

THE PID HANDBOOK

Theory and Applications of Direct-Reading
Photoionization Detectors





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**Theory and Applications of Direct-Reading
Photoionization Detectors (PIDs)**

Third Edition

Acknowledgments

We thank the many people who contributed to this book, including RAE Systems' chief technology officer, Dr. Peter Hsi; vice president of marketing and products, Thomas Nègre; and director of product management, Bobby Sheikhan. Additionally, we extend thanks and gratitude to the many contributors without whom this project would have been impossible: Tom Mulhern and James Strohecker.

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Patent Summary

- 2/95 US 5,393,979 "Photo-ionization Detector for Detecting Volatile Organic Gases" — Hsi
- 10/96 US 5,561,344 "Photo-ionization Detector for Detecting Volatile Organic Gases" (continue) — Hsi
- 6/98 US 5,773,833 "Photo-ionization Detector for Volatile Gases Measurement" — Hsi
- 3/99 US 6,313,638 "A Dual Channel Photo-ionization Detector and a Method for Eliminating Influence of Ultraviolet Intensity" — Sun & Hsi
- 6/99 US 6,320,388 Europe pending "Multiple Channel Photo-ionization Detector for Simultaneous and Selective Measurement of Volatile Organic Compound" — Sun & Hsi
- 9/99 US 6,333,632 Europe pending "Alternating Current Discharge Ionization Detector" — Yang & Hsi
- 3/00 US 6,469,303 "Non-dispersive Infrared Gas Sensor" — Sun & Hsi
- 5/01 US 6,225,633 B1 10/98 Europe 1243921 5/01 Japan 4053817 "Photo-ionization Detector and Method for Continuous Operation and Real Time Self-cleaning" — Sun & Hsi
- 1/02 US 6,509,562 9/08 EP1 229 995 B1 Europe "Selective Photo-ionization Detector Using Ion Mobility Spectrometry" — Yang & Hsi
- 6/03 US 6,967,485 "Automatic Drive Adjustment of Ultraviolet Lamps in Photo-Ionization Detectors" — Hsueh, Yeh, Sun & Hsi
- 8/03 US 7,258,773, Europe pending "Solid Polymer Electrolyte Oxygen Sensor" — Zhou, Sun & Hsi
- 12/03 US 6,661,233 B2 "Gas Analyzer with Real-time Broadband Monitoring and Snapshot Selective Detection" — Yang & Hsi
- 5/04 US 6,734,435 B2 "Photo-ionization Detector and Method for Continuous Operation and Real Time self-cleaning" — Hsi & Sun (continuation of US 6,225,633)
- 8/05 US 7,592,603, Europe pending "Combined Radiation Dosimeter and Rate Meter" — Yuzhong June Wang, Peter Hsi

China Patents Granted:

ZL 02280230.4 Photo-ionization detector
ZL 200720067821.2 Concentrator and gas sampling system
ZL 200720066496.8 Heater for the GC column
ZL 200720066495.3 Oxygen sensor
ZL 200630195809.0 Miniature gas sensor
ZL 02256504.3 Combustible gas detector
ZL 02340070.6 External appearance design for combustible gas pipeline valve
ZL 02340069.2 External appearance design for combustible gas detector
ZL200930127413.6 Radioactive Detector Gate
ZL200920246147.3 Radiation safety gate design
ZL200680032878.7 Combined radiation dosimeter and rate meter

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PCT/CN2004/00090 5 200480043755.4 Integrated photo-ionization detector
PCT/CN2006/002609 200680055975.8 VOC detection using photo-ionization detector and method
200710040807.8 Photo-ionization detector used in gas chromatograph and method
200710038443.X PCT/CN2008/070573 Integrated electrolyte gas sensor
200810036757 Formaldehyde sensor
200910045439.5 Hydrogen generator
200810207495.X Material and method to resist organic silicon poisoning in catalytic gas sensor
200810207494.5 Material and method to resist organic silicon and sulfur poisoning in catalytic gas sensor

200910055547 Electrode material, sensor and manufacturing method for sulfur dioxide gas measurement

200910247216.7 Extremely low concentration gas detector

201010131805.1 Components of carbon dioxide detectors

200480029898.X Solid polymer electrolyte oxygen sensor

Disclaimer

The use of trade names or data from a particular manufacturer's instrument is for illustrative purposes only and is not intended to indicate either an endorsement or denegation of that manufacturer's product. When tests were performed with other manufacturer's instruments, all effort was made to operate the units correctly and accurately according to the manufacturer's instructions. However, due to the limited number of experiments, no claim is made that reported results are typical for that model instrument under optimal conditions. Any negative connotations that may have been imparted to any manufacturer's products are unintended and are counter to the spirit in which this book was written.

PREFACE: FROM HUMAN NOSE TO PID

The instrumentation developed to detect chemical contamination is an extension of our human senses. One of these senses, the sense of smell, occurs primarily because chemicals volatilize. This volatilization occurs most readily at room temperature for generally light molecules. These molecules float through the air, and, upon entering nasal passages behind the nose, activate olfactory sensor neurons. The neuron activation occurs as the odorant molecule binds to the neuron's cilia. In order for the odorant to bind and ultimately be recognized, the receiving neuron must have been encoded by a specific gene to recognize a particular chemical structure.

Signals from neurons with the same receptors converge on glomeruli in the olfactory bulb located in the brain. The glomeruli's response then creates a code that is transmitted by nerve fibers to various brain regions. This transmission means that smell is interpreted both from a sensory perspective and as an initiator of memory, emotions, and behavior in the limbic system. These signals also affect the brain's cortex where conscious thought occurs.

Now to the really interesting stuff: Genes also appear to control other types of chemical sensing, such as the ability of sperm to locate an egg. Similar receptors may function in a special structure in the nose called the vomeronasal organ. The vomeronasal organ detects pheromones. These signals may then regulate hormone release, mating, and social functions in animals, including humans. The chemicals responsible for these biological processes are not the typical volatiles!

Over the course of time, these systems have protected us from rotten food, poisons, enemies, animal attack, and other "stinky" humans. Unfortunately, in our modern environment many chemicals never experienced by even our recent ancestors are used. To make matters even more complicated, these chemicals may change over time with exposure to our very dynamic ecosystem, including other contaminants; making their detection more difficult. Thus, instrumentation to detect environmental signals was and is needed, given the limitations of the human sensory system.

In response to the need to detect volatile organics, one of the first instrument components to be developed was an ionization detector. The early instrumentation relied on flame as an energy source to split molecules. The molecular structure was passed through a flame-bearing component and as energy went into the molecule, the molecule separated. The resultant molecules were then attracted to detectors based on their ionization.

Although the flame ionization detector (FID) was very effective, the flame generation via burning hydrogen gas was and is somewhat problematic. The essential problem was the need to acquire and transport compressed hydrogen gas cylinders. For obvious reasons, commercial airline pilots did not give eager environmental scientists permission to bring these cylinders onto their passenger aircraft. Consequently, unless local sources for the compressed hydrogen gas were available, the gas had to be shipped via commercial carrier to the remote sites. This process only worked well when the environmental site was near an airport, and the environmental scientist was adept at logistics.

The photoionization detector (PID) was developed in part to ameliorate the problems with on-site acquisition of flame ionization gases. These PIDs are the most frequently used on-site detection instruments for volatiles at the parts-per-million (ppm) level. Since many environmental sites are of concern due to volatiles – from petroleum products or chemical usage, including spills – the PID is a necessity.

While FIDs and PIDs had parallels in the static laboratory detection devices used, the key was to provide instrumentation that would work effectively on-site in somewhat uncontrolled locations. The reasons for this need were twofold: (1) to determine contaminant levels and (2) to provide a warning system for the workforce and other potentially exposed individuals.

Levels of personal protective equipment (PPE), including respiratory protection, for site workers or any affected humans are determined based on contaminant levels. From this information, appropriate engineering controls, PPE, and site or facility siting are chosen. Chemical information is needed for future documentation purposes on-site and in-area or surrounding environ. The PID continues to be invaluable for this environmental site work both in our exterior site realm and in indoor workplace locations.

However, as our scientific understanding has increased, nagging questions have arisen. Was the ppm detection level sufficient? What about exposure levels for sensitive populations? What about exposures that extended beyond a defined 8-hour workday? These concepts were particularly important since the permissible exposure limits (PELs) defined by OSHA were not chosen to protect workers from any chemical effect. Rather, the PELs are chemical exposure limits that, given an 8-hour workday, would not have a lasting biological effect – as long as a 16-hour recovery period occurred before the next exposure interval.

So, instrumentation that provided lower levels of detection and longer time ranges has been developed. Developments include instruments that can detect volatiles at ppb levels, and instruments that can datalog volatile trends over a 24-hour time interval (or longer). These instruments and their ppb sensors can now be used not just to detect chemical usage and spillage, but also for chemical detection related to biological risks.

Biological activity and the resultant risk associated with microbial activity can be very difficult to quantify. Of course the familiar rotting food, mildew, or sweaty feet types of smells are part of our sensory “database.” However, even these can be invisible to us after olfactory fatigue has occurred. (Olfactory fatigue is a condition in which a person’s nose, after exposure to certain odors, is no longer able to detect the odor.) So, to quantify biological activity, a persistent need has developed for real time sensing instrumentation. By using the microbial volatile organics as markers for biological activity and ultimately biological risk, the hope is that quantification of the risk associated with actively growing bacteria and fungi will be possible for some of these life forms.

Another use for the new PID technology is to predict chemical presence vis-à-vis absorption or adsorption to particulates. Think back to the last time you walked outdoors after a rainstorm. Remember that smell? The moistened air was carrying small particles, including Actinomycetes spores from formerly dry soil, on small invisible water bubbles. When inhaled, these aerosols made their way to your olfactory receptors and your brain interpreted their chemical signature as the earthy, “after-the-rain” smell. Other “after-the-rain smells” you noticed may be from the environmental degradation action of acid rain (an unfortunate side-effect of burning fossil fuels) on chemical substrates,

and the volatile oils newly emitted from plants. All of these chemicals are transferred to you on aerosolized raindrops.

Consequently, the key to many inhalation chemical exposures is the generation of both liquid and particulate aerosols. Thus, the off-gassing of the volatile component present in these aerosols can be predictive of contaminant levels both from the volatile itself and the liquid or particulate substrate. By this definition, the substrate may also include other contaminants including semi-volatile liquids, and gases. As an example, hog farm odor intensity is directly proportional to the amount of dust in the feed lot. So, the detection of airstream volatiles is an indicator not just of the volatile adsorbed to the dust, but that dust in the air is not being adequately controlled.

Fortunately, hog waste odor is one we do sense – at least until olfactory fatigue occurs. The danger is in the volatiles and semi-volatiles carried on these aerosols that we do not smell. Remembering that the “dose makes the poison,” the presence of volatiles adsorbed to particulates is often a more effective dosing vector than just inhaling the volatiles themselves. The particulates “stick” in the body and subsequent off-gassing and dissolution provide a more persistent chemical source than volatile gases that are inhaled and exhaled more readily. These same substrates may also carry semi-volatiles that off-gas at body temperature, radon gas, and biological risk components (spores, bacteria, viruses).

If exposure is occurring in our homes, hospitals, schools, and other facilities where ventilation may not be adequate and our resident time is excessive, given the potential chemical dosing effect, then all of these concerns are compounded. Thus, the PIDs which were the staple instrumentation for outdoor environmental work, have become a first line of alert for indoor environmental contaminant detection.

This book provides information as to how these PIDs function as our much-needed “extra sense.” Given that PID durability and functionality have improved as described herein, this technological transition has made PID usage easier. Calibration stability, internal diagnostic programs, and increased detector efficacy are important advances in PID instrumentation. Just to be able to use higher ionization potentials to cleave the more “difficult” molecular structures without worrying that a lamp will burn out every 30 minutes is a great step forward.

In my practice as a certified industrial hygienist, I rely on quality instrumentation to achieve my goals – to provide information that can be used to protect human life and the environment. The PID technology provided in RAE Systems instrumentation provides one of the reliable means used to determine both chemical and biological risk potential associated with volatiles. This handbook provides an excellent description of how PIDs work. Both PID potential uses and limitations are discussed. My congratulations to RAE Systems for being both scientists and teachers! I believe as an applied scientist, Certified Industrial Hygienist, and former teacher, that knowledge is power. In this case, power to make our environment better and our habitat safer.

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1. INTRODUCTION

This book describes the theory, performance and applications of direct-reading photoionization detectors (PIDs). Photoionization is a well-established detection method developed originally for use with high-performance, laboratory-size gas chromatographs (GCs). Smaller GC/PIDs described as transportable, allow measurements to be performed in the field, but generally still require a fixed power supply and have limited mobility. This book focuses on handheld, direct-reading PIDs that are battery-powered and thus provide complete freedom of movement. Some PIDs that are fixed-mounted or pre-filtered are described. However, systems with high-resolution separation prior to the PID are purposefully excluded. The book is intended to assist the user in the operation and in the interpretation of field measurements for such applications as industrial hygiene, chemical process control, emergency chemical release response, and environmental clean-up. Ultimately, we hope the book will help the industrial, government and public community to provide a safer workplace and a cleaner environment.

PIDs are broad-band sensors that respond to a large variety of organic and some inorganic compounds. The general class of compounds suitable for detection is volatile organic compounds (VOCs). For simplicity, this handbook uses the abbreviation VOC to refer to all the PID-detectable compounds, even though some volatile inorganic compounds and many semi-volatile organic compounds are also detectable, and selected VOCs are not detectable. The measurable concentrations are typically in the range 0.01 to 10,000 ppm (parts per million), while being most accurate in the lower end of that range up to about 2,000 ppm. Competing non-selective organic vapor detectors include portable flame ionization detectors (FIDs), with a range of approximately 0.5 to 50,000 ppm, infrared (IR) analyzers with a range of about 0.02 to 20,000 ppm, metal oxide semiconductors (MOS) with a range of about 1 to 10,000 ppm, and catalytic oxidation bead combustible gas (LEL) sensors, with a range of approximately 200 to 50,000 ppm. PIDs are suitable for use at lower

concentrations than are accessible to catalytic bead sensors, and where small size and ease of use make them preferable to FIDs.

Portable PIDs first came to market in 1974 with the development of the HNU Model 101, designed primarily for testing of soil vapors during environmental clean-up activities. The units were relatively bulky and heavy (e.g., 9 lbs.), and had a separate hand-held probe and a controller carried by a shoulder strap. The readout was by needle deflection, and no datalogging was available. With the advent of microelectronics and batteries with high power densities, modern PIDs are made smaller, lighter, and with sophisticated data processing and storage capabilities. The aid of intelligent power management circuitry reduces power consumption and prolongs battery life or further reduces battery size. Presently, the smallest PIDs containing an internal pump and designed for process control or environmental clean-up include the Photovac 2020, the MiniRAE 2000, the ppbRAE and the PhoCheck. These units weigh under two pounds, are about the size of a telephone handset, and in some cases can store 15,000 data points (or more). Other PIDs on the market have comparable features.

The year 1996 saw the introduction of the ToxiRAE PID, which weighs 7 ounces and is small enough to fit into a shirt pocket. This development accelerated the entry of PID use in the industrial hygiene market, where the multitude of chemicals used in and manufactured by industry are far greater than typically encountered in site remediation. As a result, correction factors for over 250 chemicals have been determined, which allow their measurement using only a single calibration gas, isobutylene. The availability of such a large list of factors has expanded the use of other, larger PIDs as well.

About 6 years ago came the introduction of PIDs capable of detecting low ppb levels of organic compounds with resolutions of 1 to 10 ppb (parts per billion). These instruments have become powerful tools in measuring ambient levels of organic vapors in general indoor air environments, such as offices, not associated with chemical processing. The need for such measurements increases as regulatory agencies begin to include total VOC limits in their indoor air quality guidelines. These measurements present new challenges in zeroing the meter because the typical ppb levels of ambient VOCs can no longer be taken as a zero point. Interpreting results is also more difficult because the identity of the organic vapors is generally unknown and may be variable.

The continuing process of miniaturization and improved PID sensitivity promises the development of a variety of new applications. In 1997 a traditional 4-gas confined space monitor was combined with a miniature PID for the first time, resulting in a VOC/LEL/O₂/CO/H₂S five-gas monitor. Such instruments protect the worker not only from gases immediately dangerous to life, but also from toxic vapors that have long-term health effects. In recent years, several new variants of the multi-gas meter with PID have appeared, some using exchangeable (i.e., disposable) PID sensors.

Another recent advance is the introduction of dual-wavelength PIDs such as 9.9/10.9 eV and 10.6/9.5 eV lamps. Although these have not found wide market favor, they offer the possibility of using multiple wavelengths and being programmed with pattern recognition for compound classification.

With further development one can envision examples of new variations such as lower-cost disposable PID sensors, PIDs embedded into articles of clothing and furniture for personal air-quality monitoring, and PID arrays for highly localized monitoring. Recently emerging applications for ppb level detection beyond Indoor Air Quality testing include: facility perimeter monitoring, detection of drugs and chemical warfare agents, and locating the source of microbially generated VOCs such as from molds in buildings. Many other currently unforeseen applications will certainly become feasible as PID technology continues to advance to smaller sizes, greater reliability, and better sensitivity and selectivity.

RAE Systems PID Related Development History

- 1993: MicroRAE introduced, the world's first personal PID monitor.
- 1994: MiniRAE professional PID introduced and US patent granted. ModuRAE continuous fixed-system PID introduced.
- 1995: ToxiRAE pocket PID introduced, the world's smallest PID.
- 1996: MultiRAE introduced, the world's first multi-sensor gas monitors to include PID.
- 1997: UltraRAE introduced, a substance-specific PID for benzene and other VOCs.
- 1998: RAE Systems awarded ISO 9001 certification. RAE Systems introduces the MiniRAE 2000 handheld PID.
- 1999: ppbRAE introduced, the world's first portable PID with parts-per-billion resolution.
- 2000: AreaRAE introduced, a multi-sensor gas detector with PID and wireless communication systems.
- 2001: MultiRAE IR and MultiRAE IAQ introduced, the world's first multi-sensor instruments to include both PID and CO₂ sensors.
- 2007: MiniRAE 3000, ppbRAE 3000, UltraRAE 3000 introduced, 3rd generation of PID with built-in wireless
- 2011: MultiRAE Family, the world's first wireless portable multi-threat monitors for visibility of chemical and radiation threat data.
- 2011: Complete closed-loop wireless solution for portable gas monitors that includes the EchoView Host Mini-Controller and the ToxiRAE Pro family of single-gas wireless monitors.
- 2012: ProRAE Guardian Real-Time Wireless Safety System that combines gas, radiation, GPS and biometric data in a rapidly deployable, secure wireless threat detection system.
- 2014: QRAE 3 introduced, the world's first 4-gas wireless detector.

2. PID THEORY AND TECHNOLOGY

2.1 Overview

The PID consists of a short-wavelength ultraviolet (UV) lamp shining onto a small cell containing the gas sample. Within the cell is a set of electrodes that have an electrical potential applied. The UV light photoionizes trace organic compounds, but not the air, resulting in electrons being ejected and forming positively charged molecules. The electrons and positive ions are propelled to the electrodes and the resulting current is proportional to the gas or vapor concentration. In general, any compound with ionization energy (IE) lower than that of the lamp photons can be measured.

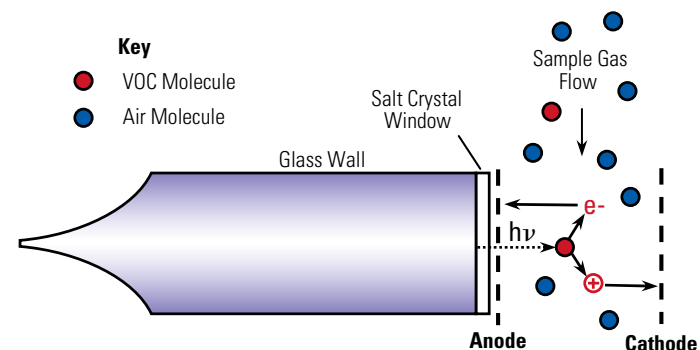


FIGURE 2.1.1. General schematic of a PID sensor

The timescale of these processes are femtoseconds to milliseconds, and therefore they are essentially instantaneous for the purposes of practical industrial hygiene and safety measurements. The response time of PID instruments (typically a few to several seconds) is usually determined by the rate at which the sample is pumped through the detection chamber and flushed completely. Adsorption processes in the instrument inlet system can slow the response time for low-volatility compounds.



CAUTION: Never look directly through the crystal at the discharge of an operating PID lamp without wearing safety glasses, as the UV light can be damaging to the eyes.

2.2 PID Lamp Design

The heart of the PID is a lamp that emits photons in the vacuum-ultraviolet region. The photon energy depends on the type of gas used to fill the lamp, and the crystal used as a transmission window.

Lamp Gases and Crystals

Table 2.2.1 lists the relevant characteristics of common gases and crystals used for PID lamps. Salt crystals are used as windows because common silica glasses do not transmit the low wavelength light required to ionize target VOCs. Inert fill gases tend to give the longest-life lamps and have emission lines at desirable wavelengths. Gas mixtures are sometimes used to ease initial turn-on and optimize output intensity. The fill gas pressure is typically below ambient. The output of the lamp increases as the fill gas pressure increases; however, an optimum value is reached, above which the output decreases. This decrease can be due to (1) the generated photons are self-absorbed by the fill gas before they exit the lamp and (2) the ions collide with other atoms before they are accelerated enough to cause excitation to a photon-emitting state. The latter effect makes the lamp more difficult both to start and to run. Practical constraints on lighting the lamp often limit the internal lamp pressure to levels below those where self-absorption becomes significant.

TABLE 2.2.1. Typical PID lamp gas and crystal characteristics

Nominal Lamp Photon Energies (eV)	Fill gas	Major Emission Lines		Relative Intens.*	Window Crystal	Crystal Transmittance λ Range (nm)**
		(eV)	(nm)			
11.7-11.8	Ar	11.83	104.8	1000	LiF	105 - 5000
		11.62	106.7	500		
10.6	Kr	10.64	116.5	200	MgF ₂	115 - 7000
		10.03	123.6	650		
10.2	H ₂	10.2	121.6	1000	MgF ₂	
		10.2	121.6	500		
9.8-10.0	Kr	10.03	123.6	650	CaF ₂	125 - 8000
9.5-9.6	Xe	9.92	125	250	BaF ₂	135 - 9900
		9.57	129.6	1000		
		8.44	147	600		
9.5	O ₂	9.52	130.2	900	CaF ₂	
		9.5	130.5	600		
		9.49	130.6	300		
8.4	Xe	8.44	147	600	Al ₂ O ₃	145 - 4500
					SiO ₂	145 - 2300

* Relative emission intensity, from CRC Handbook of Chemistry and Physics.

** Wavelength limits for 80% transmittance through a 1 mm-thick crystal.

Wavelength λ calculated as $\lambda(\text{nm}) = 1239.84 / E(\text{eV})$.

In Table 2.2.1, the most common fill gas-crystal combinations are listed opposite each other. However, other combinations are sometimes used, such as the Xe/MgF₂ lamp designated as a 9.6 eV lamp.

The lamp is usually identified by the highest-energy photons it emits. However, this nomenclature is not applied uniformly. Some manufacturers label the Ar/LiF lamp as 11.8 eV, while others call it 11.7 eV. The HNU "10.2 eV" lamp responds to compounds with IE up to 10.5 eV and has quantitatively similar response as other manufacturers' 10.6 eV Kr/MgF₂ lamps. Another supplier identifies the Kr/MgF₂ lamp as a 10.0/10.6 lamp to emphasize that the major emission line is at 10.0 eV but that there is response up to 10.6 eV. The Xe/MgF₂ lamp, designated as a 9.6 eV, would be expected to emit significant amounts of the 9.9 eV line, as can be seen in Table 2.2.1.

