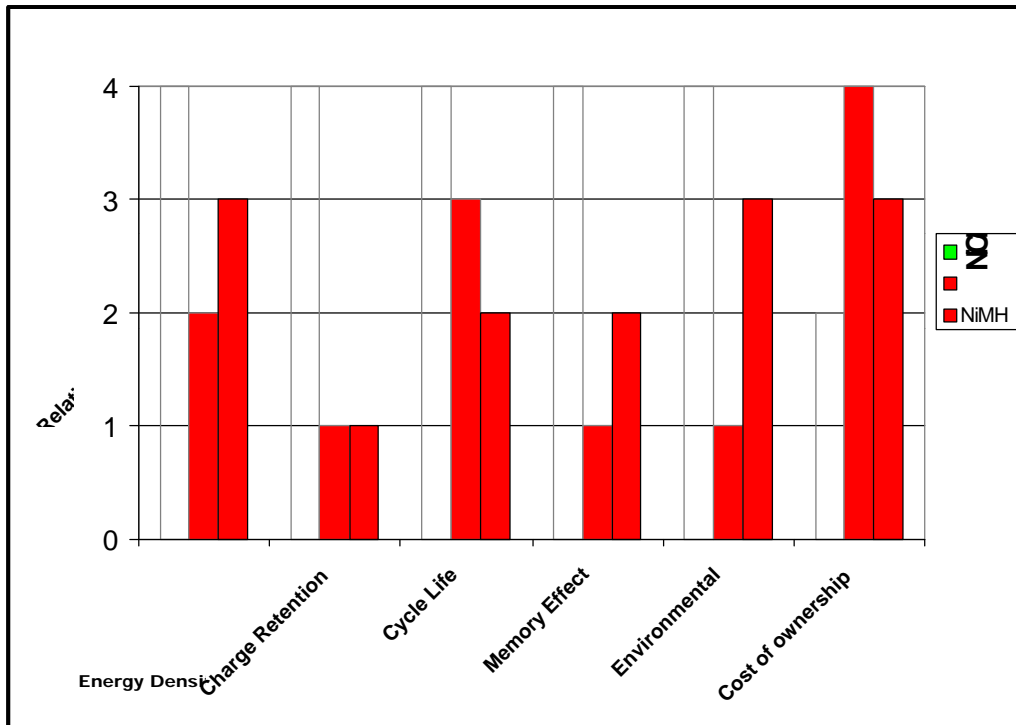


Figure 25 Relative performance attributes of lithium-ion, nickel-cadmium, and nickel-metal-hydride rechargeable batteries. (Courtesy of PolyStor Inc., Dublin, CA)

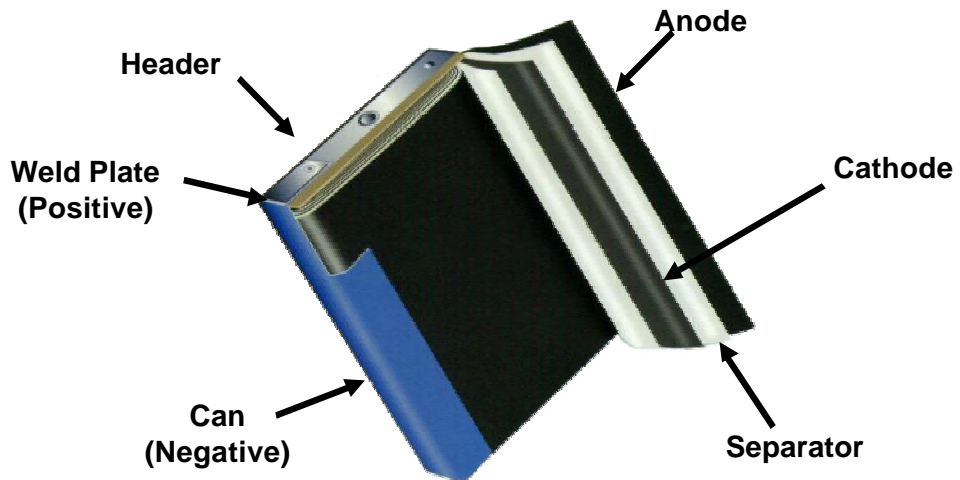


Figure 26 Cutaway view of prismatic, lithium-ion rechargeable batteries. (Courtesy of PolyStor Inc., Dublin, CA)

A typical factory guaranty from a lithium-ion battery manufacturer indicates that the battery will retain at least 80% of its original capacity even after 400 complete charging cycles.