PID lamps also emit many other wavelengths at lower energy or lower intensity than the major lines listed. Some of this light is visible as the blue/violet color seen when a lamp is on (which does not have enough energy to ionize most VOCs). In addition, the transmission of the crystal depends on its thickness, initial quality and age. Therefore, it is sometimes possible to obtain a small response from a gas that has an ionization energy higher than the nominal value for the lamp. Conversely, as lamps age, the crystal can gradually become solarized (UV-blocking crystal defects formed by light-induced crystal reorganization), corroded by moisture, or contaminated with deposits. The lamp may no longer be able to ionize some compounds near the upper limit of the nominal lamp output. These processes tend to affect the shorter wavelength limit of the crystal transmission the most, and therefore output near the edge of the transmission are more affected than at longer wavelengths.

Common Lamps

The most common, strongest, and longest-lived lamp is the 10.6 eV lamp, comprising a krypton fill gas and a magnesium fluoride window. These lamps typically have operating lives of at least 10,000 hours, for at least one year of continuous use or a few to several years of intermittent use.

Of the lamps listed in Table 2.2.1, the 11.7/11.8 eV lamp responds to the broadest range of compounds, including many chlorinated aliphatic compounds. The lower-energy lamps, such as 8.4 and 9.8 eV, offer the best selectivity. Thus, for example, a 9.8 eV lamp could be used to measure benzene selectively in the presence of pentane, or CS_2 in the presence of H_2S (see Section 4.5). An 11.7 eV lamp will measure all compounds that a 10.6 or 9.8 eV lamp measures, but not vice versa. The 11.7/11.8 eV lamps tend to have the weakest outputs and shortest lives because (1) the LiF crystal absorbs some of the main emission line, (2) the crystal is more difficult to seal onto the glass lamp housing because of a difference in thermal expansion coefficient, (3) the crystal is more prone to solarization if not highly pure, and (4) the crystal is more susceptible to etching by liquid water due to its higher solubility than other crystals.

Dual-Wavelength Lamps

Recently described are lamps that use a combination of crystals to obtain two photon energies within a single housing. In some cases the lamp is formed using a single discharge zone and attaching two additional crystals as filters on top of the main MgF_2 crystal. In another case, the lamp has two small discharge zones, each filtered by a different crystal, contained inside the main lamp housing and MgF_2 crystal. Examples of the latter include 9.9/10.9 eV and 9.5/10.6 eV dual-wavelength lamps. Such lamps allow the selective measurement of compounds in a mixture, and detection of variations of compound mixture ratios.

UV Lamp Failure Modes

Electrodeless PID lamps do not burn out the same way as incandescent bulb does, because they have no filament inside. Incandescent bulbs fail when the filament suddenly breaks, whereas PID lamps tend to lose power gradually due to gas leaks, crystal solarization, or surface degradation from organic deposits or water etching. Therefore, the strength of a lamp can usually be determined by instrument diagnostics, giving advance notice before a lamp needs replacement.

Electrode discharge lamps can also fail by corrosion of the electrodes and clouding of the lamp window by deposition of electrode metals.

Ionization of Air Components

A fundamental requirement of practical PID lamps used for environmental measurements is that they do not suffer from interference by the ambient atmosphere. Table 2.3.1 lists the ionization energy of the major components of air. Most PID lamps do not have enough photon energy to ionize any of the air components. However, with the 11.7/11.8 eV lamps there is a very slight baseline signal formed by the ionization of oxygen, the lowest IE component of air. Therefore, changes in the matrix gas oxygen levels can have some effect on the response of 11.7 eV lamps, and to a lesser extent for other lamps (see Section 3.2.1).

TABLE 2.3.1. Ionization energies of the major components of air

Gas	Mole Fraction (% by Volume)	Mole Fraction (ppmv)	I.E. (eV)
N ₂	78.084	780,840	15.58
O ₂	20.946	209,460	12.07
Ar	0.934	9,340	15.76
CO ₂	0.033	330	13.78
Ne	0.0018	18.18	21.56
He	0.000524	5.24	24.59
CH ₄	0.0002	2	12.61
Kr	0.000114	1.14	14
H ₂	0.00005	0.5	15.43
N ₂ O	0.00005	0.5	12.89
Xe	0.0000087	0.087	12.13
H ₂ O	0 - 4	0 - 40,000	12.62

2.3 Excitation Methods

Various methods of exciting the gases inside PID lamps are available. The method chosen may affect lamp design and size, mainly reflecting differences in configuration of the excitation electrodes. The UV light source usually is the single most power-hungry element in a portable PID instrument. Therefore, the excitation method strongly impacts the overall size and weight of the instrument.

DC Discharge Excitation

This type of UV lamp is typically made of a sealed glass envelope with two metal electrodes inside or embedded in the envelope, as shown schematically in Figure 2.3.1. Because the excited gas directly contacts the electrodes, a potential for corrosion exists, and therefore the choice of fill gases is more limited.

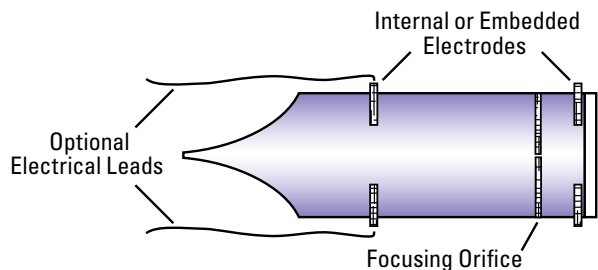


FIGURE 2.3.1. Cross-section view of DC discharge lamp

A high voltage of typically 600 to 1500 V DC is applied between the anode and cathode to initiate a glow discharge inside the lamp. A precision orifice inside the lamp is used to confine the discharge and excite the natural resonance frequencies of the gases. After the initial excitation, the voltage is reduced to about 300 V to sustain the glow discharge. A typical size of this type of UV lamp is about 2" long and 3/4" to 1" in diameter. The power consumption of DC discharge lamps is relatively high, in the range of several watts.

The heat generated by such lamps can result in a significant warm-up time for the instrument to come to thermal equilibrium. Conversely, it can be of benefit to prevent moisture condensation in the sensor cavity and lamp crystal surface.

RF Excitation

This type of UV lamp uses a radio frequency (RF) coil wrapped around the glass envelope to excite the gas (Figure 2.3.2). No metal parts contact the fill gas. The electric or magnetic field RF frequency can be in the range of hundreds of kHz to tens of MHz (14 MHz is typical). The RF coil acts as an antenna, which couples the electromagnetic energy into the gas in the lamp. A typical size for this type of lamp is about 2" long and 0.5" in diameter. The power consumption of RF Excited Lamps is usually in the range of a fraction of a watt to a few watts.

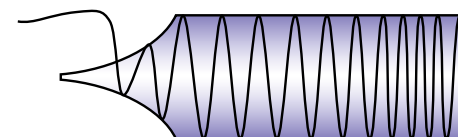


FIGURE 2.3.2. RF excited lamp

A disadvantage of RF excitation is that the antenna radiates radio waves outwardly as well as inwardly, thus potentially causing interference with other instruments or radio communication equipment. In addition, the energy coupling from the RF coil to the lamp is not very efficient unless the driving circuit is perfectly tuned. Therefore, an RF excited UV lamp requires more complex circuitry and constant tuning of the center frequency in order to maintain the coupling efficiency.

AC Electric Field Excitation

AC electric field excitation uses a pair of parallel electrodes placed outside the glass envelope, as shown in Figure 2.3.3. A high-voltage, low-frequency RF signal (<100 kHz) is applied to the electrodes to excite the lamp. Residual ions travel alternately toward each electrode and excite and further ionize the fill gas by cascading collisions. The glow discharge can be operated in a non-continuous fashion (Figure 2.3.4), but with an on-off frequency that is rapid compared to the time constant of gas flow through the ionization chamber. In this fashion, the power consumption of the PID can be reduced without affecting its measurement capability.

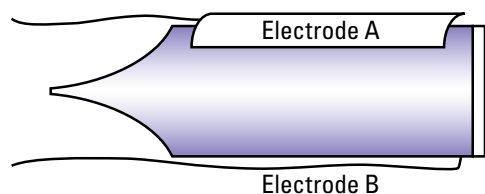


FIGURE 2.3.3. Electric field excited lamp

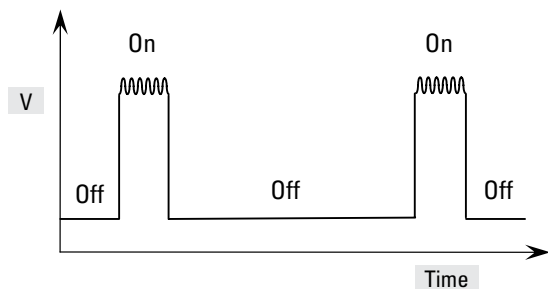


FIGURE 2.3.4. Pulsed RF excitation

Such excitation methods occasionally result in an initial difficulty in turning on the lamp. Therefore, a somewhat higher initial power is used to turn on the lamp, followed by a power reduction during the normal use. Once turned on, lamps appear to retain the ability to turn on easily for several months, presumably by retaining a trace amount of ions, by an unknown mechanism.

Another advantage of this driving method is that the low frequency of <100 kHz is well below that of most of radio communication equipment, thus reducing the possibility of RF interference.

2.4 Ionization Chamber Design

A typical ionization chamber consists of a pair of electrodes inside a small cavity in front of the UV lamp. The ionization chamber is sometimes termed the "sensor," in order to distinguish it from the UV lamp, even though the lamp often forms one wall of the chamber and is an integral part of the PID sensor. A bias voltage of up to a few hundred volts is applied between the two electrodes to collect the ions and electrons. The sensor chamber design can have a significant effect on the sensitivity, linearity, response time, and influence of matrix gas variations. In general, a longer light pathlength in the chamber increases sensitivity, but increases response time and suffers more from non-linearity (Figure 2.4.1) and matrix gas light blockage.

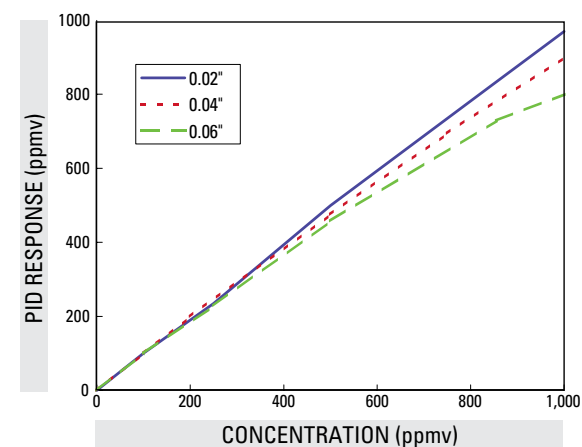


FIGURE 2.4.1. Effect of sensor light pathlength on response linearity

There are basically two different geometries used in the construction of the ionization chamber and the arrangement of the electrodes, using either long or short light path lengths.

Long Path Sensor (e.g., Cylindrical Chamber)

In one example of this design (Figure 2.4.2), the two electrodes are arranged as two concentric cylinders with the lamp shining through their axis. The sample gas flows directly towards the lamp and then exits the sides. This arrangement gives the greatest sensitivity because it provides enough pathlength to absorb and utilize most of the UV light. The larger separation

also makes small sensor manufacturing variations more tolerable, and has less susceptibility to current leakages caused by dust and humidity. However, the relatively large chamber size requires a high bias voltage because the distance between anode and cathode is relatively large. It also causes deviations from linearity at lower analyte concentrations, and suffers more from competitive light absorption by matrix gases.

With the advent of modern microelectronics capable of accurately measuring very low currents, the need to optimize light utilization efficiency has been greatly reduced. Therefore, long path sensors have been largely replaced by smaller, more linear short-path sensors.

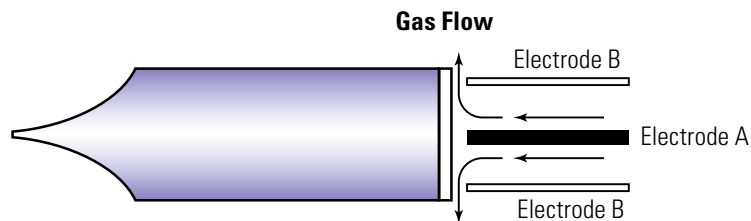


FIGURE 2.4.2. Long path PID sensor scheme

Short Path Sensor (e.g., Parallel Plate Chamber)

In this design (Figure 2.4.3), the chamber is formed by parallel plates (one of which is usually the lamp surface), separated by about 1 mm or less. In order to allow the UV light through, the electrodes are arranged as a set of wire meshes, parallel wires, or interdigital fingers. In the latter two cases the electrodes can be an alternating set of anodes and cathodes, to shorten the ion path and maximize sensitivity. This sensor design allows lower bias voltage and has better linearity and less matrix gas effects than long-path sensors.

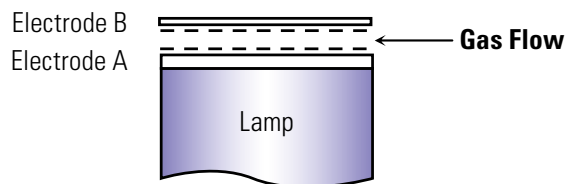


FIGURE 2.4.3. Short path PID sensor scheme

2.5 Overall Instrument Design

Figure 2.5.1 gives a typical overall design for a modern PID instrument. The monitor is powered by either disposable (alkaline) batteries or by rechargeable batteries, such as NiCd, NiMH, or Li-ion. Lead-acid rechargeable batteries are falling out of use because of their lower power densities. The user interacts with the monitor through a keypad, or it can be programmed directly from a computer. A pump draws the gas sample into the sensor and then pumps it out through the side, in some cases allowing sample collection. A liquid crystal display (LCD) or other digital display shows instantaneous readings and other parameters.

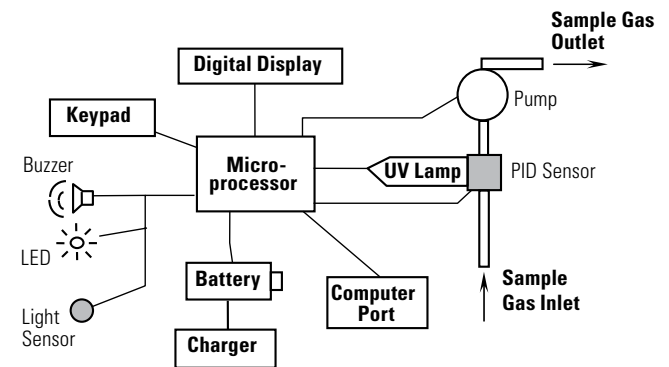


FIGURE 2.5.1. Overall PID instrument schematic

A chip microcomputer measures the PID sensor readings and calculates the gas concentrations based on calibration to known standard gases. The microprocessor is also used to control the operation of the lamp, pump, alarm buzzer, LED, light sensor and data storage. The light sensor controls a backlight, which is turned on in low light conditions for ease of reading. Alarms can often be programmed for both instantaneous concentrations and for cumulative values such as TWA and STEL. Error alarms and messages alert the user to fault conditions and assist in troubleshooting instrument problems.

The data are commonly stored in non-volatile memory with up to 20,000 data point capacity, or up to 2 weeks of continuous monitoring at a 1-minute sample interval. Newer units using memory cards can have much greater storage capacity. Infrared or RS-232 transceivers provide an interface between the monitor and a PC, so that data can be downloaded for record keeping. Figure 2.5.2 gives an example of a modern PID.



FIGURE 2.5.2. MiniRAE 3000 portable PID

2.6 Photoionization Process and Inherent Measurement Efficiency

Photoionization Process

PIDs use light in the vacuum-ultraviolet range to ionize target compounds. Table 2.5.1 illustrates the relation of vacuum-ultraviolet light to the rest of the electromagnetic spectrum.

TABLE 2.6.1. Electromagnetic spectrum*

Descriptive Name	Photon Wavelength	Possible Effects
Gamma Rays	0.0001 – 0.1 nm	Indiscriminant ionization
X-Rays	0.01 – 10 nm	Ionization from inner shell electrons
Vacuum Ultraviolet	10 – 200 nm	Ionization from outer shell electrons
Ultraviolet	200 – 380 nm	High-energy photochemical reactions
Visible	380 – 800 nm	Low-energy photochemical reactions
Infrared	0.8 – 1000 μ m	Heating; increasing rotational, vibrational and translational energies
Microwaves	1 mm – 100 cm	Sound generation; heating

* (Adapted from Smith, 1977)

The photoionization process involves the absorption of a photon by a molecule. At relatively low photon energies, the electrons in the molecule can be raised to an excited state, in which they travel in a new orbit around the nucleus at a greater average distance from it. The excited state quickly relaxes upon collision with another molecule, resulting simply in heating of the gas. However, if the photon energy is high enough, the excited electron can leave the orbit, resulting in a free electron and a positive radical ion:



The energy required to eject an electron is termed the ionization energy (often less correctly referred to as the ionization potential) and it depends strongly on the gas or VOC type. In many cases there is a rather sharp threshold of energy that needs to be exceeded before ionization will take place. However, the reported ionization energy does not always represent a sharp cut-off for the practical onset of ionization for a few reasons.

The ionization energy listed in common databases is the adiabatic ionization energy (Linstrom & Mallard, 2001). The adiabatic IE is defined as the minimum difference between the lowest energy state of the neutral molecule and the lowest energy state of the resulting ion (see Figure 2.6.1). In some cases, the ion initially formed upon absorption of a photon can relax its bond geometry to a lower energy state after forming. Therefore, the ion that is initially formed has higher energy than the lowest ionic energy state. The practical energy required to ionize a molecule is the vertical ionization energy, which is always higher than the adiabatic ionization energy.

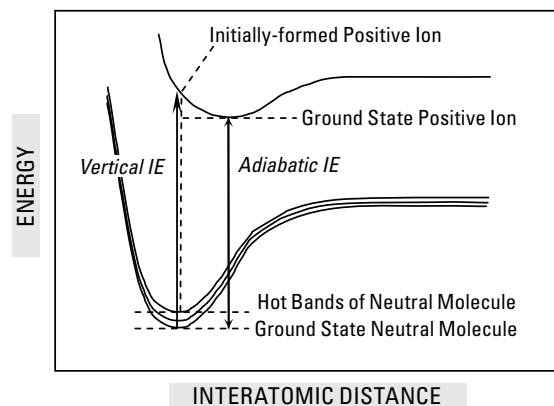


FIGURE 2.6.1. Potential energy between atoms in a molecule as a function of internuclear distance

However, the vertical IE is reduced due to the presence of hot bands. These are a series of energy levels, slightly higher than the ground state, resulting from various rotational and vibrational energy states the molecule can have. The practical energy required for ionization (indicated by the dashed line in Figure 2.6.1) is less than the vertical IE, because the starting point is one of the hotband levels. Because there are several hot band levels, the practical ionization energy is actually a range of energies, rather than a distinct value.

Photoionization in the Adsorbed Phase

Some evidence suggests that the actual photoionization process occurs predominantly when the VOC is adsorbed onto the electrode and that the gas-phase ionization component is minor (Mergemeier et al., 1998). This evidence is based partly on the observation that PID response is proportional to the surface area of the electrodes. However, some of the evidence is

also consistent with purely gas-phase photochemistry, and the relative importance of adsorbed versus gas phase processes may well depend on the concentration of the compound and its affinity for the electrode surface. In any case, simple equations derived for purely gas-phase photochemistry are useful in understanding some practical aspects of photoionization detection, such as the effects of concentration and flow rate.

Lambert-Beer Law of Light Absorption

In both gas and condensed homogeneous phases, the light absorbance is proportional to the concentration of the VOC, in accordance with the Lambert-Beer law:

$$A = \epsilon \ell c$$

$$I = I_0 10^{-A} = I_0 10^{-\epsilon \ell c}$$

Where I_0 is the initial light intensity emitted from the lamp, I is the intensity of light reaching the end the sensor cavity, A is the absorbance in units of length^{-1} , ϵ is the molar extinction coefficient in $\text{concentration}^{-1} \cdot \text{length}^{-1}$, ℓ is the pathlength (sensor cavity depth) in length, and c is the concentration. The *transmittance* T is defined as the fraction of light passing through the solution, and the *fraction absorbed*, f_A , is the complementary fraction of light absorbed by the solution:

$$\text{Transmittance } T = \frac{I}{I_0} = 10^{-\epsilon \ell c}$$

$$\text{Fraction Absorbed } f_A = 1 - T = 1 - 10^{-\epsilon \ell c}$$

This equation is plotted in Figure 2.6.2. It provides useful insights when examined at the two extremes of very low ($f_A \rightarrow 0$) and very high ($f_A \rightarrow \infty$) fractions of absorbed light.

Low Absorbance Approximation

At low total absorbance ($\epsilon \ell c < 0.1$), one may make the mathematical approximation

$$1 - 10^{-\epsilon \ell c} \approx 2.303 \epsilon \ell c$$

Therefore, at low total absorbance, as is usually the case for PID measurements (low concentration and short pathlength), we have:

$$\text{Fraction of Light Absorbed, } f_A = 2.303 \epsilon \ell c$$

Furthermore, at low concentrations, the rate of ion generation and collection is directly proportional to f_A because the chance of interaction with another ion is extremely low. Therefore, the above equation means that the electrical signal intensity is directly proportional to the concentration of the chemical being measured. This low absorbance approximation corresponds to the initial, linear portion of the curve in Figure 2.6.2.

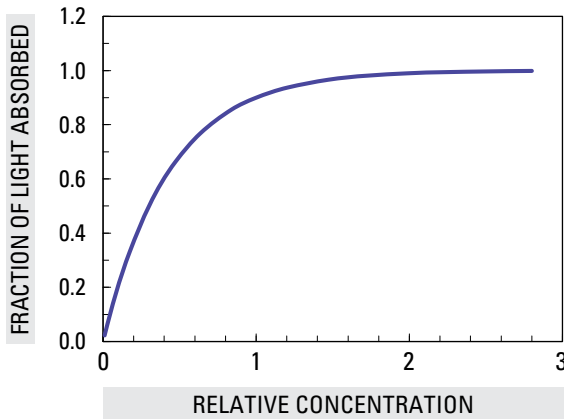


FIGURE 2.6.2. Fraction of light absorbed vs. concentration showing linear response at low concentrations and saturation by total absorbance at very high concentrations

High Concentration Limit

At high concentrations, the signal must reach an upper limit when all of the light is absorbed (Figure 2.6.2):

$$\text{Fraction Absorbed } f_A = 1 - 10^{-\epsilon \ell c} \approx 1$$

In this case, the electrical signal is limited by the light intensity and is independent of both concentration and mass flow rate.

Observed PID Response vs. Concentration

The observed PID response mimics the light absorption equations at low and intermediate concentrations. Figures 2.6.3 and 2.6.4 show that commercial PIDs have linear raw response in the ppb and ppm range, and begin to deviate slightly at approximately 500 to 1000 ppm isobutylene (this raw response is usually linearized electronically – see below). However, at very high

concentrations above about 10,000 ppm, the response actually drops with higher concentrations. This effect is not explained by a limit in ion generation due to complete light absorbance. It must be due to a decrease in the collection efficiency of ions in reaching the detection electrodes after being generated. The next section describes the chemical reactions that can account for such decreased efficiency.