- **Environmentally friendly**

Because these batteries do not include heavy metals such as lead, nickel or cadmium, they are the “greenest” available type of battery. Lithium-ion batteries are rated as non-hazardous for air transportation and disposal.

These attributes are impressive enough to have grabbed the attention of most portable gas detector manufacturers. The chief liability of lithium-ion batteries is their initial higher cost. However, their long-term performance is almost invariably associated with a substantially lower lifetime “cost of ownership”.

DURABILITY

Instruments designed for use in confined space monitoring programs must be durable. Unfortunately, many designs are less robust than they may appear on the surface. When considering whether an instrument is tough enough to take the abuse it is likely receive, consider asking the following questions.

- **Has the instrument been tested, and is it protected and constructed in a way to minimize the effects of radio frequency interference (RFI) and electromagnetic interference (EMI)?**

This is a very important consideration in light of the effect RFI can have on the output of an unshielded electrochemical sensor.

- **What are the effects of high and low temperatures on the design?**
- **How water resistant is the design?**

Is the design water resistant, or vulnerable to damage when used in the rain or

dropped in a puddle? If the manufacturer says the design is water-proof, ask for their definition.

- **Does it feel flimsy or provide unstable readings when picked up and turned on?**

Don't underestimate the amount of information the "feel" of an instrument can sometimes provide.

DATALOGGING VERSUS NON-DATALOGGING CAPABILITY

Datalogging capability is available in many single and multi-sensor instruments. In the past, successfully downloading datalogged information from the instrument to a computer sometimes required a high degree of operational expertise. Today the procedure is nearly automatic. Datalogging instruments usually are set up to retain monitoring information whenever turned on. The utility of this information for compliance and record-keeping purposes is obvious.

The information also can serve other extremely useful functions. The first is to provide information about accidents or unusual occurrences. The datalogged information provides a record about conditions that occurred. This saves the need to attempt a reconstruction of the event using costly and time-consuming activities. The datalogged information becomes a source of information that can assist in preventing recurrences. The datalogged information also verifies whether the instrument was used correctly at the time the event occurred.

The time-history of exposure indicates whether CEILING limits (floor limit in the case of oxygen) have been exceeded during work activity. The output can indicate in considerable detail about exceedences exactly when they occurred, how long they lasted and the dynamics of events that surrounded them. This information is extremely important for assessing the

significance to put on the exceedences. This capability is not available on non-datalogging instruments.

Datalogging as well as non-datalogging confined space instruments frequently include the capability to solve complex time history calculations, such as those used to compute CEILING, STEL, and TWA values. Datalogging instruments are able to retain this information after the instrument is turned off, or after the initiation of a new sampling interval. Instruments lacking datalogging capability cannot do this.

In order to create a report or display the recorded data, the datalogging instrument periodically takes a "snapshot" of the values being sensed at any given moment, and later uses these to develop a graph or tabular report of stored monitoring data. The period of time between the "snapshots" is the datalogging interval. The instrument logs only one data "snapshot" per datalogging interval. The user generally is able to select the datalogging interval that provides the optimum level of information about the contaminants being measured. For instance, if concentrations are prone to change very rapidly, the user might select a datalogging interval of one second. If concentrations are not subject to rapid change, the user might select a longer interval. The longer the datalogging interval, the less the resolution provided by the graph or tabular report. To illustrate, a datalogging interval of one hour will not show short-term spikes in concentration that last only a second or two.

Values used by the instrument for the data "snapshot" vary from manufacturer to manufacturer. Some manufacturers log the average value over the datalogging interval. Others take the more conservative approach and log the highest value noted by the instrument during the datalogging interval. This sometimes can cause confusion during interpretation of monitoring results. To illustrate the problem that can arise,

consider a datalogging instrument that logs the highest value during the datalogging interval and an interval of one hour. If 59 minutes out of the 60 were spent with an average concentration of 1 ppm and one minute was spent at 10 ppm, the tabular report would show that the concentration for that entire datalogging interval was 10 ppm.

Another question frequently asked by instrument users concerns the effect of changing the datalogging interval on running time-history calculations such as CEILING, STEL, and TWA? The answer is that the running calculations will not be affected by changing the datalogging interval. The microprocessor continuously updates these calculations many times per minute. The datalogging interval simply specifies how often the instrument stores a "snap shot" of the current readings for the purposes of generating a printed report or database file of test results.

INCLUDED ACCESSORIES

Another important consideration is accessories that are included in the purchase price for the instrument. If the instrument includes a rechargeable battery, does the price include a battery charger? Do the accessories include a sample draw kit or motorized pump? Carrying case? Training video? Calibration materials? Necessary accessories that are not included in the purchase price can considerably add to cost and user frustration.

WARRANTY

A warranty commensurate with the trust the manufacturer places in the design should accompany a quality instrument. Many manufacturers now offer a lifetime warranty on the instrument, with a one year or two year warranty on the sensors.

OPERABILITY

Probably the most important factor of all in the selection of an instrument is ease-of-operation. If the person on the shop floor is

unable to use the instrument because of unnecessary complexity, difficulty in calibration or operation - they won't.

Operability also affects the person who selected the instrument and who first must learn how to use it. This individual is the most likely to become familiar with that other part of the equipment package: the manual and associated documentation. These materials should be inclusive enough to cover the routine and the not-so-routine questions in a manner that the average technical person can comprehend without difficulty.

INSTRUMENT PERFORMANCE SPECIFICATIONS

Specifications published by manufacturers to clarify instrument performance are a valuable tool for would-be purchasers. Unfortunately, it sometimes takes a practiced eye to interpret specifications when comparing one instrument design to another. The most significant problem is the terminology used by a particular manufacturer. While some terms are straightforward and fully accepted throughout the industry, other terms have specific meanings to a particular manufacturer. A good example is published concentration ranges. Electrochemical toxic sensors have a "nominal range" in which they may be continuously used without harm or damage, and over which they are capable of accurate readings. Electrochemical sensors can be used discontinuously or for short periods of time above the nominal range as long as they are not exposed to conditions which exceed the "maximum overload" concentration. While prolonged exposure to concentrations above the nominal range may saturate the electrolyte or create other conditions which prevent the sensor from obtaining accurate readings, short exposures should not do any long term damage to the sensor. Exposure to concentrations above the maximum overload concentration may permanently harm the sensor.

Some manufacturers differentiate between nominal and maximum overload concentrations. Others list the maximum overload concentration as the upper range limit. Still others take the far more conservative nominal range as the upper range limit. They all may be using the same sensor obtained by the same manufacturer in their designs! In addition, instrument electronics and performance characteristics may also limit performance. That means the same sensor installed in a different brand of instrument may provide substantially different performance.

Another issue is trade-offs made to optimize certain performance characteristics. For instance, partial atmospheric pressure oxygen sensors usually offer slightly faster response than capillary pore sensor designs. Judging only on the basis of the sensor's T-90 (the time from initial exposure for the sensor to reach 90 % of its final stable reading), the pO₂ design might be the better choice. On the other hand, characteristics such as a longer operational life, insensitivity to changes in the ambient or barometric pressure, and smaller size may more than make up for a slightly slower response.

Product liability is a major concern to manufacturers. Conservative firms tend to minimize performance capabilities in written specifications, preferring to err on the side of caution. In some cases this leads to manufacturers dramatically understating (at least in print) the true capabilities of their design. On the other hand, less conservative manufacturers can occasionally exaggerate. The best advice is to conduct a field trial prior to purchase! There is no substitute for hands-on experience when it comes to making a purchase decision.