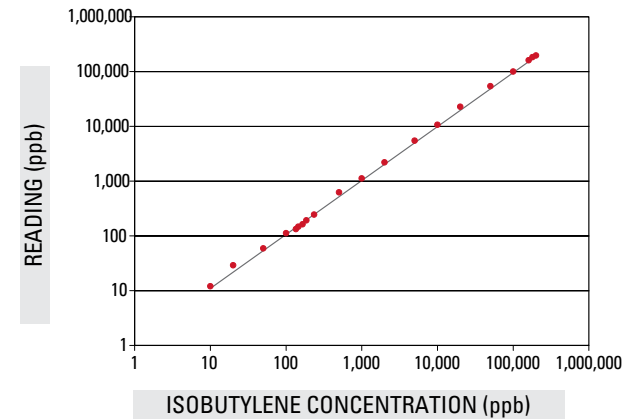


FIGURE 2.6.3. Response of a ppbRAE PID with 10.6 eV lamp as a function of isobutylene concentration in the ppb to middle ppm range

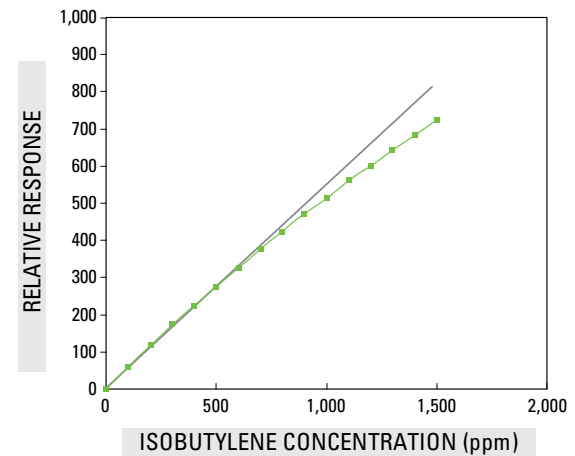


FIGURE 2.6.4. Raw response of a MiniRAE 2000 PID with 10.6 eV lamp as a function of isobutylene concentration in the high ppm range

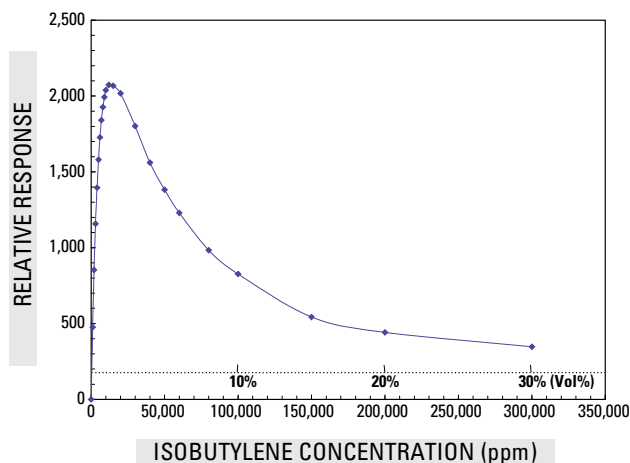
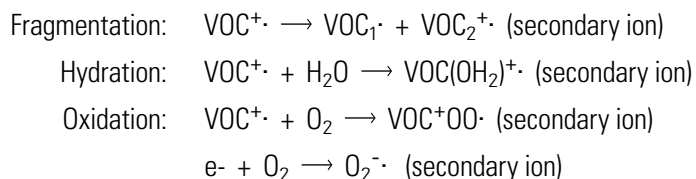


FIGURE 2.6.5. Raw response of a MiniRAE 2000 PID with 10.6 eV lamp as a function of isobutylene concentration in the volume % range

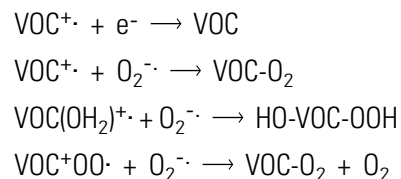
Photo-initiated Radical Reactions in the Sensor Cavity

Following their initial photo-generation, the fate of the resulting electrons and ions depends on various conditions in the sensor cavity. In the presence of oxygen and water vapor, a variety of secondary chemical reactions can occur with the initial ions before reaching the electrodes, such as:

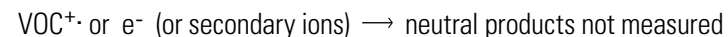
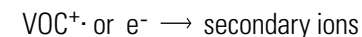
Secondary Ion Formation:



Neutralization:



Many more photochemical processes can take place; the above are examples of some of the most common ones. To summarize, the key processes are:



The time scale of the photon absorption and photoionization processes are on the order of femtoseconds (10^{-15} s) to picoseconds (10^{-12} s), and that of the subsequent ion collection and secondary chemical reactions is on the order of microseconds (10^{-6} s) to milliseconds (10^{-3} s).

At low concentrations of VOC below a few thousand ppm, ion measurement dominates over neutralization, and a significant and constant fraction of the electrons and ions reaches the electrodes and is measured. The formation of secondary ions does not reduce the response significantly because they are measured as well as the initial ions. In this case, response is quite linear, as indicated in Figures 2.6.3 and 2.6.4.

At intermediate concentrations, typically above about 500 to 1000 ppm, response begins to deviate from linearity (see Figure 2.6.4). This occurs partly because of light limitations (Figure 2.6.2) and partly because neutralization reactions begin to compete with ion collection at the electrodes. As shown before, the rate of ion formation is first-order in (directly proportional to) VOC concentration. By contrast, the rate of neutralization reactions increases with the square of the ion concentration because two ions are needed for this process. Therefore, neutralization competes more effectively at high concentrations than at low concentrations because at high concentrations there are more counter-ions present in a local region to neutralize the initial ions before they reach the sensor. In addition, the secondary ions are often heavier and have reduced mobility compared to the initial VOC ions. Therefore they have a greater chance of encountering a neutralizing ion before being detected.

At very high concentrations, the net result of light limitations and neutralizations is that the response drops, as shown in Figure 2.6.5. In this situation the photo-ions are generated at such a high local concentration that neutralization reactions occur before most of the ions can reach the electrodes to be measured. Such a drop in response at high concentrations is inherent, and is also

observed in other photochemical systems wherein the products can recombine to form undetected compounds (see for example, Lichtenthaler et al, 1989).

To summarize, the curvature and drop-off in response of PIDs at high concentrations is a superposition of two factors: a limit in ion generation (light intensity) due to high absorbance, and a reduction in ion collection efficiency due to recombination reactions.

Linearization

Most modern PIDs have built-in curve-fitting algorithms that compensate for the curvature in raw response and give a linear reading in concentration. Such corrections are successful in extending the linear range to at least a few thousand ppm, as shown in Figure 2.6.6. At higher concentrations, compensated readings are subject to increasing error. When the inherent response levels off and then drops, as shown in Figure 2.6.5 at about 10,000 ppm, corrections are difficult or impossible. Measurements at high levels are preferably performed using a dilution system to reduce the VOC concentrations closer to the linear range of the instrument.

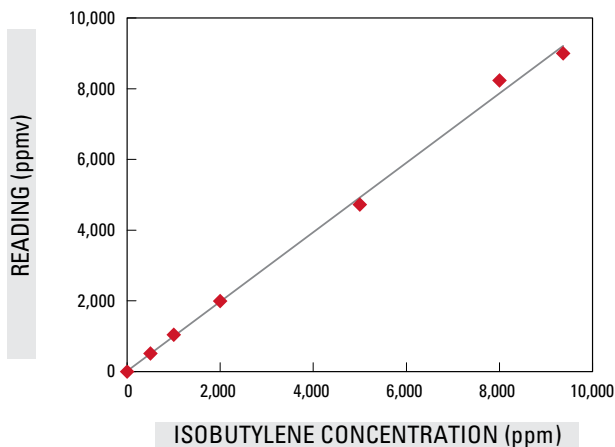


FIGURE 2.6.6. Example of linearized PID response

Photocurrent Efficiency

Certain fractions of the photons and VOC molecules entering the sensor result in ions collected by the electrometer. Photochemical efficiency can be measured from two points of view:

- a) the efficiency of VOC transformation to electrical signal (i.e., what fraction of the VOCs are consumed)
- b) the efficiency of light utilization from the lamp (i.e., what fraction of battery power results in signal) which is further broken down to:
 - i) efficiency of light generation from the power supply
 - ii) efficiency of light conversion to electrical signal from VOCs

Both of these efficiencies depend on the measurement conditions and concentrations and tend to be rather low. In case a, a low efficiency is preferable to avoid deposits and sample loss, as long as enough signal is obtained to achieve the desired sensitivity. In case b, a low efficiency is undesirable but not a great limitation because other power requirements such as the sample pump begin to dominate. The instrument designer is primarily concerned with light generation efficiency (b-i). It affects the detection limit achievable with a given lamp, sensor design and power source. This efficiency is generally below a few percent* and may be limited by the lamp crystal used to transmit the light. The light utilization efficiency (b-ii) depends strongly on the measurement conditions (i.e., analyte concentration and inherent quantum efficiency) and is largely out of the designer's control. It is often exceedingly low, and follows a pattern similar to that in Figure 2.6.5. However, these low efficiencies need not concern the user, as modern electronics allow accurate measurement of ever smaller electrical signals.

On the other hand, the operator may be concerned about the efficiency of VOC destruction (a) if it is desirable to collect a sample of the vapors for further analysis after the PID measurement. Empirical measurements show that the PID detection process is essentially non-destructive. The concentration of organic vapors exiting a PID sensor is essentially the same as that entering. We can estimate a lower limit to the ionization efficiency as follows:

At a flow rate of 0.5 L/min, a typical PID results in a photocurrent on the order of 40 pA/ppm of VOC at low VOC concentrations. From these data one can calculate that at 1 ppm the VOC amount passing through the sensor is 3×10^{-10} mol VOC/s and the photocurrent is 4×10^{-16} mol electrons/s, or 1.2×10^{-6} mol electrons/mol VOC. Thus, on the order of 0.0001% of the total VOC passing through the sensor results in a measureable photocurrent. It is possible that many more photoions are generated, but that they are simply not collected

efficiently at the electrodes. Uncollected photoions could re-neutralize or react before reaching the sensor. However, the empirical observation that the VOC concentration is essentially unchanged is in agreement with the calculation that an extremely small fraction of the VOC molecules are actually ionized. VOC^+ ions collected at the electrode may be reduced to regenerate the starting VOC. However, such regeneration is not the main reason PIDs are considered non-destructive; the reason is that only a very small fraction of VOC molecules are ionized and reach the sensor to begin with.

Sample Collection

Because of the low transformation extent in the sensor, it is often possible to collect a sample at the outlet of the instrument, such as on an activated carbon tube or in a Tedlar gas bag, for use in subsequent laboratory analysis. The ability to do this depends more on possible losses through adsorption in the sampling pump and connecting tubing than on losses due to the photoionization measurement process. For example, multi-gas instruments are more likely to have losses occurring on other sensors or in the more complex flow path. The ability to collect a sample without loss is particularly useful for making empirical correlations between PID readings and laboratory measurements, because the same sample measured by the PID can be submitted for analysis.

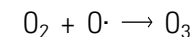
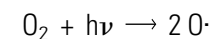
Photoproducts

From the inherent nature of the PID measurement process it is clear that photoreactions must occur in the sensor chamber in order for the desired response to be obtained. For the vast majority of cases under typical operating parameters for portable PIDs, these transformations are very minor compared to the total VOC concentration. However, in certain instances the photoproducts of these minor transformations are significant for various reasons.

First, some photoproducts can accumulate on the lamp and sensor. This can occur because photo-oxidation reactions tend to convert non-polar, volatile compounds to more-polar, less volatile photoproducts. A notable example of this is in the PID measurement of phosphine, where even tens of ppm of PH_3 can cause a reduced response in a matter of minutes. This effect is believed to be due to the photooxidation of PH_3 to phosphoric acid or polyphosphates, resulting

in a film build-up on the lamp. Further evidence with other photoionization sources lacking a lamp crystal indicates that build-up of photoproducts on the sensor electrodes also can be responsible for a loss of sensitivity. Similar effects have been observed with H_2S and methyl bromide, although to a far lesser extent and only at concentrations above a few thousand ppm.

Second, PID lamps produce some ozone from the air at ppb levels by the reactions:



As long as the pump is flowing air at typical flow rates of a few hundred cc/min, the ozone concentration remains low and generally has no significant effects. But if the lamp is on while the flow is off, ozone can accumulate and have secondary effects such as gradual damage to internal rubber or plastic components. At very low flows, several ppm of ozone may be present, which could react with some organics collected in a sample bag. However, gas-phase ozone reactions tend to be slow, and ozone decomposes catalytically on many surfaces. Therefore, the effect of such ozone can be important only when the organic vapor concentrations collected are in the low ppm range or less.

Effect of Flow Rate

PID measurements are observed to be essentially independent of flow rate, as reported by Freedman (1980) and confirmed in our laboratory and others. This result is in accord with adherence to the Lambert-Beer law of light absorption, which states that at low light intensities, the fraction of light absorbed by a fluid mixture is proportional to the concentration of the absorbing substances (not on mass flow). The concentration of substances does not change in the sensor chamber because (a) only a negligible fraction is converted to other substances and (b) the light intensities are far too low to keep a significant fraction of the substances in an excited state. The latter occurs because the speed of light and the rates of photophysical excitation and deactivation are so much more rapid than the rate of photon generation from the lamp. Therefore, a greater fraction of light cannot be absorbed by flowing more material through the cell, because the concentration is essentially the same whether the gas is flowing or standing still. By contrast, response on an FID can be flow-dependent under typical conditions where all the analyte is consumed in the sensor.

Higher flow rate can give stronger or faster response for compounds that have low vapor pressure and thus are prone to adsorption losses in the inlet probe, filters, or sensor components. This is because the adsorption sites are more quickly saturated at higher mass flows. Some filters cause significant flow reductions, and therefore for adsorbing compounds removing filters increases response rate because of both higher flow rate and less available surface for adsorption.

2.7 Linear Additivity of PID Response

At the low concentrations typical for PID measurements (ppm range), it is expected that analyte substances in a mixture will chemically behave independently. In this case, the response for all the components of a mixture should be linearly additive. Figure 2.7.1 shows the response of several mixtures of benzene, isobutylene, and H₂S, compared to the total reading predicted from the sum of the components when measured individually. In each case, the calculated and measured responses agreed within <10%, even when the benzene varied from 0 to >50% of the total response. Such tests indicate that the total response of a defined mixture can be predicted from each compound's contribution, without the need to measure responses to each type of mixture. These results are in agreement with the findings of Lee, et al. 1987. Conversely, if the total response and the ratio of components are known, this result allows back-calculation of the concentration of each component.

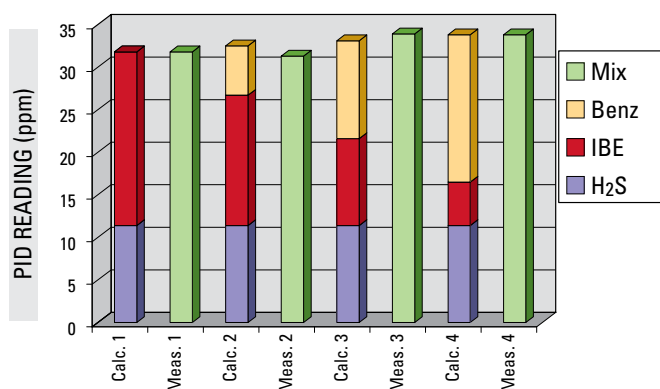


FIGURE 2.7.1. Additivity of PID response in mixtures

3. PID MEASUREMENT PARAMETERS

This chapter describes the many factors that affect the measurement and interpretation of continuous PID readings. In general, any compound with ionization energy (IE) lower than that of the lamp photons can be measured. As shown in Figure 3.0.1, the compound correction factor (CF, see definition in Section 3.1.2), which is inverse to response, increases to infinity as the upper limit of the lamp output is reached.

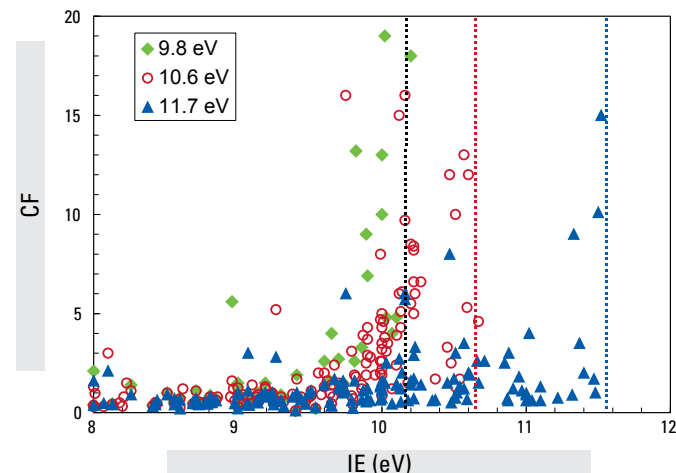


FIGURE 3.0.1. PID correction factor vs. compound ionization energy for various lamps

Compounds with IE <11.7 eV are measurable by PID, and those with lower IE are generally more sensitive (have low CFs). The response depends predominantly on the gas and crystal type; form factors such as size and shape play only a very minor role, if at all. Different manufacturers of the same type of lamp tend to have very similar correction factors, although this should not be assumed, and factors should be obtained directly from the instrument supplier.

Table 3.0.1 below lists the most-sensitive compound classes, and Appendix 3 is an extensive list of CFs for over 300 individual compounds.

TABLE 3.0.1. Approximate response of compound classes by PID

Compound Class	Relative Sensitivity
Aromatics including Heterocycles	++++
Olefins	+++
Sulfides & Mercaptans	+++
Organic Amines	+++
Ketones	+++
Ethers	+++
Silicate Esters	+++
Organic Esters	++
Alcohols	++
Aldehydes	++
Alkanes	++
Alkyl halides	
Iodides	++++
Bromides	+++
Chlorides	+
Fluorides	-
Borate & Phosphate Esters	++
H ₂ S, NH ₃ & PH ₃	+ to ++
Organic Acids	+
Noble Gases, H ₂ , CO, CO ₂ , O ₂ , N ₂ , HCN, SO ₂ & O ₃	-
Mineral Acids	-

++++ = most sensitive, + = least sensitive, - = non-detectable

Aromatics, olefins, ketones, ethers, amines, and organic sulfides are among the most sensitive commonly encountered compounds. Substituents on the aromatic ring affect the sensitivity only marginally, and many aromatics have a CF in the range 0.5±0.2. Also notable are poly-olefins such as terpenes (turpentine), multifunctional compounds such as hexamethyldisilazane, and iodine compounds. The most sensitive compound known to the author is elemental iodine (I₂), having a CF of 0.1 with 9.8, 10.6 and 11.7 eV lamps. It is a common misconception that halogenated compounds are not detected or poorly detected by PID. Fluorine substitution does reduce response, but chlorine, bromine and iodide substitution increase response. For example, chloroethane is about 14 times more sensitive than ethane itself using an

11.7 eV lamp. In other cases, a strong response is imparted to chlorinated compounds by the other functional groups, such as the double bond in perchloroethylene (CF = 0.57 @ 10.6 eV) and the aromatic nucleus in chlorobenzene (CF = 0.40 @ 10.6 eV).

Alkanes give a response that increases with chain length. Methane is not detectable with any lamp; ethane, propane and butane require an 11.7/11.8 eV lamp; and higher alkanes respond with lower CFs and lower-energy lamps as the number of carbons increases. Thus, for example, long-chain aldehydes and acids gain their sensitivity from the alkyl group rather than the functional group.

So far it has not been possible to predict correction factors from the ionization energies. For example, trans-1,2-dichloroethene (CF = 0.45 @ 10.6 eV) and decane (CF = 1.4 @ 10.6 eV) have an identical IE of 9.65 eV, yet trans-1,2-dichloroethene is 3 times more sensitive. Within a series of similar compounds with the same functional groups, such as linear alkanes (i.e., pentane, hexane, heptane, octane, and decane), it is possible to obtain a rough correlation with chain length. Simple ketones such as acetone (CF = 1.1 @ 10.6 eV), methyl ethyl ketone (CF = 0.9 @ 10.6 eV), and methyl isobutyl ketone (CF = 0.8 @ 10.6 eV) have very similar CFs. Nearly all simple benzene derivatives have a CF of 0.5±0.2. However, for many types of compounds not enough accurate data are available, either on ionization energies or on CFs for similar compounds, to make useful correlations. Therefore, when CFs are needed for new compounds they must be measured.

3.1 Calibration and Correction Factors

Most PID manufacturers recommend that instruments used for industrial hygiene measurements be calibrated each day of use. This recommendation is similar to that of the International Safety Equipment Association (ISEA) recommendation for combustible gas/ O₂/CO/H₂S monitors used for confined space entry (see Section 3.1.1). While ISEA makes no such recommendation for PIDs, the document for confined space monitors is a useful guide. The frequency of calibration can be extended based on experience in the field, but typically the interval should not be longer than 30 days.

In general, PIDs hold their calibrations for days to weeks. Various factors can cause changes in response, including lamp degradation, coating of the lamp with dust and chemicals, temperature, pressure, and matrix gases, including

humidity (see details in subsequent chapters). Different lamps have different inherent lifetimes, as noted in Chapter 2.2. For example, an 11.7 eV lamp may require daily calibration even under clean use conditions, whereas a 10.6 eV lamp may run for weeks without needing recalibration.

Lamp Self-Cleaning

Some newer PIDs offer a built-in self cleaning algorithm that turns the lamp on with the pump off during charging, or alternately turns the pump off and on during the measurements while the lamp remains on. During the pump-off periods, the lamp and sensor are cleaned by the accumulated ozone and associated photooxidation processes. Such lamp cleaning maintains the calibration and can reduce the required frequency to months (see Chapter 4 for more details).

3.1.1 ISEA Statement on Calibration for Direct Reading Portable Gas Monitors Used in Confined Spaces

1. A position statement on verification of calibration is needed to:
 - Reemphasize to OSHA and other standards writing bodies the importance of verifying the calibration of instruments used to monitor the atmosphere in potentially hazardous locations.
 - Clarify the differences between a full calibration and a functional (bump) test.
 - Clarify when daily tests are needed and when less frequent tests may be appropriate.
2. Definition of two methods of verifying calibration:
 - Functional (bump) test - 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.
 - Full calibration - The adjustment of an instrument's response to match a desired value compared to a known concentration of test gas.
3. Recommended frequency of verification of calibration:
 - 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.

- Any instrument which fails a functional (bump) test must be adjusted by means of a full calibration procedure before further use.

Note: 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.

4. If conditions do not permit daily testing to verify calibration, less frequent verification may be appropriate if the following criteria are met:
 - 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.
 - 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.
 - 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.

3.1.2 Calibration Gas Selection

The most accurate way to calibrate a PID is to use a standard gas prepared with the compound of interest, at a concentration near the expected measurement range. Isobutylene (IBE) is by far the most common calibration gas because it is inexpensive, readily available, has intermediate sensitivity, and has very low toxicity. Some manufacturers recommend benzene as a reference calibration gas, but use of benzene is decreasing because its relatively high toxicity has become recognized in recent years. Use of correction factors to adjust the scale to the compound of interest is possible. However, direct calibration with the measurement gas is always more accurate because the correction factors can vary slightly from instrument to instrument and with different use conditions such as temperature, humidity and concentration.

The calibration concentration is preferably close to the expected measurement concentration. In principle, if the instrument is perfectly zeroed and the response is perfectly linear, then any calibration concentration could be used. For practical purposes this is true for isobutylene calibration typically in the

range 100 - 2000 ppm for many PIDs. For measurements in the low ppm range, calibration at 100 ppm usually gives good precision because the response is quite linear at low concentrations. For sub-ppm measurements (10-1000 ppb), it is preferable to use a span value in the low ppm range, which is somewhat higher than the measurement range. This is because contaminants in the matrix gas begin to cause larger errors in both the zero and span gas concentrations. It is often difficult to obtain a calibration gas standard at 1 ppm certified to better than 20% accuracy.

For measurements in the 2000 - 10,000 ppm range, it is increasingly important to match the span concentration to the measurement concentration, because of the inherent non-linearity of the measurement, and thus greater variability even after firmware linearizations. Linearity may be good for isobutylene, but different for other gases, and thus the linearization scheme may under- or over- compensate the response curvature. In such cases, it may be helpful to dilute the sample gas into a more linear range. Most PID manufacturers offer a dilution probe or fitting for this purpose. Sample dilution has the additional benefit that it can modify (e.g., dry) the matrix gas, resulting in fewer matrix effect corrections and lower maintenance (e.g., lamp and sensor cleanings).

3.1.3 Calibrations with Isobutylene (IBE)



CAUTION: It is important to understand that calibrating a PID to a specific gas does not make the instrument selective to that gas. A PID always responds to all the gases that the lamp can ionize, and gives the readout in equivalent units of the calibration gas.

Correction factors have been determined that enable the user to quantify a large number of chemicals using only a single calibration gas, typically isobutylene (IBE). When the instrument is calibrated with IBE, there is no need to recalibrate it when other compounds are to be measured. Rather, a correction factor (CF) can be applied to have the PID read out in units of the new compound.

The CF is the ratio of the response to isobutylene over the response to a particular compound. Practically, it is defined as:

$$CF = CF_{VOC}^{IBE} = \frac{\text{True VOC Concentration}}{\text{PID Reading}}$$

Once the CF has been established, the true concentration can be obtained by multiplying the reading by the CF:

$$\text{True VOC Concentration} = CF_{VOC}^{IBE} \times \text{PID Reading}$$

Correction factors are inverse to sensitivity. Compounds with CF greater than 1.0 are less sensitive than isobutylene, and those with CF less than 1.0 are more sensitive than isobutylene.

CF Measurement

To measure the CF, take separate, equal concentrations of the calibration gas and the measurement gas, and measure the responses (R). Then:

$$CF_{\text{meas gas}}^{\text{cal gas}} = \frac{R_{(\text{cal gas})}}{R_{(\text{meas gas})}}$$

For example, on a PID 100 ppm isobutylene reads 98, and 100 ppm benzene reads 185. The CF = 98/185 = 0.53.

If the isobutylene concentration is different than the test gas concentration during CF determination:

$$\text{Isobutylene based CF for benzene} = CF_{\text{benz}}^{IBE} = \frac{R_{IBE}}{C_{IBE}} \times \frac{C_{\text{benz}}}{R_{\text{benz}}}$$

For example, on a PID 100 ppm isobutylene reads 96 and 50 ppm benzene reads 91, the CF = (96 x 50)/(100 x 91) = 0.53.

CF Application

Further measurements no longer require the isobutylene check. For example, a reading of 23 in benzene-laden air would correspond to:

$$23 \text{ ppm}_{(\text{isobutylene equivalents})} \times 0.53_{(CF)} = 12 \text{ ppm}_{(\text{benzene})}$$

Many instruments now allow the user to call up and apply the CF from an on-board library. Thus, the instrument would be calibrated with isobutylene but read directly in units of benzene or other desired compounds. Note that this factor does not make the monitor selective for a particular compound; it still responds to all detectable compounds, but quantitates them on a different scale.

3.1.4 Converting CFs to Other Calibration Compounds

CFs are always relative to the calibration gas. To estimate CFs for other calibration gases, simply divide the isobutylene CF for the measurement compound by the CF for the new calibration compound. Thus, a new scale of calibration factors can be determined for any compound with known isobutylene CF.

$$\text{Isobutylene based CF for hexane} = CF_{\text{hex}}^{\text{IBE}} = \frac{R_{\text{IBE}}}{C_{\text{IBE}}} \times \frac{C_{\text{hex}}}{R_{\text{hex}}}$$

Where R_{IBE} = Response to isobutylene at a concentration C_{IBE}

R_{hex} = Response to n-hexane at a concentration C_{hex}

$CF_{\text{hex}}^{\text{IBE}}$ = CF for hexane calibrated to Isobutylene

At equal concentrations of hexane and isobutylene (tested separately), this equation reduces to:

$$\text{Isobutylene based CF for hexane} = CF_{\text{hex}}^{\text{IBE}} = \frac{R_{\text{IBE}}}{R_{\text{hex}}} (= 4.3)$$

$$\text{Likewise, the isobutylene based CF for toluene} = CF_{\text{tol}}^{\text{IBE}} = \frac{R_{\text{IBE}}}{R_{\text{tol}}} (= 0.5)$$

By analogy, the toluene-based CF for hexane is:

$$CF_{\text{hex}}^{\text{tol}} = \frac{R_{\text{tol}}}{R_{\text{hex}}} = \frac{R_{\text{IBE}}}{R_{\text{hex}}} \times \frac{R_{\text{tol}}}{R_{\text{IBE}}} = \frac{CF_{\text{hex}}^{\text{IBE}}}{CF_{\text{tol}}^{\text{IBE}}} = \frac{4.3}{0.5} = 8.6$$

Where R_{tol} = Response to toluene at a concentration C_{tol}

$CF_{\text{tol}}^{\text{IBE}}$ = CF for toluene calibrated to isobutylene

$CF_{\text{hex}}^{\text{tol}}$ = CF for hexane calibrated to toluene

Thus, all the CF values from Appendix 3 can be converted to a toluene scale (toluene calibration) by dividing the 10.6 eV lamp values by 0.5 (multiplying by 2). Or, they could all be converted to a hexane scale by dividing the 10.6 eV lamp values by 4.3.

In some instruments where CFs are built into the firmware, all the user needs to do is call up the calibration gas and the measurement gas. Then the instrument will calculate the modified factors for the non-isobutylene calibration gas and apply them to the readings.

3.1.5 Conversion of ppmv Readings to Other Units (mg/m³)

PIDs typically give a response in units of ppmv, or parts per million by volume, as opposed to ppmw or parts per million by weight. In this manual the term ppm is taken to be synonymous with ppmv. Because dilute gas samples follow the ideal gas law closely, ppmv is equivalent to ppm by mole.

More precisely, portable PIDs typically give a response in the same units as the calibration gas supplied. The most common calibration gas is 100 ppm isobutylene, which is manufactured as 100 ppmv. However, the monitor is usually insensitive to the concentration units; therefore if the gas standard concentration is defined in other units, such as mg/m³, then the response will be in mg/m³ equivalents of the calibration gas. Likewise if the standard gas is supplied in %LEL or lbs./MMCF (lbs./million cubic feet), then the PID response will be in %LEL or lbs./MMCF equivalents, respectively, of the calibration gas.

Appendix 9 gives a table of conversion factors between different gas phase concentration units. Additional tables are provided in Appendix 9 to correct the conversion factors for various temperatures and pressures. The conversion between ppmv and mg/m³ requires the compound molecular weight (m.w.) and, at room temperature 25°C (77°F) and sea-level atmospheric pressure, reduces to:

$$\text{Conc. (ppmv)} = \frac{24.46 \times \text{Conc. (mg/m}^3\text{)}}{\text{m.w. (g/mol)}}$$

$$\text{Conc. (mg/m}^3\text{)} = 0.041 \times \text{Conc. (ppmv)} \times \text{m.w. (g/mol)}$$

Example 1: Conversion from Compound ppmv to mg/m³

Convert 46 ppmv of ethyl acetate (m.w. = 88.1) and 100 ppm IBE (m.w. = 56.1) to mg/m³ at room temperature and atmospheric pressure:

$$\text{Conc. (mg/m}^3\text{)} = 0.041 \times 46 \text{ ppmv} \times 88.1 \text{ g/mol} = 166 \text{ mg/m}^3$$

$$\text{Conc. (mg/m}^3\text{)} = 0.041 \times 100 \text{ ppmv} \times 56.1 \text{ g/mol} = 230 \text{ mg/m}^3$$

Example 2: Calibration with a Standard Directly in mg/m³

A PID is calibrated using a cylinder of 100 ppmv IBE, but the span value is set to 230 (mg/m³). The unit then reads directly in mg/m³ of isobutylene.



CAUTION: When calibrating a PID in mg/m³ units, one cannot use the CFs in Appendix 3 for converting to mg/m³ units of another gas, because Appendix 3 applies only to ppmv to ppmv conversions. It is necessary to convert the readings from mg/m³ IBE back to ppmv before the CFs from Appendix 3 can be applied, and then reconvert the ppmv value of the new compound to mg/m³.

To make the unit display in mg/m³ of another compound, either calibrate directly with that compound, setting the span value to its mg/m³ concentration, or calibrate with isobutylene and use the procedure in Example 3.

Example 3: Conversion from Isobutylene Equivalent to mg/m³

A PID with 10.6 eV lamp is calibrated to isobutylene (IBE) in ppmv and reads 10 ppmv on a sample of ethyl acetate. According to Appendix 3, the correction factor for ethyl acetate is 4.6. Therefore, the true concentration is 10 x 4.6 = 46 ppmv of ethyl acetate. From the Example 1 above, 46 ppmv equals 166 mg/m³.

An overall correction factor can be calculated to convert directly from IBE equivalent ppmv to compound mg/m³:

$$\text{Conc. (mg/m}^3\text{)} = 0.041 \times \text{IBE equiv. (ppmv)} \times \text{CF} \times \text{m.w. (g/mol)}$$

$$\begin{aligned} \text{Conc. (mg/m}^3\text{)} &= \{0.041 \times \text{CF} \times \text{m.w. (g/mol)}\} \times \text{IBE equiv. (ppmv)} \\ &= \text{CF}^* \times \text{IBE equiv. (ppmv)} \end{aligned}$$

$$\text{CF}^* = 0.041 \times \text{CF} \times \text{m.w. (g/mol)}$$

In this example, the new CF* value is 0.041 x 4.6 x 88.1 = 16.6. Therefore, the 10 ppm reading equals 10 x 16.6 = 166 mg/m³. This new CF* can often be programmed into the PID to allow direct reading of ethyl acetate mg/m³ after calibration to a ppmv standard isobutylene.

Example 4: Conversion from Isobutylene Equivalent to mgC/m³

First convert the IBE equivalent ppmv readings to true ppmv of the compound. Then convert ppmv to mg/m³ as in Examples 1 and 3. Finally, multiply by the weight fraction of carbon in the compound. For ethyl acetate the four carbons make up a molecular weight fraction of 48/88.1 = 54%. Thus, the 166 mg/m³ in Example 3 correspond to 0.54 x 166 = 90.4 mgC/m³.

Example 5: Conversion from Isobutylene Equivalent to mg/m³ and mgC/m³ for Compound Mixtures

In the case of compound mixtures, first convert the mixture response to ppmv of each individual component, as described in the Section 3.1.6. Then convert each individual component to mg/m³ by multiplying by the molecular weight and dividing by the gas molar volume as in Example 1. Then add all the mg/m³ values to obtain total concentration in mg/m³.

Given a PID reading of 100 ppmv isobutylene equivalents on a mixture comprised of 5% benzene and 95% n-hexane, calculate the total concentration in mg/m³ as follows. The CF for this mixture is 3.2, as described in Example 1 of Section 3.1.6. The total VOC concentration is thus 100 x 3.2 = 320 ppmv, consisting of 16 ppmv benzene and 304 ppm hexane.

$$\text{Benzene m.w.} = 78.1 \text{ g/mol or } 72.1 \text{ gC/mol}$$

$$0.041 \times 16 \text{ ppmv} \times 78.1 \text{ g/mol} = 51 \text{ mg/m}^3$$

$$\text{Hexane m.w.} = 86.2 \text{ g/mol or } 72.1 \text{ gC/mol}$$

$$0.041 \times 304 \text{ ppmv} \times 86.2 \text{ g/mol} = 1074 \text{ mg/m}^3$$

TABLE 3.1.1. Conversion from ppmv to mg/m³ for mixtures

Compound	ppmv	mg/m ³	mgC/m ³
Benzene	16	51	47
Hexane	304	1074	899
Total	320	1125	946

Thus, after calibration to isobutylene, a response of 100 ppmv on the PID corresponds to 320 ppmv, 1125 mg/m³, and 946 mgC/m³ of the mixture.

Unknown Compound Mixtures

For unknown compound mixtures, it is not possible to convert rigorously to ppmv, mg/m³ or mgC/m³. In such cases, average or estimated molecular weights and carbon mole fractions may prove useful. However, it is incorrect to use the molecular weight and carbon mole fraction of the calibration gas (e.g., isobutylene) for these conversions.

3.1.6 Measurement of Vapor Mixtures

Because the PID is a non-specific measurement technique, mixtures of compounds give a weighted total response of all detectable compounds. Usually it is desirable to know the concentration of each individual compound, or at least the most toxic one. Numerous examples exist, such as benzene in gasoline, butadiene in the presence of solvents used in rubber and plastics manufacture, formaldehyde in paint solvents, and CS₂ in the presence of H₂S during plastics manufacturing.

1. GENERAL CONSIDERATIONS FOR MIXTURES

Human Exposure Limits for Mixtures

According to the ACGIH (1997), exposure effects are, to a first approximation, taken to be the sum of the effects of the individual components. Exceptions occur where individual components act in separate organs and effects are less than additive, or when they act synergistically, and effects are more than additive. Making the assumption of additivity allows the calculation of TWAs for mixtures, and thus the recommended alarm limit setpoints for a PID.

Calculated CFs for Mixtures

Tests have shown that the response of PIDs to mixtures of compounds are linearly additive (see Section 2.7 and Lee, et al. 1987). Therefore, it is possible to calculate an overall correction factor based on the exact mixture composition from the CFs of the individual components. Part 3 of this section describes the equations used, and further examples of CF calculations for mixtures are given in Chapter 4 and in Appendix 4. The concentration of the individual components can then be extracted from a simple measurement of the total VOC concentration, even if some of the components are not detectable.

Empirically Measured CFs for Mixtures

Alternatively, if the mixture is very complex or not precisely known (but reproducible, e.g., gasoline), the CF can be measured empirically using the equations in Section 3.1.3. A common method is to evaporate a known weight of a liquid mixture into a known volume of air. In such cases it is necessary to determine the CF in non-standard units (e.g., (mg/m³)/ppmv), or to use an estimated average molecular weight to calculate the CF in the standard dimensionless units (ppmv/ppmv). Another method of establishing a known vapor concentration is to collect a typical gas sample on a charcoal tube or in a gas bag and submit it for laboratory analysis. One method that has been successful is to attach a charcoal sorbent tube to the effluent of the PID and thus measure the PID response at the same time as the sample collection (Drummond, 1997).

Surrogate Compound Measurement

In some cases, the most toxic compound is a detectable but minor component of the mixture, such as 1% benzene or tetraethyllead in gasoline. In other cases, the target compound does not respond on the PID at all, such as when using an 11.7 eV lamp to measure undetectable methane in natural gas from the response of the minor components ethane and propane. In these cases, it is impossible to distinguish the minor or undetectable component from the much higher response of other detectable compounds. However, if the percentage of the minor or undetectable component is constant, the other detectable compounds provide a marker for the target compounds and a surrogate measurement can be made. Given that the fraction of the target component is constant and known, mixture CFs can be used to determine both the total vapor concentration and the concentration of a trace or undetectable component.

2. VARIABLE MIXTURES

Both calculated and measured CFs are suitable only if the mixture composition is constant. If the mixture ratio varies, it is not possible to determine either the individual or total concentrations using a single sensor (whether it be PID, FID, IR, or any other technique). In such cases it is necessary to either employ multiple sensors with different detection

abilities, or to apply a separation technique before detection. Examples of the latter include portable GCs or simpler scrubbers, such as RAE-Sep tubes or cellulose filters, to select for the component of interest.

Controlling Compound Approach

Alternatively, one can set the alarm limit to that for a controlling compound. This is a conservative approach, which sets the alarm to a low enough level to ensure that the user is protected in a worst-case scenario. The controlling compound is often, but not necessarily, the most toxic compound. In this method, the unit is calibrated to isobutylene and equivalent alarm concentrations for each compound in the mixture are calculated as:

$$\text{Alarm Limit} = \text{Exposure Limit} / \text{CF}$$

The calculated isobutylene equivalent alarm limits are then compared and the alarm set to the lowest value. For example, in the mixture in Table 3.1.2, ethyl acrylate is the most toxic compound and controls the alarm, which would be set at 10 ppm. Overprotection is provided for toluene and hexane and the possibility for false positive alarms exists, but the operator is assured protection for all compounds at any mixture ratio.

TABLE 3.1.2. Controlling compound evaluation #1

Chemical Name	10.6 eV CF	OSHA PEL (ppm)	IBE Equivalent Alarm Limit (ppm)
Ethyl acrylate	2.4	25	10
Toluene	0.50	200	400
n-Hexane	4.3	500	116

TABLE 3.1.3. Controlling compound evaluation #2

Chemical Name	10.6 eV CF	OSHA PEL (ppm)	IBE Equivalent Alarm Limit (ppm)
Ethanol	12	1000	83
Toluene	0.50	200	400
Acetone	1.1	1000	910

In the example in Table 3.1.3, toluene is the most toxic compound, but ethanol is the controlling compound because of its low sensitivity (high CF). Therefore, if the PID is set to an alarm of 83 ppm, it will protect workers from all three chemicals no matter what the relative concentrations are.

Appendix 5 Lists isobutylene equivalent alarm limits for a range of compounds, including many from the OSHA Z-List. If the alarm is set to that for any one compound, the user will be warned against overexposure to any other chemicals above it on the list. All exposure limits are listed as the OSHA PEL, except that the nerve agents at the end of the table also include the LC50, or the 50% lethal concentration after one minute exposure. Using a PID for these chemicals cannot protect at 8-hour exposure levels, but can be useful in warning against potentially lethal concentrations.

3. CF & ALARM LIMIT CALCULATIONS FOR SIMPLE GAS MIXTURES

The PID response of a mixture is weighted to the relative sensitivity and relative concentration of each compound:

$$\begin{aligned} \text{CF}_{\text{mix}} &= 1 / (X_1/\text{CF}_1 + X_2/\text{CF}_2 + X_3/\text{CF}_3 + \dots X_i/\text{CF}_i) \\ \text{TLV}_{\text{mix}} &= 1 / (X_1/\text{TLV}_1 + X_2/\text{TLV}_2 + X_3/\text{TLV}_3 + \dots X_i/\text{TLV}_i) \\ \text{Alarm Setting} &= \text{TLV}_{\text{mix}} / \text{CF}_{\text{mix}} \end{aligned}$$

where X_i , TLV_i , and CF_i are the mole fraction of total VOCs, TLVs, and CFs of the individual components, respectively.

Example 1: All Compounds Detected

Air contaminated with ppm level VOCs distributed as 5% benzene (CF = 0.53, TLV = 0.5 ppm) and 95% n-hexane (CF = 4.3, TLV = 50 ppm) has a correction factor of

$$\text{CF}_{\text{mix}} = 1 / (0.05/0.53 + 0.95/4.3) = 3.2$$

A reading of 100 would then correspond to 320 ppm of the total mixture, comprised of 16 ppm benzene and 304 ppm hexane. The TLV for this mixture is

$$\text{TLV}_{\text{mix}} = 1 / (0.05/0.5 + 0.95/50) = 8.4 \text{ ppm}$$

corresponding to 8.0 ppm hexane and 0.4 ppm benzene. The alarm setting for an instrument calibrated with isobutylene is

$$\text{TLV reading} = 8.4 / 3.2 = 2.6 \text{ ppm}$$

A common practice is to set the lower alarm limit to half the TLV reading, and the higher limit to the TLV. In this case, one would set the lower and higher alarms to 1.3 and 2.6 ppm, respectively.

Example 2: Not All Compounds Detected (Surrogate Method)

Air-VOC mixture containing 30% phenol (CF = 1.0, TLV = 5 ppm) and 70% methylene chloride (CF = No Response, TLV = 25 ppm) has a correction factor, TLV, and alarm setting of

$$\begin{aligned}CF_{\text{mix}} &= 1 / (0.3/1.0 + 0.7/\infty) = 3.3 \\TLV_{\text{mix}} &= 1 / (0.3/5 + 0.7/25) = 11.4 \text{ ppm} \\TLV \text{ reading} &= 11.4 / 3.3 = 3.4 \text{ ppm}\end{aligned}$$

The suggested low and high alarm settings are 1.7 and 3.4 ppm. The TLV mixture corresponds to 30% of 11.4 = 3.4 ppm phenol and 70% of 11.4 = 8.0 ppm methylene chloride. In this case, the PID with a 10.6 eV lamp does not respond to the methylene chloride and all the response is due to the phenol. The alarm setting of 3.4 ppm is lower than the TLV of the phenol alone (5 ppm), because the methylene chloride contributes to the toxicity of the mixture even though it is not measured.



CAUTION: If the percentage of the toxic component is variable, the surrogate measurement method can lead to serious inaccuracies, and a more specific detection method is required.

Selective measurement methods include using a separation tube in front of the PID (e.g., UltraRAE), portable GCs, laboratory GCs, and gas detection tubes with prelayers that remove interferences.

4. CF & ALARM LIMITS FOR MIXTURES FROM AN EVAPORATING LIQUID

Determination of CFs for an evaporating liquid mixture present some special challenges that can be addressed using some limiting assumptions for headspace vapors and evaporated spills.

Usually liquid mixtures are identified in terms of weight percent. Calculation of CFs and exposure limits in ppmv then requires that the concentrations first be converted to mole percent (i.e., mole fraction). This is done as follows:

$$\frac{(Wt\% A)/(m.w. A)}{(Wt\% A)/(m.w. A) + (Wt\% B)/(m.w. B) + (Wt\% C)/(m.w. C) + \dots \text{etc.}}$$

where wt% is the weight percentage of component A and m.w. is its molecular weight in g/mol.

Example 3: Conversion of Weight % to Mole %.

For example, a liquid mixture has the following weight percentages:

60% Ethyl acetate (EA)	m.w. = 88.1 g/mol
25% Methyl ethyl ketone (MEK)	m.w. = 72.1 g/mol
15% Toluene (Tol)	m.w. = 92.1 g/mol

TABLE 3.1.2. Conversion of Wt.% to Mol% for liquid for mixtures

Compound	Wt. % (g/kg liq)	m.w. (g/mol)	(Wt%)/(m.w.) (mol/kg liq)	mol %
Ethyl acetate (EA)	600	88.1	6.81	57.2
Methyl ethyl ketone (MEK)	250	72.1	3.47	29.1
Toluene (Tol)	150	92.1	1.63	13.7
Total	1000	-	11.91	100.0

In this example, the weight percentages and mole percentages are similar. When the molecular weights and CFs of the components are similar, the conversion of weight percent to mole percent typically has little effect on the CF calculation for the mixture. The conversion is necessary for mixtures of components of substantially differing molecular weights.

a. Vapors From a Large Liquid Reservoir

CAUTION: The concentration of vapors directly above a tank of organic liquid is often too concentrated to measure directly. As shown in Figure 2.6.5, some PIDs may give a false low response when exposed to percent levels of VOCs. Therefore, the PID is more suitable for measuring such vapor mixtures after they are some distance from the tank headspace and are diluted.

General Equations. Vapors above a large liquid reservoir have a different equilibrium composition than that of the liquid mixture, as can be calculated by Raoult's Law:

$$P_T = P_1X_1^{\ell} + P_2X_2^{\ell} + P_3X_3^{\ell} \dots + P_nX_n^{\ell}$$

where P_T is the total vapor pressure of organic compounds above the liquid, P_1 is the vapor pressure of Component 1 if it were a pure liquid, and X_1^{ℓ}

is the mole fraction of Component 1 in the liquid mixture, P_2 is the vapor pressure of Component 2, and so on.

The mole fraction in the gas phase is $X_n^g = \frac{P_n X_n^l}{P_T}$

The mole fractions thus calculated refer only to the fraction of total vaporized compounds without regard to the air or other matrix gas. Raoult's Law is most applicable for mixtures of similar compounds and is most exact at high mole fractions.