Commonly used terms in instrument specifications include:

Accuracy: The percentile agreement between the instrument reading and the true concentration. Accuracy may be expressed as a function of the full scale reading, a

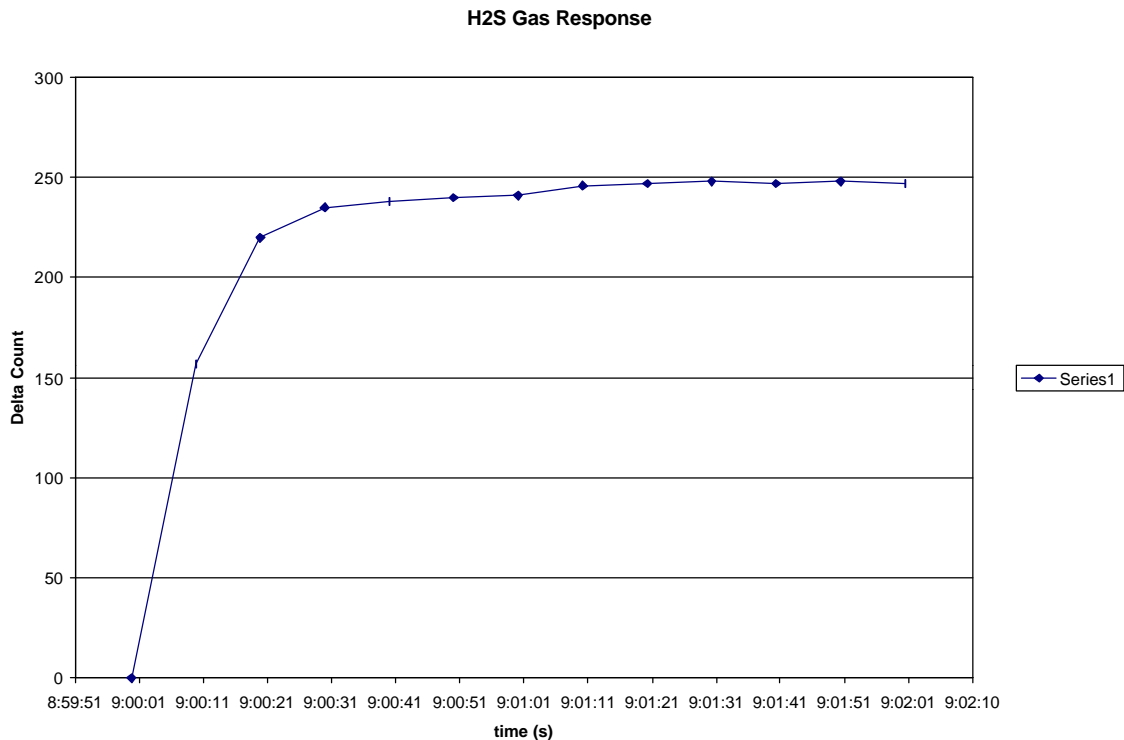


Figure 27. Electrochemical sensor output showing response and recovery times for hydrogen sulfide sensor installed in a typical confined space instrument. (Courtesy RAE Systems Inc., Sunnyvale, CA)

percentage of the actual reading, or a specific unitary value. For instance consider a carbon monoxide instrument with a full scale deflection of 0 - 500 ppm which is exposed to a concentration of 50 ppm calibration gas.

If the published accuracy of the instrument is $\pm 10\%$ of the actual reading, the expected reading in a properly calibrated instrument should fall within 45 - 55 ppm. On the other hand, if the accuracy is $\pm 10\%$ of the full scale deflection, the reading could fall anywhere within 0 - 100 ppm and still be within tolerance! The most straightforward approach is to use a unitary value. A unitary approach to the accuracy of a carbon monoxide sensor might be ± 2 ppm over a range of 0 - 250 ppm. Of course, any published accuracy is specific to the design!

Resolution: Lowest concentration of the substance being measured which can be reliably detected by the instrument.

Increments of measurement: The least significant measurement unit used to display readings. The increment of measurement can sometimes exceed the resolution of the instrument. For instance, some confined space instruments can be provide toxic readings in either 1.0 or 0.1 ppm increments. A sensor which shows poor resolution below 1.0 ppm step-change should not be used to obtain 0.1 ppm readings.

Response time: The time from initial exposure for the sensor to reach its final stable reading. (Figure 27) Response time is usually given as a T-90 (time to 90 % of final stable reading) or T-95 (time to 95 %

of final stable reading) value. Make sure the specification is clear as to the method used!

Recovery time: The time necessary for the sensor to recover after exposure to a step-change in concentration.

Repeatability: The maximum percentage variation between repeated, independent readings on a sensor, (using a gas mixture within the nominal range and under identical conditions).