Dilute Solutions. For dilute solutions, the solute behavior often deviates from Raoult's Law and it is more accurate to apply Henry's Law to the solute and Raoult's Law to the solvent. This approach requires knowledge of the Henry constant (H_{Solute}) for the solute:

$$P_{\text{Solute}} = H_{\text{Solute}} X_{\text{Solute}}^l$$

$$P_T = H_{\text{Solute}} X_{\text{Solute}}^l + P_{\text{Solvent}} X_{\text{Solvent}}^l$$

But since X_{Solvent}^l is nearly 1.0, the second term approaches the vapor pressure of the pure solvent:

$$P_T = H_{\text{Solute}} X_{\text{Solute}}^l + P_{\text{Solvent}}$$

The mole fractions are then:

$$X_{\text{Solute}}^g = \frac{H_{\text{Solute}} X_{\text{Solute}}^l}{P_T} \quad \text{and} \quad X_{\text{Solvent}}^g = \frac{P_{\text{Solvent}}}{P_T}$$

Example 4: Conversion of Liquid to Vapor Mole Fractions

Using the mixture in Example 3 above, the liquid mole fractions are 0.572 for ethyl acetate, 0.291 for MEK, and 0.137 for toluene. The vapor-phase mole fractions are calculated as in Table 3.1.3.

TABLE 3.1.3. Calculation of vapor mole fraction from liquid mole fraction

Compound	X_n	$P_n @ 20^\circ\text{C}$ (mm Hg)	$P_n X_n^l$ (mm Hg)	X_n^g
Ethyl acetate (EA)	0.572	73	41.7	0.619
Methyl ethyl ketone (MEK)	0.291	78	22.7	0.337
Toluene (Tol)	0.137	22	3	0.044
Total	1	-	67.4	1

The average CF and alarm limits are then calculated using the equations in subsection 1 of this chapter (see Example 1). The average CF is 1.6 calculated from the gas-phase mole fractions, compared to 1.4 calculated from the liquid-phase mole fractions.

TABLE 3.1.4. CFs and alarm limits vs calculation method

Factor	Calc. By Vapor mol% (large reservoir)	Calc. By Liq. mol% (small spill)	Calc. By Liq. Wt.% (small spill)
Correction Factor	1.6	1.4	1.4
TLV (8-hr TWA)	244 ppm	178 ppm	174 ppm
Alarm Setpoint (cal to IBE)	150 ppm	131 ppm	126 ppm

Note that in this example there is little difference between the CF and alarm setpoints for calculations using liquid mole % or liquid weight %. This is generally true for mixtures of compounds with similar molecular weights. However, as the component molecular weights and vapor pressures diverge, it becomes increasingly more important to perform the conversions to vapor-phase mole percentages before calculating the CFs and exposure limits.

b. Vapors From a Small Spill or Liquid Leak

If the liquid release is small, compared to the gas-phase volume, all the liquid will evaporate and there will no longer be an equilibrium with a liquid phase. If evaporation occurs quickly, then the vapor will have the same composition as the original liquid. In Example 4, a CF of 1.4 would be more appropriate to use for a small spill or leak that evaporates quickly.

If evaporation occurs slowly, the composition of the vapor mixture varies with time. Then the vapor composition and CF will initially be closer to those of the most volatile components and later resemble more the least volatile components.

3.1.7 PID Correlations with FID Measurements

Introduction

Many regulatory agencies request inventories of chemicals released to the air to be provided in units of methane or hexane equivalents. This is done as

a way of normalizing the overall environmental impact of a broad variety of different chemical types to a common unit, i.e., the total number of carbon atoms released. Traditionally, methane equivalents of a mixture of organic compounds have been measured using a laboratory gas chromatograph (GC) calibrated with methane using a flame ionization detector (FID). Portable FIDs and PIDs provide a convenient, cost-saving method of making measurements in the field. Portable FIDs function on the same principle as the laboratory FIDs; however the sample inlet designs of many portable FIDs often result in responses that are not proportional to the number of carbons in the organic compound. Therefore, methane equivalents measured on a portable FID do not necessarily correspond to the desired laboratory FID equivalents, which are proportional to carbons.

Portable PIDs offer advantages over portable FIDs in their ease of use, smaller size and weight, lower cost, and lack of need for hydrogen cylinders. In addition, a PID does not have interference from methane, which is exempt from most regulatory emissions limits. Methane is prevalent from both biogenic sources and from natural gas distribution leaks, and thus use of a PID will reduce the number of false positive responses due to methane. This chapter describes methods for converting PID measurements to laboratory GC-FID methane equivalents. Conversion of PID readings to hexane equivalents is performed by analogous equations.

Empirical Correlations

The conceptually simplest conversion approach is to simultaneously make PID measurements while taking gas samples that are sent to a laboratory for GC-FID analysis. When the results are compared, a PID-FID correlation factor or curve can be developed. For example, Coy, et al. (2000) found the following correlation when calibrating the PID to isobutylene and sampling with charcoal for GC:

$$\log(\text{GC total ppm}) = -0.042 + 1.05 \cdot \log(\text{PID ppm})$$

This calibration applied to vapors from painting operations, including such compounds as petroleum distillates, mineral spirits, isobutyl acetate, isobutyl alcohol, isopropanol, toluene, xylenes, ethylbenzene, and MEK.

Drummond (1997) studied gasoline vapors measured by a PID worn by a tanker truck driver during loading. The average benzene concentration

determined by charcoal tubes and lab GC correlated with the isobutylene-calibrated PID as follows:

$$\text{Benzene ppm} = 0.20 \cdot (\text{PID ppm})$$

In these cases, the GC results gave actual concentrations of the individual components in ppm, but could have easily given methane equivalents by calibrating the GC-FIDs to methane.

The advantage of this approach is its simplicity and accuracy once the correlation has been obtained. It also can be used on highly complex and unknown mixtures. The disadvantage is that it applies to only one mixture, and more laboratory tests are needed to establish a new correlation for each new mixture encountered. The methods described below allow estimation of PID-FID conversion factors for many mixtures without the need for sampling and laboratory measurements.

PID Lamp Selection

A variety of lamps are available for general hydrocarbon monitoring (see Chapter 2.2). The 10.6 eV lamp responds to pentane and higher hydrocarbons, and the 11.7 eV lamp responds to ethane (weakly), propane and higher hydrocarbons. As mentioned above, methane and ethane are exempt from most regulations. Unless propane or butane are specifically known to be present, the 10.6 eV lamp is preferred because it responds broadly to many solvents and fuels and has a considerably longer working life than the 11.7 eV lamp. Even if propane or butane are present, their proportion of the total hydrocarbons can be measured in a few laboratory tests and then the ratio used to correct the 10.6 eV PID readings. Therefore, the 10.6 eV lamp is recommended unless compounds that require an 11.7 eV lamp dominate the emissions scenario. Appendix 3 is an extended list of compounds and their responses on these two lamps.

Procedure

To convert PID readings to methane equivalent FID readings, proceed as follows:

- 1) Calibrate the PID to isobutylene using the standard procedures
- 2) Measure the gas or gas mixture.
- 3) Multiply the observed readings by the PID-FID Correction Factor listed in one of the last two columns in the Tables in Appendix 6.

Ideally, the value selected is the measured factor in the second-to-last column. In the absence of a measured value, an upper limit to the methane-equivalent response can be estimated from the number of carbons in the molecule (last column).

PID-FID Correction Factor Derivation for Methane Equivalents

The rationale behind the PID-FID correction factors (CFs) is as follows:

The PID CF is defined as the value by which the readings are multiplied in order to obtain the true ppmv concentrations, when the unit has been calibrated to isobutylene:

$$\text{True ppmv} = \text{PID reading} \times \text{PID CF} \quad (1)$$

The Lab FID Response Factor (RF) is defined as the relative response of the compound compared to methane. The methane equivalent FID response is

$$\text{CH}_4 \text{ Equivalents} = \text{True ppmv} \times \text{FID RF} \quad (2a)$$

An estimate of the FID RF is the number of carbon atoms in the molecule, in which case Eq (2a) becomes:

$$\text{CH}_4 \text{ Equivalents} = \text{True ppmv} \times \#C \text{ Atoms} \quad (2b)$$

Combining Eqs (2a) or (2b) with Eq (1) yields:

$$\text{CH}_4 \text{ Equivs} = \text{PID read} \times \text{PID CF} \times \text{FID RF} \quad (3a)$$

$$\text{CH}_4 \text{ Equivs} = \text{PID read} \times \text{PID CF} \times \#Cs \quad (3b)$$

The PID-FID CFs are thus:

$$\text{PID-FID CF (Meas.)} = \text{PID CF} \times \text{FID RF} \quad (4a)$$

$$\text{PID-FID CF (Calc.)} = \text{PID CF} \times \#Cs \quad (4b)$$

If the PID is calibrated using the gas of interest, then it reads directly in true ppmv and therefore it is not necessary to multiply by the PID CF, only by the FID RF or the number of carbon atoms. In other words, the PID gives the true ppmv used in Eq. 2a or 2b.

Example 1: Single Compound

1. Toluene is the only compound being measured. The Lab FID RF is available in Table 5.6.1 and therefore the PID-FID CF is known (col. 5).

- a) The reading is 10 ppm with the PID calibrated to isobutylene. The lab FID equivalent is $10 \times 2.6 = 26$ ppm methane units.
- b) With the PID calibrated directly to toluene (or calibrated to isobutylene but using the built-in correction factor to read in toluene units) the display reading is 5 ppm. The lab FID equivalent is $5 \times 5.1 = 26$ ppm methane units.

2. Methyl cellosolve (2-methoxyethanol) is the only compound. The Lab FID RF is not available, and therefore the PID-FID CF is estimated from the number of carbon atoms (Table 5.6.1, column 6). The PID reading of 10 ppm corresponds to $10 \times 7.2 = 72$ ppm FID equivalents. This value can be considered a safe upper limit because the true factor is almost certainly less than the 7.2 estimated from the number of carbons.

Example 2: Compound Mixture (Methane Equivalents)

The vapors consist of the following mixture:

- 60% Ethyl acetate (EA)
- 25% Methyl ethyl ketone (MEK)
- 15% Toluene (Tol)

The unit is calibrated to isobutylene and the reading is 50 ppm. As described in Chapter 3.1.6, the average CF for this mixture is calculated as:

$$\begin{aligned} \text{CF}_{\text{mix}} &= 1/(X_{\text{EA}}/\text{CF}_{\text{EA}} + X_{\text{MEK}}/\text{CF}_{\text{MEK}} + X_{\text{Tol}}/\text{CF}_{\text{Tol}}) \quad (5) \\ \text{CF}_{\text{mix}} &= 1/(0.60/4.6 + 0.25/0.86 + 0.15/0.50) = 1.4 \end{aligned}$$

The true total concentration is $50 \times 1.4 = 70$ ppm, which consists of 42 ppm ethyl acetate, 17.5 ppm MEK, and 10.5 ppm toluene. Multiplying each compound by its respective FID RF factor from Table 5.6.1:

$$\text{CH}_4 \text{ Equivalents} = 42 \times 2.0 + 17.5 \times 2.2 + 10.5 \times 5.1 = 176 \text{ ppm}$$

To simplify, an average FID RF can be calculated for the mixture as:

$$\begin{aligned} \text{RF}_{\text{mix}} &= X_{\text{EA}} \times \text{RF}_{\text{EA}} + X_{\text{MEK}} \times \text{RF}_{\text{MEK}} + X_{\text{Tol}} \times \text{RF}_{\text{Tol}} \quad (6) \\ \text{RF}_{\text{mix}} &= 0.60 \times 2.0 + 0.25 \times 2.2 + 0.15 \times 5.1 = 2.5 \end{aligned}$$

Then, according to Eq. 3a:

$$\begin{aligned} \text{CH}_4 \text{ Equivs} &= \text{PID read} \times \text{PID CF} \times \text{FID RF} \quad (3a) \\ \text{CH}_4 \text{ Equivs} &= 50 \times 1.4 \times 2.5 = 175 \text{ ppm} \\ \text{CH}_4 \text{ Equivs} &= \text{PID reading} \times 3.5 = 175 \text{ ppm} \end{aligned}$$

Example 3: Mixture with Non-Responding Compounds

The vapors consist of the following mixture:

- 60% Ethyl acetate (EA)
- 25% Methylene chloride (MC)
- 15% Toluene (Tol)

The unit is calibrated to isobutylene and the reading is 50 ppm. There is no response to methylene chloride with the 10.6 eV lamp; therefore, its correction factor is infinite. The average CF for this mixture is calculated as:

$$CF_{mix} = 1/(X_{EA}/CF_{EA} + X_{MC}/CF_{MC} + X_{Tol}/CF_{Tol})$$

$$CF_{mix} = 1/(0.60/4.6 + 0.25/\infty + 0.15/0.50) = 2.3$$

The average FID RF is calculated as (Eq. 6):

$$RF_{mix} = 0.60 \times 2.0 + 0.25 \times 0.94 + 0.15 \times 5.1 = 2.2$$

According to Eq. 3a:

$$CH_4 \text{ Equivs} = 50 \text{ ppm} \times 2.3 \times 2.2 = 253 \text{ ppm}$$

Note that the 50 ppm PID response is equivalent to a higher methane equivalent response in this example than in Example 2 because the PID is blind to 25% of the total VOC.

Example 4: Mixture with Unknown FID RF

If the lab FID RFs were unknown in Examples 2 and 3 above, one would estimate the RFs as the number of carbons, which usually leads to a safe overestimation:

For Example 2:

$$RF_{mix} = 0.60 \times 4 + 0.25 \times 4 + 0.15 \times 7 = 4.5$$

$$CH_4 \text{ Equivs} = 50 \text{ ppm} \times 1.4 \times 4.5 = 315 \text{ ppm}$$

compared to a value of 175 ppm from actual RFs.

For Example 3:

$$RF_{mix} = 0.60 \times 4 + 0.25 \times 1 + 0.15 \times 7 = 3.7$$

$$CH_4 \text{ Equivs} = 50 \text{ ppm} \times 2.3 \times 3.7 = 426 \text{ ppm}$$

compared to a value of 253 ppm from actual RFs.

It is clear that the availability of accurate response factors will help avoid false-positive alarms.

PID-FID Correction Factor Derivation for Hexane Equivalents

Although a PID with 10.6 eV lamp can be calibrated with hexane, the resulting PID hexane equivalents are different than FID hexane equivalents. Therefore, the same procedures should be used for hexane as described above for methane, by substituting the factors in Table 5.6.2 in place of those in Table 5.6.1.

Example 5: Compound Mixture (Hexane Equivalents)

For the same compound mixture as in Example 2, the unit is calibrated to isobutylene and reads 50 ppm:

- 60% Ethyl acetate (EA)
- 25% Methyl ethyl ketone (MEK)
- 15% Toluene (Tol)

$$CF_{mix} = 1/(0.60/4.6 + 0.25/0.86 + 0.15/0.50) = 1.4$$

The true total concentration is $50 \times 1.4 = 70$ ppm, which consists of 42 ppm ethyl acetate, 17.5 ppm MEK, and 10.5 ppm toluene. Multiplying each compound by its respective FID RF factor from Table 5.6.2:

$$\text{Hexane Equivalents} = 42 \times 0.42 + 17.5 \times 0.48 + 10.5 \times 1.1 = 38 \text{ ppm}$$

To simplify, an average FID RF can be calculated for the mixture as:

$$RF_{mix} = X_{EA} \times RF_{EA} + X_{MEK} \times RF_{MEK} + X_{Tol} \times RF_{Tol} \quad (6)$$

$$RF_{mix} = 0.60 \times 0.42 + 0.25 \times 0.48 + 0.15 \times 1.1 = 0.54$$

Then, analogous to Eq. 3a:

$$\text{Hexane Equivs} = \text{PID read} \times \text{PID CF} \times \text{FID RF}$$

$$\text{Hexane Equivs} = 50 \times 1.4 \times 0.54 = 38 \text{ ppm}$$

$$\text{Hexane Equivs} = \text{PID reading} \times 0.76 = 38 \text{ ppm}$$

3.2 Effect of Humidity and Other Matrix Gases

Aside from the basic components of air, matrix gases including water vapor (Chelton et al., 1983; Maslansky, 1993), methane (Nyquist et al., 1990; Maslansky, 1993) and oxygen variations (Mouradian & Flannery, 1994) can affect the response of a PID. PIDs are commonly calibrated using a dry

calibrations gas and then used to measure in ambient air with various degrees of relative humidity. Biogenic methane and carbon dioxide are sometimes present in landfill gases at the percent level, enough to affect PID response. PIDs are often used to measure organic compounds in industrial process streams, where matrix gas concentrations can be quite high, e.g., at the volume percent level. The most common matrix gases include hydrogen, helium, argon, carbon dioxide, butane, chlorofluorocarbons, nitrogen, and methane. These gases do not respond on the PID themselves, but may affect (usually reduce) the response to detectable vapors.

3.2.1 Oxygen Effects

Figure 3.2.1 shows the effect of varying oxygen concentration on the response of several commercial PIDs using 10.6 eV lamps. Most PIDs show a moderate quenching by oxygen, such that the response in pure oxygen (100% O₂) is about 60-80% of that in air. In pure nitrogen (0% O₂) the response may rise or fall compared to that in air with 20.9% O₂, but typically the difference is less than 25%. Possible mechanisms for these quenching effects include absorption of UV light by O₂ and the trapping of free electrons generated from the photoionization process, to produce O₂⁻ radical ions, as described in Chapter 2.6. O₂ can also react with the positive VOC ions to produce peroxyradical ions (VOC⁺ + O₂ → VOC⁺OO⁻). These secondary ions move more slowly toward the electrodes and thus can be neutralized more easily before being measured.

The Thermo Environmental 580 series PIDs are an exception and exhibit much larger oxygen effects, as reported by Mouradian and Flannery (1994). These authors noted a PID response to isobutylene that was 325% as high in pure nitrogen than in air. They pointed out correctly that calibration gas standards in “air” are often prepared commercially by mixing pure nitrogen with pure oxygen, rather than from purified air. Oxygen contents can thus vary, in their case ranging from 14% to 23%, which would have caused PID calibration errors of up to 17%. However, these oxygen effects are not reproducible in other PIDs, and in our experience, O₂ concentrations in synthetic air calibration gases are rarely outside the range of 19.5% to 22.5%. This oxygen variation would cause at most a 2% to 3% error in most PID responses, and therefore the user usually need not be concerned about O₂ variations in the calibration gas.

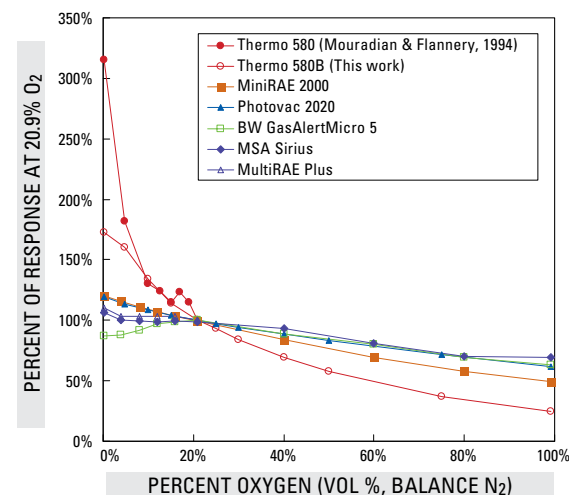


FIGURE 3.2.1. Effect of oxygen on various PID responses to 100 ppm isobutylene

Several results point to differences in sensor design as the cause of differences in oxygen dependence. Note that some of the instruments used for Figure 3.2.1 show a small drop in response in pure nitrogen, while others show a rise. These instruments have different sensor styles but nearly all had nominal 10.6 eV lamps. Moreover, Figure 3.2.2 shows that the MiniRAE Plus exhibits no oxygen dependence whatsoever between 0% and 20.9% oxygen, for the three different compounds tested. By contrast, the MiniRAE 2000 shows a rise of about 20% in pure nitrogen, compared to air (Figure 3.2.1). These two instruments use exactly the same lamp, and therefore the response differences must be due to the somewhat different sensor designs rather than lamp type.

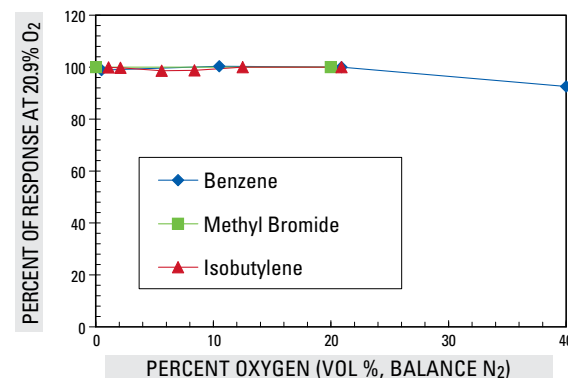


FIGURE 3.2.2. Effect of oxygen on MiniRAE Plus PID response to various compounds with a 10.6 eV lamp

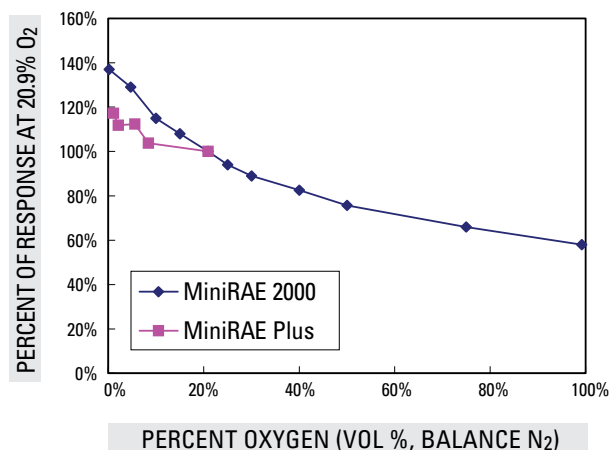


FIGURE 3.2.3. Effect of oxygen on MiniRAE PID response to 100 ppm isobutylene with an 11.7 eV lamp

Figure 3.2.3 shows that with an 11.7 eV lamp, the effect of O₂ on a MiniRAE instrument is about the same as with a 10.6 eV lamp above 21% O₂, but somewhat greater below 21% O₂. The reason for these differences in oxygen effect are unknown.

In conclusion, it is clear that oxygen effects vary from manufacturer to manufacturer and therefore the supplier should be consulted before making any corrections for changes in oxygen level.

3.2.2 Effects of Methane and Other Gases

Landfill and other excavation sites may evolve methane and CO₂, generated from anaerobic biological activity. The question is sometimes raised whether a PID can be used to measure VOCs such as mercaptan odorants in natural gas. In still other cases PIDs are used in industrial process streams containing a number of possible matrix gases. Clearly, water vapor is present ubiquitously, and its effects need to be considered.

Figure 3.2.4a shows that methane reduces the response on various PIDs by about the same amount. The negative readings for the HNU instrument in Figure 3.2.4b indicate a baseline shift with elevated methane. Figure 3.2.5 shows the effect of various gases in the lower volume % range. There is no effect of CO₂, Ar, He, or H₂ up to 5 volume %. In contrast, methane, water vapor, methanol, butane, and R-123 (2,2-dichloro-1,1,1-trifluoroethane) show

a reduction in response to either isobutylene or toluene. Figure 3.2.6 shows the matrix gas effect up to higher concentrations approaching 100%. All PIDs show a reduced response when methane is present above about 1% or 10,000 ppm. Measurements in natural gas, which is >85% methane, will give extremely low response and thus are impractical. The lack of major effect of CO₂, Ar, He, or H₂ suggests that these gases do not absorb the UV light very strongly. The fact that all organic matrix gases tested, including methane, showed a reduction in response, suggests that these all absorb the 9.8 eV and 10.6 eV light. It further suggests that any other organic matrix vapors will exhibit similar reductions in response (e.g., Figure 2.6.5 for isobutylene).

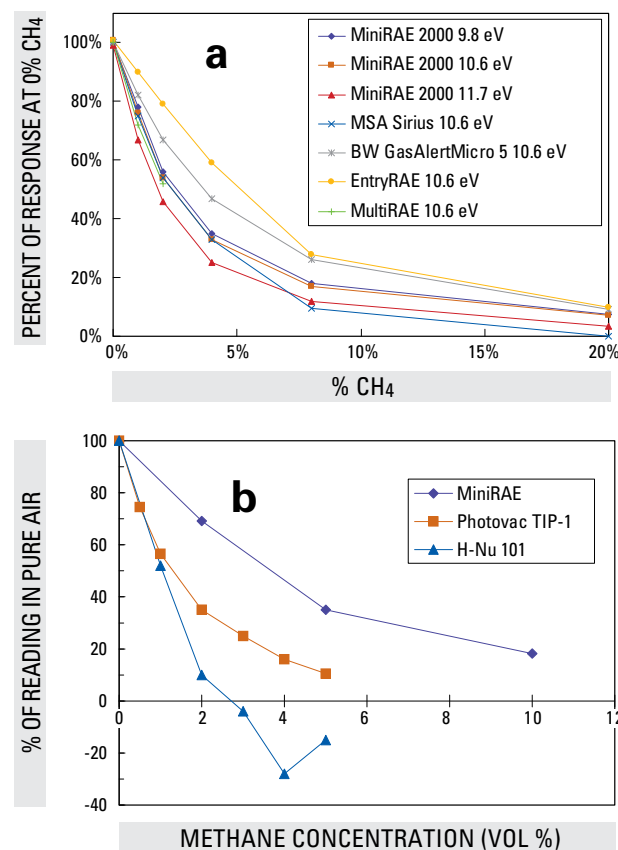


FIGURE 3.2.4. Effect of methane on the response of various PIDs with 10.6 eV lamps. Data for the Photovac TIP-1 and HNU-101 are adapted from Nyquist et al. (1990)

The curves in Figures 3.2.5 and 3.2.6 for Ar, He and H₂ used nitrogen as a balance gas instead of air in order to avoid complications with the oxygen effects described before. Figure 3.2.7 shows the response to increasing argon in a practical situation where air is likely to be the balance gas. The apparent increase in response at higher argon concentrations in air is due to the depletion of oxygen rather than an enhancement due to argon. The same result should occur with hydrogen and helium.

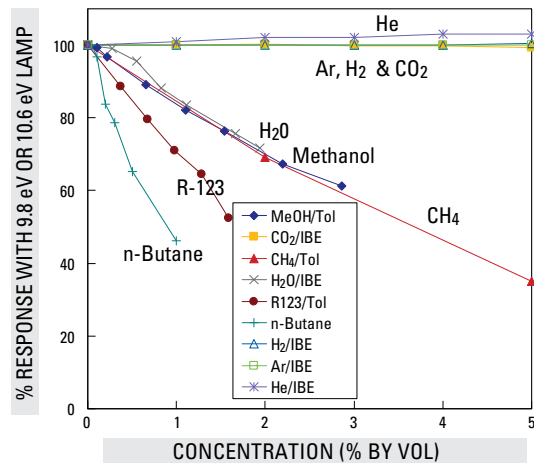


FIGURE 3.2.5. Effect of matrix vapors on MiniRAE PID Response to 50 ppm toluene, 100 ppm IBE, or butane self-quenching. All experiments except those of H₂, He, Ar, and butane had pure air as the balance gas. The others had N₂ as the balance

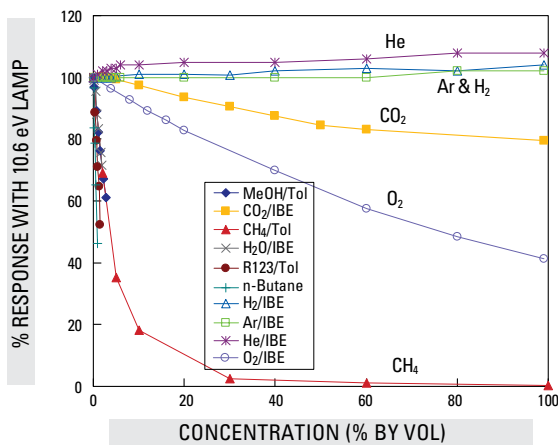


FIGURE 3.2.6. Effect of various gases on MiniRAE PID response with a 10.6 eV lamp. The 9.8 eV lamp has similar effects with CH₄ and O₂

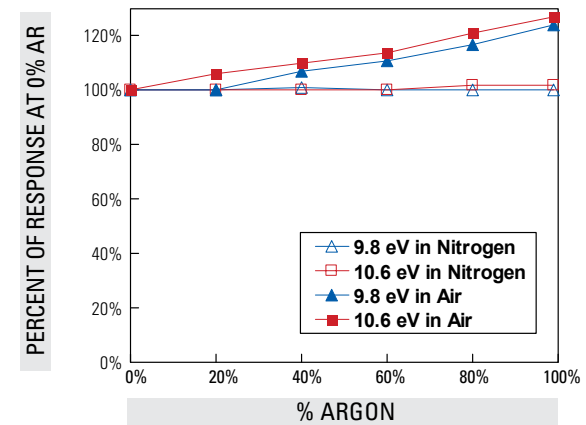


FIGURE 3.2.7. Comparison of argon effect on PID response to IBE in air vs. N₂

Thus, in the common situation where the PID is calibrated using a standard gas in dry air, and argon is used to purge air from a vessel, an apparent increase in response would be observed as the air (i.e., oxygen) is displaced. If the PID had been calibrated using humid air instead of dry air, the apparent rise in Figure 3.2.7 would have been even greater as both the oxygen and water vapor are displaced.

The butane effect in Figure 3.2.5 is an example of self-quenching. That is, butane is both the measured gas and the matrix quenching gas. The values plotted are the ratio of the observed response to the response expected assuming a linear rise with concentration. A similar plot for self-quenching could be obtained from the data for isobutylene shown in Figure 2.6.5. Thus, non-linearities at high concentrations of detectable gases are essentially the same phenomenon as the quenching effects of non-detectable matrix gases. As described above, these phenomena are high absorbance of the active light (Figure 2.6.2) and increased neutralization reactions due to high local ion concentrations (Chapter 2.6).

3.2.3 Humidity Effects

Water vapor is ubiquitous in ambient air and can reduce PID response, as shown in Figures 3.2.5 and 3.2.7(a). A secondary effect that is a common occurrence is the condensation of water vapor on the PID sensor, causing a false-positive “leak” current. These two phenomena have opposite effects on the response and must be distinguished carefully.

Water Vapor Quenching

Figure 3.2.7(a) shows that various PIDs have similar reduced response at high relative humidity. The quenching effect is independent of lamp type for 10.6 and 11.7 eV lamps. Compensation using a humidity sensor is possible, but complicated by the fact that the response times of most RH sensors are much slower than those of modern PIDs with built-in electronic pumps. Therefore, compensation is not commonly employed.

PIDs are commonly calibrated with dry calibration gas and then used to measure in ambient air with various degrees of relative humidity. In this case, corrections are necessary if the absolute concentration of the measured vapor is desired. Alternatives to performing corrections are to either humidify the calibration gas, or to dry the sample gas during measurements. Drying the sample gas using dessicant filter tubes is possible for non-polar compounds like gasoline and trichloroethylene, and is described in more detail in Chapter 4.13. These tubes are of great advantage in removing both quenching and “leak current” effects during continuous PID readings, and reduce the need for sensor cleanings. However, heavy and polar compounds tend to adsorb to the reagent, causing slower response, particularly at low temperatures and low concentrations. Some compounds such as amines absorb completely and cannot be measured using the dessicant tubes.

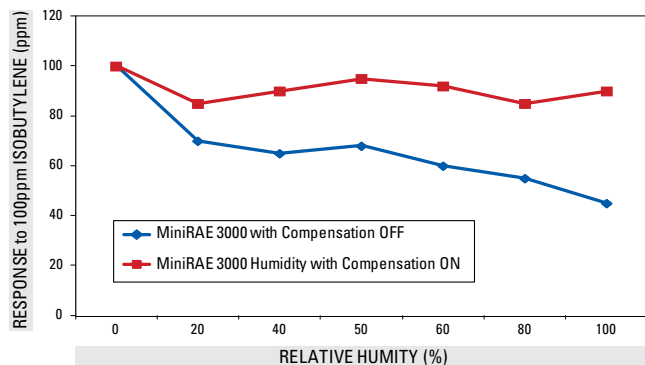


FIGURE 3.2.7(a). Effect of humidity PID response

Correcting the response by humidifying the calibration gas is possible using moisture exchange tubes consisting of a Nafion membrane. Such tubes allow humidification of the calibration gas close to the ambient level. Use of moisture exchange tubes is described in more detail in Chapter 4.14.

The moisture exchange tube has limitations: the humidity equilibration is not exact, and it only compensates correctly at one humidity, but not when humidity changes. Such changes are commonly encountered when a PID is calibrated indoors and then used outdoors for measurements. Nevertheless, the readings will be closer than if no compensation were performed at all, and may be adequate for many purposes.

Procedures for correcting VOC readings to ambient RH are described in the following section. Because the quenching depends on the absolute concentration of water vapor, rather than the relative humidity, the data in Figure 3.2.8 can be used to calculate curves for other temperatures at the same total water content.

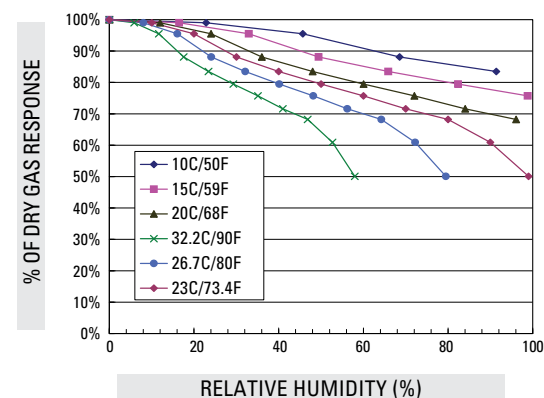


FIGURE 3.2.8. Calculated PID humidity effect curves vs. temperature for MiniRAE 2000

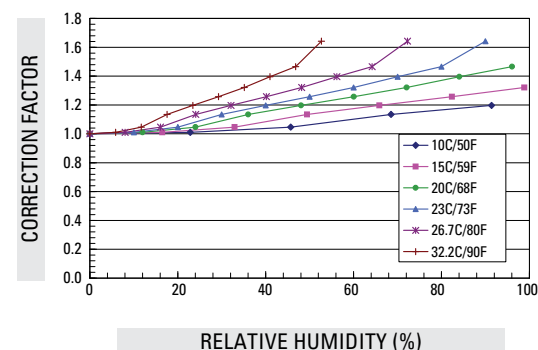


FIGURE 3.2.9. Correction factors for humidity vs. temperature for MiniRAE 2000

Figure 3.2.9 and Table 3.2.1 give correction factors derived from Figure 3.2.8. When the unit is calibrated in dry gas, multiply the CF by the observed reading at ambient RH to obtain the true concentration. For other PIDs, the manufacturer should be consulted to obtain humidity correction tables.

Humidity-Induced Current Leakage

When making measurements at high relative humidity, PIDs may exhibit an apparent response that appears as a rising drift. This signal is due to a current leakage between the electrodes in the sensor, caused by condensation on the sensor. A similar phenomenon, although usually less severe, can occur when some high-boiling compounds deposit onto the sensor. When water vapor deposits, it causes a slight short-circuit that results in current leakage and an apparent VOC response. Condensation occurs most obviously when a PID is brought from a cool, dry indoor environment to a warm, humid outdoor environment. This condition can be avoided by warming the PID to the measurement temperature before entering the humid environment.

Water vapor can only condense on a clean sensor when the relative humidity is very close to 100%. However, water can be absorbed by dust particles when the RH is somewhat lower. Therefore, the current leakage is exacerbated when minute, invisible dust or dirt particles collect on the sensor. Most humidity-induced drift problems can be solved by a thorough cleaning of the sensor, preferably using an ultrasonic cleaner. Thus, maintaining a clean sensor is usually very important when working in high-humidity environments. Additional aids include ensuring the sensor is not bent or corroded, and use of drying filters to condition the sample gas. Chapter 4 gives more information for working in humid environments.

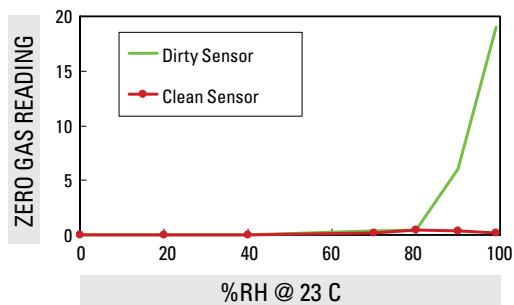


FIGURE 4.13.2. Response to zero gas vs. humidity on “dirty” vs “clean” sensor

TABLE 3.2.1. Humidity correction factors for MiniRAE 2000

%RH	10°C	15°C	20°C	23°C	26.7°C	32.2°C
	50°F	59°F	68°F	73°F	80°F	90°F
0.0	1.00					
22.8	1.01					
45.7	1.05					
68.5	1.14					
91.4	1.20					
0.0		1.00				
16.5		1.01				
32.9		1.05				
49.4		1.14				
65.9		1.20				
82.4		1.26				
98.8		1.32				
0.0			1.00			
12.0			1.01			
24.0			1.05			
36.0			1.14			
48.0			1.20			
60.0			1.26			
72.1			1.32			
84.1			1.40			
96.1			1.47			
0				1.00		
10				1.01		
20				1.05		
30				1.14		
40				1.20		
50				1.26		
60				1.32		
70				1.40		
80				1.47		
90				1.64		
0.0					1.00	
8.0					1.01	
16.1					1.05	
24.1					1.14	
32.1					1.20	
40.1					1.26	
48.2					1.32	
56.2					1.40	
64.2					1.47	
72.3					1.64	
0.0						1.00
5.9						1.01
11.7						1.05
17.6						1.14
23.4						1.20
29.3						1.26
35.1						1.32
41.0						1.40
46.8						1.47
52.7						1.64

3.3 Temperature and Pressure Effects

Corrections for temperature and pressure tend to be minor and are often ignored in PID measurements. However, for accurate quantitation, they must be taken into consideration. No correction is necessary if the instrument is calibrated at the same temperature and pressure as the subsequent measurements. Therefore, the discussion below applies only when the unit is calibrated at a different temperature or pressure as those present during subsequent measurements.

PIDs respond proportionally to absolute concentration, whereas the conventional desired reading is in ppmv, 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. As the gas density decreases, the apparent response is reduced because there are fewer molecules per unit volume sampled. Thus, a correction is needed when gas density changes after calibration.

Temperature Effects

Photochemical reactions generally have low temperature coefficients. Therefore, the effect of temperature is expected to be primarily due to a change in gas density, and thus concentration. Figure 3.3.1 shows that the response decreases as the temperature increases, but by somewhat more than would be expected from gas density changes alone. The cause for the temperature effect is unknown.

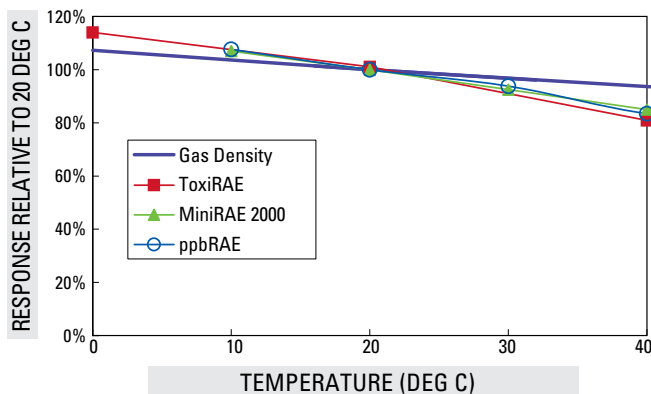


FIGURE 3.3.1. Effect of temperature on three PIDs

Pressure Effects

Rapid pressure changes are encountered in such instances as when descending a mine shaft or in a submarine, or when rising in an elevator or aircraft. In some cases, a PID is calibrated at a central location and then transported for use at a high elevation without recalibration. The following equations can be used to correct for gas density effects due to pressure changes.

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

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

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

If the calibration is performed at a pressure different from one atmosphere, the values 760 mm Hg, 101.3 kPa, and 14.7 psi should be substituted by the calibration pressure. The pressure in mm Hg can be estimated as a function of altitude using the equation:

$$P \text{ (mm Hg)} = 760 \exp(-0.1286[\text{alt}(\text{km})]) \text{ below 2 km}$$

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

TABLE 3.3.1. Pressure corrections

Example Location	Altitude (km)	Altitude (feet)	Pressure, (mm Hg)	CF
San Francisco, CA	0	0	760	1.00
Atlanta, GA	0.3	1000	731	1.04
Spokane, WA	0.6	2000	703	1.08
Rapid City, SD	0.9	3000	676	1.12
Salt Lake City, UT	1.2	4000	650	1.17
Denver, CO	1.5	5000	625	1.22
Colo. Springs, CO	1.8	6000	601	1.27
Santa Fe, NM	2.1	7000	578	1.32
Alta, UT	2.4	8000	555	1.37
Winter Park, CO	2.7	9000	534	1.42
Keystone, CO	3.0	10000	514	1.48

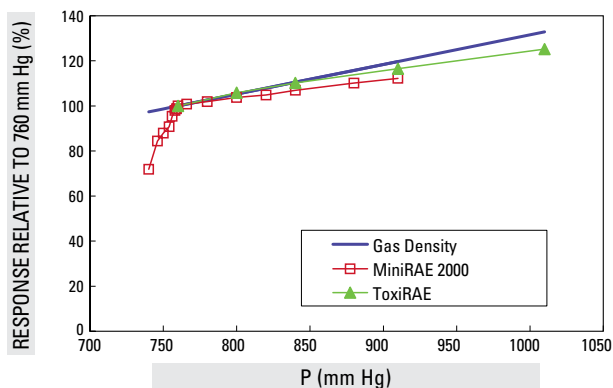


FIGURE 3.3.2. Pressure dependence for two PIDs

Figure 3.3.2 shows that the pressure dependence observed for two commercial PIDs is similar to the dependence expected from gas density above ambient pressure. The dependence deviates at pressures below ambient for unknown reasons. In these experiments, the entire instrument and calibration gas bag are placed at subambient pressures. Therefore, the deviation is not caused by leaks. These results emphasize the importance of calibrating at the same pressure as the measurements, thus compensating for such deviations as shown in Figure 3.3.2.

3.4 Effects of Sampling Equipment and Procedures

The measurement ability of any instrument can only be as good as the sampling process involved in moving the sample to the PID sensor. This chapter considers the effect of sampling procedures, sample pressure, adsorption losses, and other pressure effects.

Spatial and Temporal Variations of the Sample

The samples themselves may vary in location and in time. Therefore, it is difficult to correlate readings from instruments that have different pump flow rates and in some cases, even slightly different locations. For example, measurements taken in ambient air with a gas detection tube, which may require a few minutes, may not agree with those from a PID whose response time is a few seconds, due to variations in ambient air mixing. It is usually only possible to obtain comparable readings by two different instruments when the gas is drawn from exactly the same source, such as from a Tedlar gas bag.

Sample Tubing, Filters and Adsorption Losses

When a sample is drawn from a distance, the sample tubing can cause a delay in response and losses due to adsorption. Adsorption of VOCs is significant for most types of plastic or rubber tubing, even though such tubing may be supplied with standard confined space entry kits and is adequate for sampling CO, H₂S, CH₄, and O₂. For VOCs, metal or perfluorinated plastic (Teflon or PTFE, PFA, etc.) tubing is highly recommended. A second choice, polyurethane tubing, is often adequate. The importance of the tubing material choice depends on the length of tubing, the absorbability of the compound and the flowrate. Ten feet (3 m) of Tygon tubing will completely absorb low-volatility compounds like jet fuels. Several inches of Tygon has no effect on volatiles like benzene or isobutylene; 100 feet (30 m) of Teflon tubing has little effect on isobutylene, but does cause enough adsorption to delay the response by a few seconds more than that required to displace the air in the tubing.

For very high molecular weight compounds, even the inlet probe and sensor block can cause enough adsorption to affect the readings. Typically, compounds with a boiling point above about 300°C are not possible to measure quantitatively with most portable PIDs, unless the entire system is heated. For example, MDI, an isocyanate used in polymer manufacturing, has a boiling point of about 370°C. On a MiniRAE 2000 or ppbRAE, its response time to full response is very slow (>15 minutes), but these instruments have proven useful for detecting leaks on heated MDI pipelines.

The effect of adsorption losses can be reduced by setting the instrument to the highest flow rate available, thus saturating the adsorption capacity more quickly. In addition removing filters may reduce adsorption. Some PIDs use filters made of cellulose or other materials that can absorb or react with some chemicals. For example, cellulose reacts with hexamethyldisilazane and acyl chlorides, making these compounds difficult or impossible to measure quantitatively with the filters in place. Removing the filters usually is at the cost of shortening the pump life or more frequent lamp cleanings, but it may be necessary for proper measurement.

Sample Tubing Volume and Delay Time

Tables 3.4.1 to 3.4.3 give the wait times that need to be considered when using extension tubing, to allow the gas sample to reach the instrument, at typical flows of 300, 500 and 650 cc/min. The times assume that the sample

line has not been pre-filled with the air sample of interest. Smaller diameter tubing has the least delay time, but causes a pressure drop for long tubing. Only the smallest-diameter tubing (1/8" o.d.) exhibits a reduced flow rate due to pressure drop. For many instruments wider tubing is recommended to reduce strain on the pump, avoid leaks, and give better consistency.

Pump Flow Curves

Figure 3.3.3 below shows curves of flow vs inlet vacuum for RAEGuard and ppbRAE. MiniRAE 2000 has the same flow characteristics as the ppbRAE. Although the pumps can draw down to about 100" of H₂O (74 mm Hg) without leaks, this creates a significantly reduced flow rate. To avoid excessive strain on the pump and to reduce the chance of leaks developing when parts are worn, typically no more than 40 inches of H₂O (30 mm Hg) vacuum should be applied.