Linearity: The measure of how well the concentration response curve of an instrument fits the equation for a straight line. It's important to note that it is not necessary for the sensor output to be exactly linear in order to provide linear readings. As long as the sensor output is mathematically predictable, instrument electronics may be able to linearize the readings.

Linear range: That portion of the concentration range over which the instrument's concentration response matches (or approximates) a straight line.

Noise: Random fluctuation in signal which is independent of the concentrations being measured.

Drift: Slow or long term changes in the instrument reading which are not caused by immediate changes in the concentration of the substance being measured.

ALARM SETTINGS

A primary use of confined space instruments is to alert workers about the need to take action when conditions become unsafe. Generally, that action is to leave the confined space immediately, and to return only after further testing determines that the area once again is safe for occupancy.

A very important consideration in the use of instruments is the set-point for the alarm. Alarm set-points should be set conservatively. Alarms should activate before the onset of toxicological effects that might reduce the worker's ability to self-rescue. Setting the alarms at the point above

which a hazardous atmospheric condition exists may not be adequately conservative. Workers must have enough time to get to a position of safety before conditions become so hazardous that the ability to self-rescue is impaired.

As an example, OSHA specified 10 % of LEL as the concentration above which the atmosphere is deemed to be hazardous. (OSHA 1993) This actually is the maximum allowable concentration at which the alarm can be set in this jurisdiction. OSHA used 5 % of LEL as an action limit in the compliance document. (OSHA 1995)

Possibilities for alarm settings for other gases and vapors are the TWA, STEL, CEILING, AVERAGE, EXCURSION limit or some fraction of these values. The TWA is the most conservative set-point where a STEL or an EXCURSION limit also exists. Setting the set-point at the TWA would ensure that the TWA never would be exceeded during normal work activity provided that the alarm did not sound. The TWA could be exceeded as a result of evacuation during an alarm condition. Setting the alarm level higher could lead to overexposures during work activity because the alarm would not sound until the TWA was exceeded. Setting the alarm to a level below the TWA could lead to needless work stoppages.

Substances with a CEILING designation, or a floor (oxygen, for example) pose a difficult dilemma. Where the concentration changes rapidly as in gas-shielded welding, the alarm condition could develop and clear in less than one minute.

Atmospheric conditions in confined spaces can change rapidly. Conditions can easily go from safe to hazardous in a matter of moments. Datalogged information about normal and abnormal conditions becomes an invaluable resource for understanding what is occurring in the space. This can form the basis for an informed decision about a reasonable alarm setting. Other factors to consider include:

- Distance from the work area to the position of safety
- Rapidity of increase in concentration of contaminant that triggers alarms
- Effects of overexposure

If there is the slightest doubt use a more conservative setting. Use "factory default" settings only if they are appropriate. Finally, be alert to changes in the job or environment that may require changes in monitoring procedures,

CALIBRATION

All instruments require maintenance and calibration. The only way to achieve assured results is to follow the manufacturer's instructions. Regardless of the use of the instrument accuracy must be verified on an on-going basis. This is absolutely important with instruments designed for use in confined spaces, given their use: detection and measurement of potentially life-threatening atmospheric conditions.

The atmospheric conditions that lead to accidents and fatalities during work in confined spaces often provide no sensible warning. The only way to ensure conditions are safe is to use an accurate atmospheric monitor. The only way to know that the readings are accurate is to expose the instrument to known concentration of test gas. This verifies that readings on the display and those that trigger the alarms are correct. Accuracy is very important. Hexane is fully flammable at 1.1 percent by volume. A flammable/combustible alarm set to 10% of LEL must activate when the concentration reaches 0.1 percent by volume. This is a very low concentration from the standpoint of the catalytic hot bead sensors used for this purpose. Toxic gases require action from the instrument at even lower concentrations. In the case of chlorine, the TLV is 0.5 ppm. This is an extremely low concentration to register.

The atmosphere in which the instrument is used can have profound effect on the sensors or detector element. PID windows become degraded or dirty. Electrochemical and hot-bead sensors can be poisoned or suffer degraded performance when exposed to certain substances. The kinds of conditions that affect the accuracy of sensors vary from one type to the next. For example, oxygen sensors can be affected by prolonged exposure to "acid" gases such as carbon dioxide. Some electrochemical toxic sensors actually consume themselves as they function. Catalytic hot bead sensors are affected by exposure to silicones, the tetraethyl lead in "leaded" gasoline, chlorinated solvents, hydrogen sulfide, and high (fully flammable) mixtures.

Calibration verifies that the instrument is accurate. If exposure to test gas indicates a loss of sensitivity, the instrument needs to be adjusted. The important thing to understand is that without challenging the instrument with known concentration of contaminant, there is no way of know whether adjustment is needed. For all of these reasons, the most prudent course of action is to verify the accuracy of instrument by exposure to a known concentration before each day's use.

Calibration should be simple and straight-forward. Calibration usually is a two-step procedure. First the instrument is taken to clean air or exposed to contaminant-free "zero air" from a cylinder. If the readings differ from zero, a "zero" adjustment is required. The second step is to expose the sensor to a known concentration of contaminant. If the readings are the same, the instrument requires no further adjustment. Where a discrepancy exists, the instrument should be "span"-adjusted before further use.

The user should follow the manufacturer's instructions carefully. Incorrect flows produced by an improperly set regulator or improvised fittings can

produce inaccurate readings. Adjustment because of these readings could lead to dangerous incorrect readings.

Bump test

Most manufacturers strongly recommend verifying the calibration of their confined space instruments with a known concentration test gas before use. The "bump" test is very simple and takes only a few seconds to accomplish. Most manufacturers agree that it is not necessary to make a calibration adjustment unless readings are off by more than some percentage of the expected value. While advice may differ between manufacturers, several suggest using $\pm 10\%$ as the criterion for determining whether adjustment is required.

Lengthening the interval between calibration checks

One of the most frequent questions a manufacturer of confined space targeted instruments hears from its customers is whether there are circumstances that would allow lengthening the period between calibration checks. There has never been a consensus among manufacturers about the approach to take to this vexing issue. One of the industry associations to which many gas detection manufacturers belong is the Industrial Safety Equipment Association (ISEA). In May 1996 the ISEA published a protocol to clarify the minimum conditions for lengthening the interval between calibration checks for direct reading portable gas monitors used in confined spaces.

The ISEA protocol begins by clarifying the difference between a functional (bump) test and a full calibration:

- a. A functional (bump) test is defined as a means of verifying calibration by using a known concentration of test gas to demonstrate that an

instrument's response to the test gas is within acceptable limits.

- b. A full calibration is defined as the adjustment of an instrument's response to match a desired value compared to a known concentration of test gas.

The protocol goes on to recommend the frequency for verification, of calibration:

- a. A functional (bump) test or full calibration of direct reading portable gas monitors should be made before each day's use in accordance with the manufacturer's instructions using an appropriate test gas.
- b. Any instrument which fails a functional (bump) test must be adjusted by means of a full calibration procedure before further use.
- c. If environmental conditions which could affect instrument performance are suspected to be present, such as sensor poisons, then verification of calibration should be made on a more frequent basis.

The protocol then goes on to identify the specific minimum circumstance under which the interval between verification checks can be lengthened. If conditions do not permit daily testing of the gas detector to verify calibration, the ISEA protocol permits less frequent verification of calibration only if the following criteria are met:

- a. During a period of initial use of at least 10 days in the intended atmosphere, calibration is verified daily to be sure there is nothing in the atmosphere which is poisoning the sensor(s). The period of initial use must be of sufficient duration to ensure that the sensors are exposed to all conditions which might have an adverse effect on the sensors.

- b. If the tests demonstrate that it is not necessary to make adjustments, then the time interval between checks may be lengthened but should not exceed 30 days.
- c. The history of the instrument since last verification can be determined by assigning one instrument to one worker, or by establishing a user tracking system such as an equipment use log.

The ISEA protocol has been accepted by many confined space instrument manufacturers. The user should verify with the manufacturer that the procedure intended for use is in accordance with instructions from the manufacturer of the specific instrument before commencing a calibration schedule. Remember that any conditions, incidents, experiences, or exposure to contaminants that might adversely affect the calibration should trigger immediate reverification before further use. Most importantly, if there is any doubt about the calibration of the sensors, expose them to a test gas of known concentration before further use.