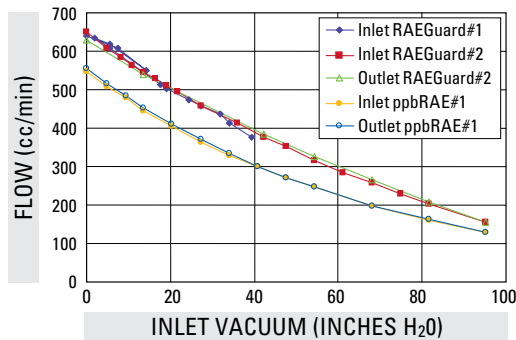


FIGURE 3.3.3. Flow-vacuum curves for ppbRAE (lower curve) and RAEGuard (upper curve)

TABLE 3.4.1. Sample tubing delay times at 300 cc/min

Nominal Tubing Size					Volume			Delay Time @ 300 cc/min				
in OD	in OD	in ID	cm OD	cm ID	cc per cm	cc per m	cc per ft	1'	10'	30'	100'	300'
1/8	0.125	0.063	0.318	0.159	0.020	2.0	0.60	0.1	1	5*	29*	--
4 mm	0.157	0.110	0.400	0.280	0.062	6.2	1.88	0.4	4	11	38	113
3/16	0.188	0.127	0.476	0.323	0.082	8.2	2.49	0.5	5	15	50	149
1/4	0.250	0.190	0.635	0.483	0.183	18.3	5.58	1.1	11	33	112	335
5/16	0.313	0.248	0.794	0.630	0.312	31.2	9.50	1.9	19	57	190	570
3/8	0.375	0.311	0.953	0.790	0.490	49.0	14.94	3.0	30	90	299	896
1/2	0.500	0.436	1.270	1.107	0.963	96.3	29.36	5.9	59	176	587	1762

* Corrected for decrease in flow rate due to pressure drop in tubing

TABLE 3.4.2. Sample tubing delay times at 500 cc/min

Nominal Tubing Size					Volume			Delay Time @ 500 cc/min				
in OD	in OD	in ID	cm OD	cm ID	cc per cm	cc per m	cc per ft	1'	10'	30'	100'	300'
1/8	0.125	0.063	0.318	0.159	0.020	2.0	0.60	0.1	1	2	7	22
4 mm	0.157	0.110	0.400	0.280	0.062	6.2	1.88	0.2	2	7	23	68
3/16	0.188	0.127	0.476	0.323	0.082	8.2	2.49	0.3	3	9	30	90
1/4	0.250	0.190	0.635	0.483	0.183	18.3	5.58	0.7	7	20	67	201
5/16	0.313	0.248	0.794	0.630	0.312	31.2	9.50	1.1	11	34	114	342
3/8	0.375	0.311	0.953	0.790	0.490	49.0	14.94	1.8	18	54	179	538
1/2	0.500	0.436	1.270	1.107	0.963	96.3	29.36	3.5	35	106	352	1057

TABLE 3.4.3. Sample tubing delay times at 650 cc/min

Nominal Tubing Size					Volume			Delay Time @ 650 cc/min				
in OD	in OD	in ID	cm OD	cm ID	cc per cm	cc per m	cc per ft	1'	10'	30'	100'	300'
1/8	0.125	0.063	0.318	0.159	0.020	2.0	0.60	0.1	1	3*	13*	--
4 mm	0.157	0.110	0.400	0.280	0.062	6.2	1.88	0.17	1.7	5	17	52
3/16	0.188	0.127	0.476	0.323	0.082	8.2	2.49	0.23	2.3	7	23	69
1/4	0.250	0.190	0.635	0.483	0.183	18.3	5.58	0.5	5	15	51	154
5/16	0.313	0.248	0.794	0.630	0.312	31.2	9.50	0.9	9	26	88	263
3/8	0.375	0.311	0.953	0.790	0.490	49.0	14.94	1.4	14	41	138	414
1/2	0.500	0.436	1.270	1.107	0.963	96.3	29.36	2.7	27	81	271	813

Pressure Drop in Tubing

Pressure drop in extension tubing depends on the inner diameter, the number and severity of bends, and total flow rate. Typical pressure drop for different types of tubing and flow rates are summarized in Table 3.4.4 below. The "Max Flows" in Table 3.4.4 are the nominal flows with no tubing or only short sections. To calculate the flow rate with tubing attached, use the value in Table 3.4.4 to estimate the vacuum in the tubing and then read the flow drop off of Figure 3.3.3. For example, a 10' section of 1/16" i.d. tubing will cause a pressure drop of 1.3 x 10 = 13" of water in a ppbRAE or MiniRAE with nominal flow rate of 500 cc/min. Figure 3.3.3 shows that at a vacuum of 13" H₂O the flow rate drops from 540 to 450 cc/min. For 100' of 2.8-mm i.d. tubing a RAEGuard with nominal 650 cc/min flow will result in 0.1 x 100 = 10" H₂O vacuum, and thus a flow drop from 650 to about 550 cc/min. These estimates

give only a rough idea of the flow rates expected and vary with the user's exact configuration. Because of the high pressure drop in 1/16" i.d. tubing, we recommend using this tubing only if the length is less than a few meters, and using wider-bore tubing for longer distances.

TABLE 3.4.4. Pressure drop in various sizes of tubing

Tubing ID (inches)	Tubing ID (mm)	Max flow 500 cc/min	Max flow 650 cc/min
1/16"	1.6	1.3" H ₂ O/ft.	1.6" H ₂ O/ft.
1/9"	2.8	0.10" H ₂ O/ft.	0.13" H ₂ O/ft.
1/8"	3.2	0.083" H ₂ O/ft.	0.10" H ₂ O/ft.

Maximum Vacuum or Pressure

The maximum vacuum obtained on most PIDs with a built-in pump is about 280 mm Hg (150" of H₂O). On the outlet side, these instruments can push against a pressure of up to about 6 psi or 170" of H₂O (310 mm Hg). Note that the flow will be close to zero or very low at these maximum values, and it is not recommended to operate the pump for long periods under such conditions.

Aerosols, Mists and Dusts

Most PIDs are not designed to measure mists and dusts. Dusts tend to be trapped in instrument filters or the inlet sample train and thus do not reach the sensor efficiently. If dust particles do reach the sensor, they may ionize. However, they are so large as to have exceedingly poor mobility in the sensor and thus are poorly detected. In some cases high-molecular-weight chemicals such as dioxins and PAHs exist to a large extent adsorbed onto dusts in ambient air. It is possible that chemicals in the adsorbed phase ionize in the sensor chamber, but again, the ions are unlikely to be collected at the electrodes before being neutralized or swept out of the chamber.

Aerosols and mists are tiny droplets of pure liquid. They likewise tend to be trapped in the filters or the inlet sample train and are poorly detected. In addition, they tend to coat the lamp, causing reduced real response and increased current leakage.

Pressure Operation

If a sample is drawn from a pipe or vessel that is not at ambient pressure, high or low readings can be obtained if no precautions are taken. In addition to the pressure effects on the readings described in the previous chapter, sampling procedures may need to be modified.

For a high-pressure vessel or pipe, a valve can be attached to release a limited flow of the sample gas. The flow should be higher than the instrument pump draw, but not so high that the pump or sample train is damaged, preferably in the range of 110% to 200% of the pump draw. A safe way to achieve this is through an open cup, releasing excess flow past the inlet probe of the PID. As a rule of thumb, if the open cup diameter is no more than 4 times the diameter of the probe, then inserting the probe by at least 2 cm is adequate when the flow is at least 110% of the sample draw. If the cup is wider than that, air entrainment into the sample is possible unless flow is increased or the probe inserted further.

If emission of the sample gas to the ambient air is dangerous or otherwise undesirable, it is often possible to plumb the effluent from the PID back into the sample train. This option is usually available only for low-pressure systems, because of possible damage when the entire PID sample train will be pressurized.

Vacuum Operation

Sampling from vessels under vacuum is often limited by the capacity of the pump to draw against a vacuum. Most PID pumps are not designed to draw against more than a few inches of Hg negative pressure. To avoid these pump limitations, the effluent can be plumbed back into the sample train. However, the leaks into the sensor can still occur because the instrument is under negative pressure. Without leaks, the pressure dependence curves such as in Figure 3.3.2 are followed. Again, it is desirable to calibrate at the same pressure as the measurement in order to avoid the need for pressure corrections.

4. SPECIFIC APPLICATIONS

4.1 Environmental Applications for PIDs

One of the earliest uses of portable PIDs was to screen for organic compounds emitted from potentially contaminated soils and leaking storage drums. Environmental contractors and consultants use PIDs to monitor the remediation of industrial waste sites and closed military bases. Other environmental applications include perimeter monitoring and fugitive emissions monitoring.

4.1.1 Hazardous Waste Monitoring

Toxic Hazardous Waste Monitoring

Hazardous waste contractors and industrial hygienists concerned with occupational health determine levels of toxic vapors or volatile organic compounds. PIDs allow pinpointing of the most hazardous areas at old disposal sites, disused industrial plants, and closed military bases, and during hazardous waste transportation. PIDs can help determine the correct level of personal protective equipment (PPE) to use, and whether a self-contained breathing apparatus (SCBA) is necessary.

Drum Monitoring

Hazardous waste contractors and environmental engineers can easily determine drum and other container contents at old disposal, landfill and garbage sites, as well as closed industrial plants and military bases.

4.1.2 PIDs for EPA Method 21 Compliance

EPA Method 21 is a standard for monitoring leaks, calibrating field monitoring equipment, and principles for monitoring fugitive emissions in pipelines and chemical processing equipment. Properly designed PIDs meet the specifications for leak-monitoring equipment called for in Method 21. For more information on Method 21, see Chapter 4.9.

4.1.3 Soil Remediation

Leaking Underground Storage Tanks

Portable PIDs are ideal for detecting BTEX (benzene, toluene, ethylbenzene, and xylene) and TPH (total petroleum hydrocarbons) in gasoline, diesel and jet fuel that may be present at leaking underground storage tanks. Both environmental engineers and the petroleum industry use PIDs to monitor gas stations, industrial sites, commercial transportation refueling sites and defense bases.

Real Estate Transfers

Environmental engineers and consultants can use PIDs for environmental soil contamination monitoring at industrial real estate sites and military base closures. A PID enables them to determine, before the sale of land, whether the soil is contaminated by VOCs. Due diligence and environmental impact studies, prior to purchase, allow for safe rezoning to homes, shops and parks.

Environmental Remediation and Contaminated Air Treatment

A common method of treating contaminated sites is to use a soil vapor extraction system that pumps air laden with organic contaminants out of the ground using a large vacuum pump. In most states, the generated air must be treated before it can be released to the atmosphere. Contaminated air streams are also produced in a large variety of industrial processes. Common treatment processes include liquid scrubber absorption, activated carbon adsorption, thermal oxidation, and incineration. PIDs are useful in determining the treatment process by measuring the VOC content before and after. In some cases, a dilution is necessary on the influent to bring the sample concentration into the linear PID range and reduce the humidity to acceptable levels.

4.1.4 Headspace Screening

Although PIDs cannot be used to measure VOCs in water or soil directly, they are often employed indirectly to measure concentrations in these media by measuring the vapors emitted from them. For example, Hewitt and Lukash (1999) reported linear correlations between headspace PID response

and soil concentrations of benzene, toluene, xylenes, dichloroethylenes, trichloroethylene and perchloroethylene. The concentration in the headspace, measured in ppmv, does not equal the soil or water concentration, measured in mg/kg or mg/L. The vapor concentration depends on such factors as soil-to-headspace weight and volume ratio, soil permeability, affinity of the compound to the soil, temperature, equilibration time, and dilution during the measurement procedure. Therefore, it is important that these factors are controlled as closely as possible if quantitative soil or water concentrations are desired.

Toxic VOCs in Drinking Water Sources

Hydrologists and environmental engineers often use PIDs to monitor chlorinated solvents (e.g., carbon tetrachloride) and VOCs (e.g., toluene) in groundwater at drill and well sites or closed industrial plants, military bases or nuclear facilities, etc. PIDs can also be used to monitor water stripper effluents and off-gases from wastewaters.

Soil and Water Headspace Screening

In a typical procedure, a sample of soil or water is filled approximately halfway into a jar with a ring-type lid. A piece of aluminum foil is placed over the mouth of the jar and held in place with the lid ring. The jar and its contents are brought to room temperature. The influent probe (and effluent line) of the portable PID is then poked through the foil and the VOC concentration measured in the headspace of the jar.

Procedures for Optimum Performance of PIDs

Soil and water headspace sampling requires special attention beyond that needed for typical ambient air monitoring. Stripper effluents and soil vapor extraction streams are typically near 100% RH (relative humidity), and soil samples are often dusty and humid. Such conditions can cause high, drifting readings on many PIDs if not properly maintained. Interferences are usually traceable to condensation in the sensor, causing a current leakage across the electrodes and thus a false-positive signal. This situation is exacerbated when the sensor is contaminated by soil dust or condensed, high-boiling organic compounds.

- a) Keep the sensor clean using high-purity methanol, preferably using an ultrasound bath. Flush the residual solvent from the sensor with a rapid stream of clean air, and clean the lamp housing area that contacts the sensor when in place.
- b) On sensors with interdigital fingers, check that the metal electrode fingers do not contact the Teflon sensor walls. Bend them out carefully if necessary. Replace the sensor if the electrodes are corroded.
- c) Keep the lamp clean using high-purity methanol. Never use acetone on 11.7 eV lamps.
- d) Perform frequent changes of the dust filters (daily to monthly, depending on usage and dirtiness).
- e) Use additional external filters (e.g., Teflon “water trap”) as an extra precaution, especially in dusty or moist environments.
- f) Start sampling by using a dilution attachment, especially for highly contaminated soils. This minimizes the amount of dust, water, and high-boiling organics condensing on the sensor and lamp. If the concentrations are too low to give a reading, remove the attachment to obtain an undiluted reading.
- g) Avoid situations in which the PID is colder than the soil being sampled, such as heating the soil samples to increase the headspace organic concentration, or bringing a cold PID into a warm room without allowing time for temperature equilibration. If anything, try to keep the PID warmer than the soil samples.
- h) To obtain more stable readings, plumb the effluent flow from the PID back into the sample container to prevent diluting the sample. Use Teflon or metal tubing for this purpose so as to prevent adsorption to Tygon or other plastic tubing. Losses will not be stopped altogether but will be greatly reduced.
- i) If humidity problems persist, use a humidity filtering tube to absorb moisture (see Chapter 4.13).

Response of PIDs and FIDs to Semi-volatiles on Soils

Often repeated is the statement that PIDs do not respond to semi-volatile organic compounds. This statement seems to be an old piece of “common knowledge” that may have been true at one time for an old PID used for soil headspace measurements, but is no longer true in general. The larger the

organic molecule (and thus less volatile), the lower the IE and the greater the PID sensitivity. However, there is a point of diminishing sensitivity when adsorption losses in the instrument sample lines and filters begin to dominate over this sensitivity increase. This is true for any instrument including FIDs and PIDs if they are not specifically designed to handle semi-volatile compounds. New PIDs have higher flow rates and better sensor designs that reduce such losses, and therefore most compounds up to a boiling point of about 300°C can be detected on the MiniRAE 2000. Boiling points for fuel oils, diesels, and kerosenes range from about 170°C for #2 Fuel Oil to 260°C for #5-6 Fuel Oils. As the oil weathers and the light ends evaporate, the response time increases and the overall response drops because less organic vapor is present. The response may drop to zero before all the oil is removed from a soil sample, because only non-volatile components remain. Again, this effect is the same for FIDs and PIDs. In such cases, a direct measurement of the oil contamination may be needed – for example, using a solvent extraction procedure followed by laboratory gas chromatography. For such high-boiling compounds it is also important not to use any rubber or Tygon tubing to draw in samples, as several inches of such tubing can completely absorb heavy fuels. Teflon or metal tubing is preferred.

4.2 PIDs for Industrial Hygiene

The recent advent of PIDs with small size and weight and with datalogging capability has opened a host of new applications for industrial hygiene. The small size allows workers to wear the monitor while freely moving about, including climbing on ladders and scaffolding, and entering narrow, confined spaces. Advanced programming features are commonly available that allow the hygienist to set up the monitor parameters and calibrate it, using password protection to prevent tampering by the user. Programming of alarm limits allows the user to set one or more alarm levels, usually giving warning by both visual and audio alarms. Some manufacturers supply vibration alarms for operations in high-noise environments.

4.2.1 Definition of TWA, STEL and Ceiling

This section discusses the terms TWA (time-weighted average), STEL (Short-Term Exposure Limit), Ceiling, and running average, because these parameters are often misunderstood.

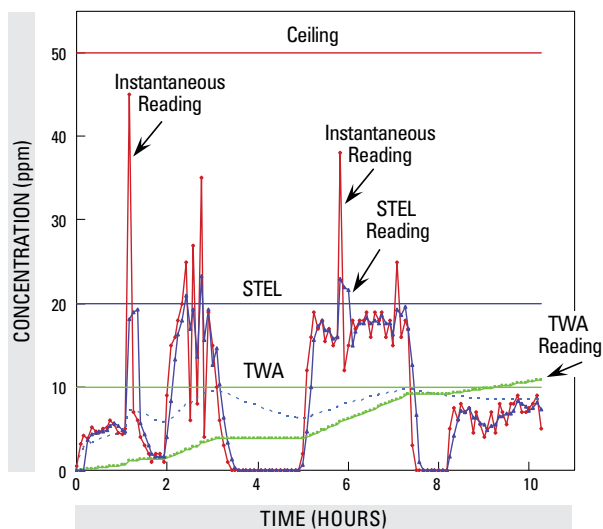


FIGURE 4.2.1. Exposure limit illustration: TWA vs. running average

Figure 4.2.1 illustrates these concepts for a hypothetical compound with a TWA of 10 ppm, STEL of 20 ppm, and Ceiling of 50 ppm. The Ceiling value is the concentration that should never be exceeded, even for an instant. An instantaneous reading may exceed the TWA and STEL as long as it never exceeds the Ceiling. A STEL reading may exceed the TWA, but action must be taken when the STEL limit is reached. A STEL is the average concentration over the immediately previous 15-minute period.

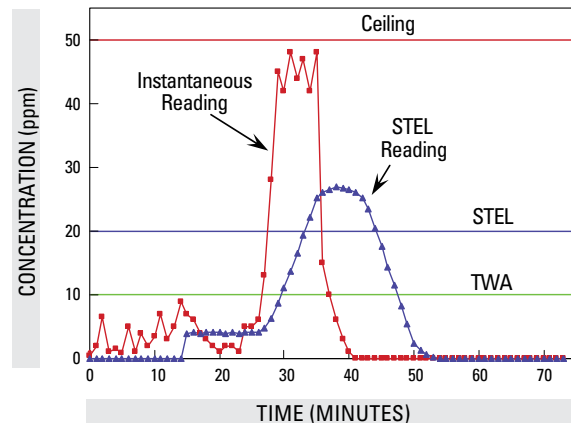


FIGURE 4.2.2. Exposure limit illustration: STEL

Figure 4.2.2 shows that the STEL reading tracks the instantaneous reading, except that it has a lag and is dampened. Once the STEL reading exceeds the STEL limit (at about 33 minutes in Figure 4.2.2), the exposure must be removed until the STEL reading drops below the limit again. At most, four such exposures may occur in a given working day, as long as there is at least one hour between consecutive cases exceeding the STEL limit. Note also in Figure 4.2.2 that the STEL reading is undefined until a 15-minute period has elapsed, and thus the reading is reported as zero.

The TWA is very different from all the other parameters because it is an accumulated exposure dose instead of an instantaneous concentration. Although the TWA is usually listed in units of ppm, which is a concentration unit, it is understood that the actual units are equivalent to ppm-days. It is calculated as the running average concentration times the number of hours exposed, divided by the hours in a working day. OSHA and ACGIH define the number of hours in a working day as 8 hours, while NIOSH uses 10 hours to define its recommended TWAs. Thus, if one is exposed to 20 ppm of a substance for two hours, the TWA reading is calculated as:

$$\text{TWA} = (2 \text{ h exposed} \times 20 \text{ ppm}) / (8 \text{ h/day}) = 5 \text{ ppm-days}$$

Figure 4.2.3 illustrates the difference between running average and the TWA readings. Like the STEL reading, the running average concentration (dashed line in Figure 4.2.3) tracks the instantaneous readings and can rise and fall. In contrast, the TWA is a cumulative dose that can never fall until it is reset to zero when the worker leaves work for the day. In Figure 4.2.3, it can be seen that the TWA reading rises steadily during the first 3.5 hours when some exposure occurs, and then from 3.5 to 5 hours, the concentration is zero and the TWA reading remains constant.

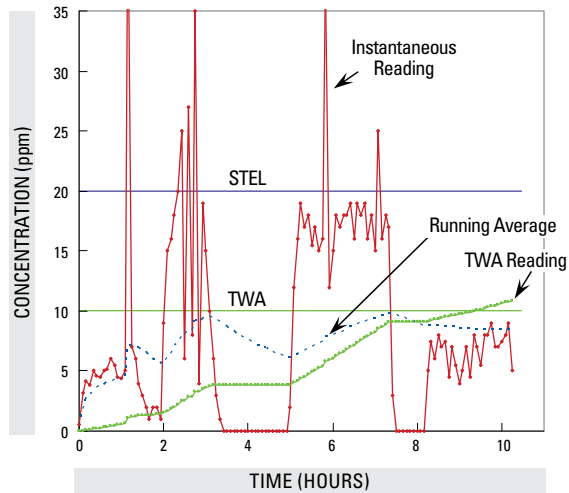


FIGURE 4.2.3. Exposure limit illustration: TWA vs. running average

After a full day (typically 8 hours), the TWA reading is equal to the running average. However, if work continues beyond the 8 hours, the TWA reading continues to accumulate and will exceed the running average. For very long exposures, it is even possible that the TWA reading is greater than the peak concentration for the exposure period, as shown in Figure 4.2.4.

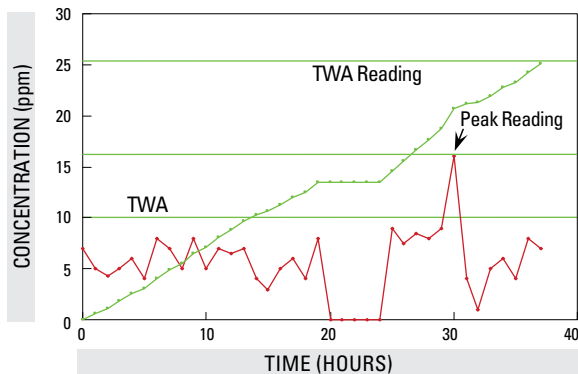


FIGURE 4.2.4. Exposure limit illustration: TWA exceeds peak

TWA and instantaneous concentrations are analogous to a recommended daily allowance of a food component such as fat and the rate at which it is eaten. Let's say the daily allowance is 100 grams. During breakfast one might

eat 20 grams, lunch 35 grams, and dinner 45 grams. During meals the rate of intake (i.e., concentration) is relatively high, and the amount eaten (TWA reading) rises steadily. Between meals, the rate of intake (concentration) drops to zero but the amount consumed (TWA reading) during the day remains constant. If a heavy lunch is taken and the amount of fat eaten (TWA reading) exceeds 100 g (TWA) already, then one needs to stop eating (remove the exposure).

4.2.2 TWA and STEL Datalogging

This section gives details on how TWAs, STELs and other concentration data are determined and datalogged by a PID.

The ability to datalog exposure concentrations, calculate TWA and STEL values, and download them to a personal computer affords a permanent record of the exposures that can be used for hygiene improvements and legal protection. It is also useful in correlating exposure levels with work activities and thus to modify work behavior to reduce subsequent exposure. Figure 4.2.5 and Table 4.2.1 show examples of datalog records for a miniature PID worn in the workers' breathing zone.