CONFINED SPACE MONITORING SEQUENCE

Regulatory and other standards on confined space entry require all "permit required" confined space entry procedures to be performed in accordance with a written program centered on the issuance and use of an entry permit. Confined space regulations explicitly define monitoring requirements. The OSHA Standard on confined spaces for general industry requires testing of all permit spaces for oxygen, combustible gas, and any toxic gases potentially present. Testing must occur prior to entry, as well as on a continuing basis until the entry is completed. (OSHA 1993) Besides indicating the kind of hazards for which the space must be tested, the Standard also specifies

the sequence of testing: oxygen, followed by flammable/combustibles, followed by toxic substances. The reason behind this sequence is that flammable/combustible sensors cannot detect in the absence of oxygen. The oxygen concentration should always be noted prior to obtaining readings from a catalytic hot bead sensor.

When testing confined spaces prior to entry, note that two out of three explosions involving confined spaces occur at the time the space is first disturbed. (NIOSH, 1979) This usually is before the entrants have actually entered the space. For this reason the OSHA Standard on general industry stresses not to open or disturb the space should not be opened or disturbed until proven safe to do.

The best means for assessing conditions in an undisturbed space is to use a remote sample kit to obtain an air sample through holes in the lid or hatch of the space. If holes are not available the space should be opened cautiously just enough to obtain a sample. Gases and vapors tend to form vertical density dependent layers in the atmosphere. Gases (such as methane) and vapors that are less dense than air tend to rise and accumulate near the roof of the space. Gases (such as hydrogen sulfide) and vapors that are denser than air tend to sink and accumulate near the lowest point in the space. Once initial readings indicate that work can proceed in safety, additional readings should be obtained for all vertical levels between the entrance and the deepest point in the bottom of the space. Unless all areas of the space are sampled, the existence of a dangerous layer or pocket may not be noted.

Remember that monitoring is only one aspect of confined space entry procedures. Another very important element is use of forced air ventilation. Even if all tests are within allowable limits, the confined space atmosphere should still be purged with a fresh air ventilator blower before entry. 'the atmosphere should be

tested again after the initial purge ventilation. Monitoring and ventilation go hand in hand. The safest course of action is to continuously ventilate and continuously monitor for the entire duration of the entry, Monitoring determines that the atmosphere is safe while ventilation keeps it that way. Confined space monitors are designed to be operated continuously, take advantage of it!

SUMMARY

Instruments and monitoring are central to assessing conditions in confined spaces and maintaining them safe for entry and work activity. Practitioners of today are fortunate to have available a broad range of technologies for pursuing this end.

REFERENCES

American Conference of Governmental Industrial Hygienists: 1997 TLVs and BEIs, Threshold Limit Values for Chemical Substances and Physical Agents, Biological Exposure Indices. Cincinnati, OH 45240-1634: American Conference of Governmental Industrial Hygienists, 1997. 148 pp.

American Industrial Hygiene Association: Manual of Recommended Practice for Combustible Gas Indicators and Portable Direct Reading Hydrocarbon Detectors. Akron, OH 44311: American Industrial Hygiene Association, 1980. 56 pp.

American National Standards Institute (ANSI): Standard No. Z117.1-1995, "Safety requirements for confined spaces." Des Plaines, IL.: ANSI, 1995.

Chambers G, DeVany G, DeVany M C, Henderson R E, Krug T and Weems W. Second Edition, 2001. Confined Space Entry: An AIHA Protocol Guide. American Industrial Hygiene Association: Fairfax, VA.

City Technology Ltd.: Product Data Handbook, Volume I: Safety. Portsmouth, England: City Technology Ltd., 1997.

George, Eric (editor), Boissevain, A. L., Henderson, R. E., Claybaugh, D. J., Massey, C., Morton, J. R., Britain, B. J. and Bethel, B.B.: Corporate Health and Safety: Managing Environmental Issues in the Workplace. Southampton, PA: Ergonomics, Inc., 1996.

Henderson, Robert E., Editor: RAE Systems Handbook of Gas Detection Tubes and Sampling Pumps. RAE Systems Inc., Sunnyvale, California. 2000

Moseley, P. T. and B. C. Tofield: Solid State Gas Sensors. Bristol, England: IOP Publishing Ltd., 1987.

Moseley, P. T., Morris, J. O. W. and Williams, D. E.: Techniques and Mechanisms in Gas Sensing. Bristol, England: IOP Publishing Ltd., 1991.

National Fire Protection Association: NFPA 306: Control of Gas Hazards on Vessels (1993 edition). Quincy, MA 02269-9101: National Fire Protection Association, 1993. 15 pp.

National Fire Protection Association: Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids. Boston, MA.: NFPA, 1977.

National Institute for Occupational Safety and Health: Criteria for a Recommended Standard - Working in Confined Spaces (DHEW/PHS/CDC/NIOSH Pub. No. 80-106). Cincinnati, OH 45228: National Institute for Occupational Safety and Health, 1979. 68 pp.

National Institute for Occupational Safety and Health: Worker Deaths in Confined Spaces (DHHS/PHS/CDC/NIOSH Pub. No. 94-103). Cincinnati, OH 45226-1998: National Institute for Occupational Safety and Health, 1994. 273 pp.

Nyquist, J. E., Wilson, D. L., Norman, L. A., and Gammage, R. B.: Decreased sensitivity of photoionization total organic vapor detectors in the presence of methane. American Industrial Hygiene Association Journal 51(6): 326-330 (1990).

Occupational Safety and Health Administration: Selected Occupational Fatalities Related to Fire and/or Explosion in Confined Work Spaces as Found in OSHA Fatality/Catastrophe Investigations. Washington, D.C. 20210: U.S. Department of Labour, Occupational Safety and Health Administration (U.S. DOL/OSHA), 1982. 76 pp.

Occupational Safety and Health Administration: Selected Occupational Fatalities Related to Toxic and Asphyxiating Atmospheres in Confined Work Spaces as Found in Reports of OSHA Fatality/Catastrophe Investigations. Washington, D.C. 20210: U.S. Department of Labour, Occupational Safety and Health Administration (U.S. DOL/OSHA), 1985. 230 pp.

Occupational Safety and Health Administration: Selected Occupational Fatalities Related to Welding and Cutting as Found in Reports of OSHA Fatality/Catastrophe Investigations. Washington, D.C. 20210: U.S. Department of Labour, Occupational Safety and Health Administration (U.S. DOL/OSHA), 1988. 225 pp.

Occupational Safety and Health Administration: Selected Occupational Fatalities Related to Ship Building and Repairing as Found in Reports of OSHA Fatality/Catastrophe Investigations. Washington, D.C. 20210: U.S. Department of Labour, Occupational Safety and Health Administration (U.S. DOL/OSHA), 1990. 195 pp.

Occupational Safety and Health Administration: "Permit-Required Confined Spaces for General Industry; Final Rule," Federal Register 58: 9 (14 January 1993). pp. 4462-4563.

OSHA: "Air contaminants," Federal Register 54: 36767 (Sept. 5, 1989); 54 FR 41244 (Oct. 6, 1989); 55 FR 3724 (Feb. 5, 1990); 55 FR 12819 (Apr 6, 1990); 55 FR 19259 (May 9, 1990); 55 FR 46950 (Nov. 8, 1990); 57 FR 29204 (July 1, 1992); 57 FR 42388 (Sept. 14, 1992); 58 FR 35340 (June 30, 1993); 61 FR 56746 (Nov. 4, 1996); 62 FR 42018 (August 4, 1997).

OSHA: "Confined and Enclosed Spaces and Other Dangerous Atmospheres in Shipyard Employment; Final Rule," Federal Register 59: 141 (25 July 1994). pp. 37816-37863.

OSHA: Compliance Directive (CPL 2.100) for Confined Space Entry. Washington, D.C. 20210: U.S. Department of Labour, Occupational Safety and Health Administration (U.S. DOL/OSHA), May 5, 1990.

Weast, Robert C.: Handbook of Chemistry and Physics. Cleveland, OH.: CRC Press, 1977.

Workers' Compensation Board: Occupational Health and Safety Regulation, Core Requirements (BC Regulation 296/97). Richmond, BC: Workers' Compensation Board of BC, 1998.