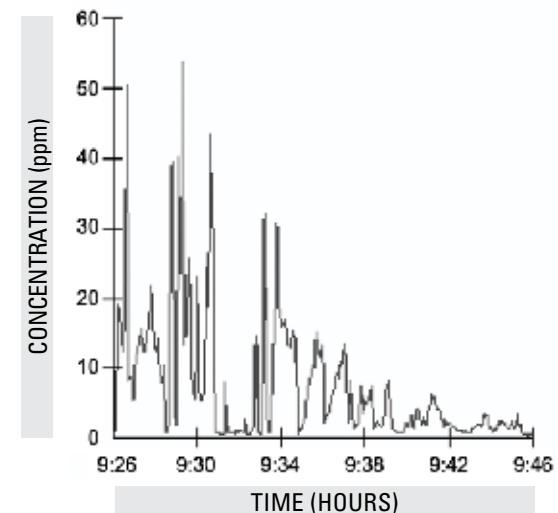


FIGURE 4.2.5. Real-time datalogging of vapor concentrations

TABLE 4.2.1 Example of logged data

Instrument: ToxiRAE (PGM30)		Serial Number: 001410			
User ID: 1	Site ID: 1				
Data Points: 28	Sample Period: 120 sec				
Last Calibration Time: 09/05/2001 18:31		Value: 100.0 ppm			
Last Check Time: 09/05/2001 18:47		Value: 100.1 ppm			
Measurement Type:	Min (ppm)	Avg (ppm)	Max (ppm)		
High Alarm Levels:	100.0	100.0	100.0		
Low Alarm Levels:	50.0	50.0	50.0		
Line#	Date	Time	Min (ppm)	Avg (ppm)	Max (ppm)
1	09/06/01	08:36	0.5	1.6	2.0
2	09/06/01	08:38	0.6	1.4	1.9
3	09/06/01	08:40	0.5	0.7	0.9
4	09/06/01	08:42	0.2	2.2	4.0
5	09/06/01	08:44	0.6	0.7	0.8
6	09/06/01	08:46	3.9	5.5	6.9
7	09/06/01	08:48	0.2	0.6	0.8
8	09/06/01	08:50	0.0	0.5	2.5
9	09/06/01	08:52	0.9	0.9	0.9
10	09/06/01	08:54	0.2	0.7	0.9
11	09/06/01	08:56	0.9	0.9	1.0
12	09/06/01	08:58	0.3	0.7	0.9
13	09/06/01	09:00	3.6	5.3	7.1
14	09/06/01	09:02	3.5	7.3	15.2
15	09/06/01	09:04	1.8	2.1	5.2
16	09/06/01	09:06	0.8	0.8	0.9
17	09/06/01	09:08	0.7	1.3	15.1
18	09/06/01	09:10	1.3	7.9	28.0
19	09/06/01	09:12	0.7	1.2	3.5
20	09/06/01	09:14	1.1	9.7	58.5L
21	09/06/01	09:16	0.7	14.0	51.3L
22	09/06/01	09:18	23.7	30.3	35.0
23	09/06/01	09:20	32.2	36.1	39.8
24	09/06/01	09:22	41.2	44.9	49.0
25	09/06/01	09:24	51.1L	75.4L	103.1H
26	09/06/01	09:26	4.8	74.3L	102.2H
27	09/06/01	09:28	0.6	1.0	4.6
28	09/06/01	09:30	0.6	0.7	0.8

Figure 4.2.5 shows that a worker is more severely exposed during the first 10 minutes of the datalog event than in the second 10 minutes, a fact that might be missed with badge measurements or if relying on the worker to record unusual concentrations manually. Table 4.2.1 is an example of data taken at a 2-minute sampling interval, showing that minimum, average, and maximum values during each interval can be recorded. The “L” and “H” next to some values warn the reader that the low and high alarm limits were exceeded. In this case, the record can be used to prove that these limits were exceeded only for short periods.

Example 1: Instantaneous warning for transient exposures

Adsorptive tests using activated charcoal or passive samplers average-out changes in concentration and therefore may underestimate short-term exposures. For example, suppose a nail salon is located in a storefront under a law office. Vapors periodically filter into the law office with every new nail salon customer. These transient exposures may exceed the 15-minute STEL, but the averaging by adsorptive sampling techniques would miss this short-term exposure. A PID can datalog these quick, high transient responses and help IAQ investigators quickly identify and solve the problem.

Example 2: Datalogging PIDs document exposure versus time

PID datalogged results can be used in conjunction with worker schedules or even video tracking to correlate elevated VOC levels with the type of worker operations. For example, consider an office building with a small print shop in the basement. During the winter, the building manager decided to save money by decreasing the amount of outside air introduced into the HVAC system so that the air in the building was recirculated. Over the course of a workday, the solvent vapors from the print shop built up in the building until they reached levels over the TWA limit. Workers in the building didn't smell the vapors because they had grown accustomed to them over the course of the workday (olfactory fatigue). The logged PID data elucidated the low solvent exposures in the morning coupled with the high exposures in the afternoon. Therefore, it was only necessary to increase ventilation in the afternoon when outdoor temperatures were higher, thus maintaining some energy and cost savings.

4.2.3 TWA and STEL Data Processing

This section gives details on how TWAs, STELs and other concentration data are determined and datalogged by a PID. The algorithms apply specifically to the ToxiRAE PID, Model PGM-30, but are similar on most other portable PIDs with datalogging features. Depending on the datalogging options chosen, there may be differences between the instantaneously displayed values and the final datalogged values, as described below. All averages are calculated as arithmetic, rather than geometric, averages.

Displayed Values

- **Second Values:** Every second, the signal is sampled for several milliseconds, and the data are averaged to give the instantaneous reading. This value is used for calculation of the Minute Value and then overwritten when the next instantaneous reading is made.
- **Minute Average:** The Second Values are added to a running sum, and every minute this sum is divided by 60 to obtain a minute average. The Minute Average is not displayed, but is used to calculate the TWA and STEL.
- **STEL:** The Minute Average values are stored in a rolling buffer for 15 minutes to calculate the STELs and then overwritten. The STEL is updated every minute as an average of the most recent fifteen Minute Averages.
- **TWA:** The Minute Average values are also used to update the TWA every minute, by adding to a running sum and dividing by the number of minutes in an 8-hour day (480). The TWA is the value accumulated from the time the instrument is turned on until the time of the last Minute Average; it assumes no further exposure from then on. The TWA continues to accumulate after eight hours until the instrument is turned off.
- **Peak Value:** The Peak Value is updated every second and is the highest measured Second Value since the unit was turned on.
- **Running Average:** Some instruments store a running average in addition to (or instead of) a TWA. The running average is simply the arithmetic average of the concentration since the instrument or datalogging session was turned on.

Logged Values

The instrument software downloads minimum, average, and/or maximum values within a defined datalogging period. The datalogging period is defined as a time interval within the total datalogging event. The user programs the datalogging period, typically in one-second increments from one second up to one hour.

- The Minimum Value is the lowest Second Value measured during each datalogging period.
- The Average Value is the arithmetic average of all Second Values measured during each datalogging period.
- The Maximum Value is the highest Second Value measured during each datalogging period.
- The STEL is calculated as the average of the maximum logged results of the previous fifteen-minute window:

$$\frac{\sum (\text{All max logged values in last 15 min})}{\# \text{ values in 15 min} = (15 * 60) / \text{period (sec)}}$$

- The TWA is calculated as:

$$\frac{\text{Previous TWA} + \text{max logged value} * \text{period (sec)}}{480 * 60}$$

STEL and TWA values are sometimes not downloaded directly, but may be recalculated from the downloaded minimums, averages or maximums. Therefore, the logged values can be different from the displayed values if inappropriate datalogging parameters are chosen. The program often uses the highest values available to calculate the TWA and STEL. To ensure that the displayed and logged values are identical, the user should chose a datalogging period of 15 minutes or less. It is also suggested that the user log average only or average and minimum values, but not peak values.

Example 3: Typical Results

Table 4.2.2. gives an example of datalogged results showing TWA and STEL values. TWA values always increase because they are cumulative values, even though average concentrations may decrease. STEL values are calculated

correctly because the datalog period is <7.5 minutes and divides evenly into fifteen. The first 14 minutes of STEL values are not valid and always increase because they assume zero concentration before the first time-point. After 15 minutes, STEL values are correct.

Example 4: Datalog Period Too Short

Table 4.2.3 shows datalogged values that give incorrect STEL values due to data processing. In this example, the STEL does not average the most recent 15-minute window correctly. This is because STEL cannot be back-calculated correctly from the stored values when the datalog period is >7.5 minutes.

TABLE 4.2.2. Datalogged results showing TWA and STEL values

S/N: 001403		User ID: 1		Site ID: 1		Cal: 9/20 16:56		00.4 ppm	
Year: 2001		Period(s): 60		Data Pts: 20		Chk: 9/20 14:40		100.5 ppm	
Date	Time	Min	Avg ppm	Max	High 100.0	Low 50.0	STEL 25.0	TWA 10.0	
11/05	10:52	-	10.7	-			0.7	0.0	
	10:53	-	9.7	-			1.4	0.0	
	10:54	-	8.7	-			1.9	0.1	
	10:55	-	8.0	-			2.5	0.1	
	10:56	-	7.4	-			3.0	0.1	
	10:57	-	7.0	-			3.4	0.1	
	10:58	-	6.7	-			3.9	0.1	
	10:59	-	6.4	-			4.3	0.1	
	11:00	-	6.2	-			4.7	0.1	
	11:01	-	6.0	-			5.1	0.2	
	11:02	-	5.8	-			5.5	0.2	
	11:03	-	5.7	-			5.9	0.2	
	11:04	-	5.5	-			6.3	0.2	
	11:05	-	5.4	-			6.6	0.2	
	11:06	-	5.3	-			7.0	0.2	
	11:07	-	5.2	-			6.6	0.2	
	11:08	-	5.1	-			6.3	0.2	
	11:09	-	5.0	-			6.0	0.2	
	11:10	-	4.9	-			5.8	0.3	
	11:11	-	4.8	-			5.7	0.3	

TABLE 4.2.3. Datalogged results showing incorrect STEL values

S/N: 001403		User ID: 1		Site ID: 1		Cal: 6/20 45:29		106.6 ppm	
Year: 2001		Period(s): 600		Data Pts: 10		Chk: 4/3 15:41		100.3 ppm	
Date	Time	Min	Avg ppm	Max	High 100.0	Low 50.0	STEL 25.0	TWA 10.0	
5/10	11:24	-	2.7	3.6			3.6	0.1	
	11:34	-	1.7	2.7			2.7	0.2	
	11:44	-	1.6	2.7			2.7	0.2	
	11:54	-	2.2	4.4			4.4	0.3	
	12:04	-	3.9	4.6			4.6	0.4	
	12:14	-	4.1	5.4			5.4	0.5	
	12:24	-	2.9	3.8			3.8	0.6	
	12:34	-	1.4	1.9			1.9	0.6	
	12:44	-	2.2	4.0			4.0	0.7	
	12:54	-	3.0	3.9			3.9	0.8	

4.3 PIDs for Hazardous Materials Spill Response

Many HazMat (Hazardous Material) incidents involve spills or releases of VOCs that vaporize. Until recently, emergency responders were primarily concerned with the immediate hazards of the release or fire, including oxygen depletion, CO toxicity, and explosivity. Therefore, most responders relied on CO and O₂ electrochemical sensors and combustible gas detectors for broadband organic vapor detection. However, increasing awareness of the long-term toxicity of the many VOCs has led to a rapid growth in use of PIDs for HazMat response, either as stand-alone instruments or in combination with the other sensors listed above. PIDs measure VOCs at low ppm levels that can be toxic but are not detectable by standard LEL sensors. Also, recent improvements in PID ruggedness, reliability and affordability have made them more accessible to local HazMat teams. PID's are a valuable tool for making HazMat decisions including:

- Initial PPE assessment
- Leak detection
- Perimeter establishment and maintenance
- Spill delineation
- Decontamination
- Remediation

Because of these developments, more HazMat responders may want to consider adding PIDs to their inventory of gas monitors.

Common HazMat VOCs

Chemicals commonly encountered in hazardous material releases are the same as those that are commonly used in industry, including:

- Fuels
- Solvents, paints
- Heat transfer fluids
- Degreasers
- Plastics, resins and their precursors
- Oils, lubricants

Initial PPE Assessment

When approaching a potential HazMat incident, the responder must make a personal protective equipment (PPE) decision. Some potential incidents may not be an “incident” at all and may not require any PPE. Some incidents may initially appear to have no contamination yet require significant levels of PPE. PIDs are useful aids in this decision-making process.

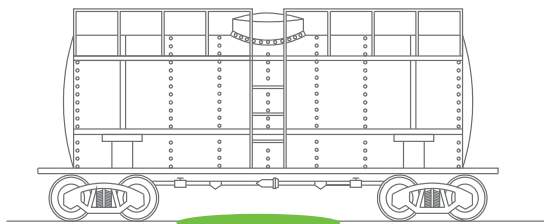


FIGURE 4.3.1. Apparently leaking benzene rail car

For example, a HazMat contractor was called by a railroad company to respond to a leaking tank car on a hot (95°F), humid (95%RH) summer day. According to the manifest, the tank car was loaded with benzene. Due to the carcinogenic nature of benzene (PEL of 1 ppm) the HazMat contractor chose to dress-out in Level A. However, because it was a hot summer day, this potentially exposed the responders to heat stress injuries. In the assessment of the “leaking” tank car it was found that the puddle under the car was coming from condensation, not dripping benzene. The car had been loaded

at 65° F and the high relative humidity coming into contact with the cool rail car produced a puddle of water from condensation, which was mistaken as a benzene leak.

Using a PID would have helped the contractor quickly rule out the presence of benzene vapors, reducing the cost of the response and preventing the potential of heat-stress injuries from dressing in full Level A encapsulation.

Leak Detection with a PID

A leak is often not readily apparent and must first be located before it can be effectively stopped. As the gas or vapor disperses and dilutes, a concentration gradient is established with the highest concentration at the source and decreasing outwardly until it can no longer be detected. The PID can be used like a Geiger Counter to quickly follow the concentration gradient to the vapor source.

“See” the Concentration Gradient

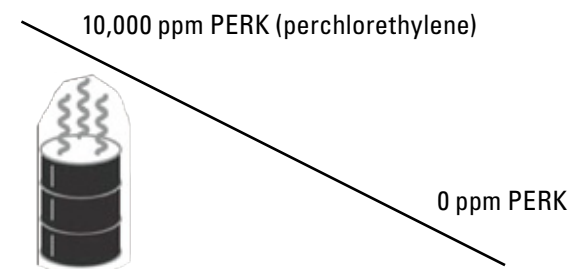


FIGURE 4.3.2. Concentration gradient from a vapor source

Perimeter Monitoring with a PID

HazMat technicians assess the incident and set a perimeter based upon the toxicity of the gas or vapor, the temperature, wind direction, and other factors. However, perimeters are usually manned by personnel without a high degree of experience.

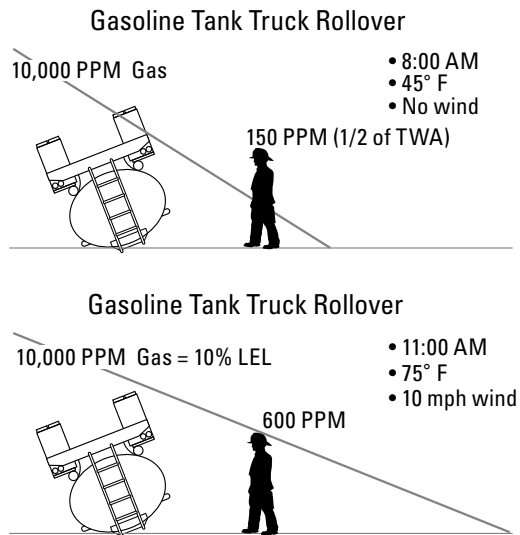


FIGURE 4.3.3. Perimeter variation due to changing weather conditions

As conditions change, perimeters often are not adjusted because perimeter workers do not have the experience to recognize that the conditions have changed. The experienced HazMat technicians are typically focused upon the problem of dealing with complications of the original spill. Therefore, perimeter workers are often unprotected from changing conditions that may require movement of a perimeter away from the spill site. For many HazMat incidents, a PID allows those manning a perimeter line to adjust the line in response to changing conditions. PIDs can provide instantaneous alarms that warn perimeter workers when to retreat from the incident.

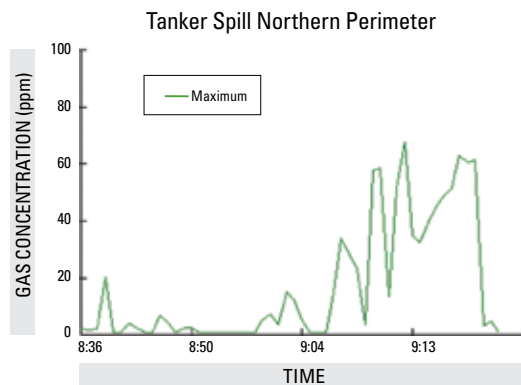


FIGURE 4.3.4. Datalogged PID response at a HazMat incident perimeter

Datalogging as a Tool

Datalogging PIDs provide supervisors with documentation of exposure levels and provide evidence to justify evacuations, should they be required. Some HazMat teams already datalog their incidents where there has been a chemical release.

However, most teams only datalog those incidents when the datalog showed positive results. This misses more than half of the value of datalogging. Many times a negative result on a datalog is more beneficial than a positive result, as it can later prove that a spill of an ionizable compound was promptly and properly contained. This can save time and money if the spill ever results in legal action.

PIDs for Spill Delineation

In the course of a HazMat incident many liquids can be present, such as water, fuel, engine fluids and firefighting foam. As described previously for the benzene rail car, PIDs allow responders to distinguish the released chemical from water, saving both time and absorbent. It also helps delineate a spill where the chemical adsorbed to surfaces and not clearly visible.

PIDs can help separate the “water” from the “oil,” so that limited absorbent can be efficiently used on just the diesel spill

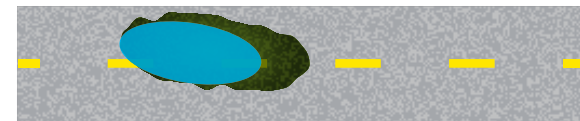


FIGURE 4.3.5. Delineating a spill

Using a PID for Decontamination

After a HazMat incident clothing and PPE may require decontamination of the hazardous materials. For ionizable compounds like fuels and other VOCs, PIDs provide a quick and effective means of determining if materielle require decontamination, and if the decontamination is complete. A PID is swept over areas of suspected contamination will respond positively to areas that are contaminated with ionizable compounds and it will not respond to clean or properly decontaminated areas.



PIDs can help answer these questions:

- Is the worker contaminated?
- Is decontamination complete?
- Can we reuse the suit?
- Is my turn-out contaminated with fuel products?

FIGURE 4.3.6. PID for decontamination monitoring

Often a first responder to a fuel spill incident gets gasoline on his flame-retardant turnout clothing. Absorbed gasoline compromises the flame-retardant properties of turnout gear. A PID quickly responds to contamination and identifies this dangerous condition so that the turnout gear can be properly laundered before going into a structural firefighting situation. This same sensitivity to hydrocarbons makes PIDs ideally suited to arson investigations.

Using a PID for Remediation

While the goal of any HazMat response team is to contain and prevent spills, hazardous materials often evade containment, contaminating nearby soil and water. Many jurisdictions (counties, states, countries) have defined the concentration at which remediative action must take place. If there has been a fuel spill that has been contained to the road surface and it has been completely removed by absorbent, further remediative action may not be required. However, if fuel product has evaded the best efforts for containment, the fuel may have contaminated the surrounding soil or water. Some jurisdictions have an action level of 100 ppm TPH (Total Petroleum Hydrocarbons) in a sample headspace for further remediation. If soil samples show only 10 ppm of contamination in the headspace of a sample, remediation may not be required. Soil samples of 200 ppm would require further remediation. The usefulness of PIDs for environmental remediation is described in Chapter 4.1.

4.4 Using PIDs For LEL Measurements

One of the many requirements for entering confined spaces (OSHA Standard 29 CFR 1910.146) is that the level of flammable gases be below 10% of LEL (Lower Explosive Limit). The most common sensor used for measuring LEL is the Wheatstone bridge/catalytic bead/pellistor sensor. However, catalytic bead LEL sensors have poor sensitivity to high-molecular-weight compounds. Furthermore, they are subject to deactivation by commonly present chemicals including silicones, sulfur compounds, chlorinated solvents, leaded gasoline, and phosphorous compounds. In these circumstances, PIDs provide an alternate, accurate means of measuring 10% of LEL for confined space entry. A notable exception to this is that there is no response to methane, and a PID should not be used for LEL judgments if methane approaching LEL levels may be present. Some examples are described below.

Aircraft Maintenance: Jet Fuels & Solvents

Many commercial and military aircraft maintenance programs are standardizing on PIDs for confined space entry into wingtanks. Catalytic bead LEL sensors have poor sensitivity to low-vapor-pressure jet fuels, and are readily poisoned by the silicones present in many chemicals used, including hydraulic fluids and sealants. 10% of LEL for jet fuel is approximately 800 ppm. Because jet fuel standards are not readily available, PIDs can be calibrated with hexane or isobutylene and set to read in units of jet fuel by internally applying a correction factor. The PID alarm is set to 800 in units of jet fuel. This setting provides 10% LEL protection not only for jet fuels, but also for most other flammable liquids used in aircraft maintenance, including aromatics and ketones.

Pulp & Paper Plant: Turpentine

Turpentine is a low-vapor-pressure/high flash point flammable liquid that is difficult to measure with a catalytic bead LEL sensor. The mercaptans and sulfides present in pulp mills can deactivate the sensor. An experienced worker measured a confined space prior to a welding operation in a paper plant and detected no flammable vapors. However, the welding operation ignited turpentine vapors that went undetected by the properly functioning and calibrated catalytic bead LEL sensor. This facility subsequently

standardized on PIDs with a high alarm set to 800 ppm (10% of LEL) for confined space entries.

Deodorant Filling Plant: Acute Silicone Poisoning

In addition to flammable solvents and propellants, deodorants contain sizable amounts of silicone compounds. Catalytic bead LEL sensors typically last days or weeks in these applications. PID optics are unaffected by these conditions and provide a reliable tool for 10% of LEL measurement. Due to the nature of some propellants, 11.7 eV lamps may be needed. While an 11.7 eV lamp does not last as long as the standard 10.6 eV PID lamp, it can last longer than catalytic bead sensors in these environments.

Gasoline Tank Remediation: TEL Poisoning

Tetraethyllead (TEL) historically was used as an octane booster in gasolines but is no longer allowed in the US because of its human toxicity. However, TEL still can be found in old underground storage tanks and contaminated sites. One contractor repeatedly replaced LEL sensors until it was determined that the old tanks contained trace amounts of TEL. For underground work it is important to use a catalytic bead LEL sensor because of the possible presence of methane, which PIDs cannot measure. But the most immediate threat during the tank remediation is gasoline flammability, and the PID provides consistent, reliable results even when TEL is present.

Styrene Plants: Chronic Styrene Poisoning

Styrene monomer can polymerize on hot catalytic bead LEL sensors, gradually rendering them inoperable. Exposure to clean air can help to reverse this process, but air that is completely free of styrene is rarely found in plants producing styrene. Therefore, catalytic bead LEL sensors have short lives in these facilities. PIDs have been used in many styrene plants to provide continuous monitoring of styrene vapors for daily exposure limits (20, 50, and 100 ppm for AGCIH, NIOSH, and OSHA, respectively). A high PID alarm of 900 ppm in styrene units provides a convenient, reliable alarm for 10% LEL also, without the need for a second instrument.

Setting PID Alarms for 10% LEL

Table 4.4.1 lists 128 NFPA 325 chemicals and 178 total flammable chemicals. The table shows the concentration of the compound in ppm at 10% of the LEL, in column 5. The rightmost column shows the equivalent PID reading when the unit is calibrated to isobutylene with a 10.6 eV lamp (calculated as 10% LEL/CF). When the alarm is set to the 10% LEL equivalent value for any chemical, it provides a warning also for all other chemicals on the list that are above it. The unit alarms at <10% LEL for these chemicals. A PID set to the following alarms and not beeping provides 10% of LEL protection for:

- 1000 ppm alarm: 75 NFPA 325 chemicals, including major solvents like xylene, toluene, acetone, and MEK, MPK.
- 500 ppm alarm: 96 NFPA 325 chemicals, from isobutyl acetate to vinyl bromide.
- 250 ppm alarm: 116 NFPA 325 chemicals, from n-hexane to vinyl bromide.
- 100 ppm alarm: 126 NFPA 325 chemicals, from naphtha to vinyl bromide.

For most common industrial chemicals, a setpoint of 1000 ppm in isobutylene units is an appropriate alarm for 10% of LEL. This will provide a conservative setpoint for all liquid fuel products, aromatics (benzene, styrene, xylene, etc.), ketones (MEK, MIBK, etc) and many other common industrial chemicals. Some chemicals, like the alcohols, require more conservative setpoints. Of course, setting an alarm to 100 ppm would provide the highest level of protection, but also a greater tendency for false alarms.

TABLE 4.4.1. 10% LEL response for NFPA chemicals by PID

Note: NFPA 325 Chemicals are in *Italics*

Chemical Name	10.6 eV CF	LEL (Vol %)	LEL (ppm)	10% LEL (ppm)	10% LEL Response w/IBE Calibration
<i>Vinyl bromide</i>	0.40	9	90000	9000	22500
Dichloroethene, t-1,2-	0.45	9.7	97000	9700	21600
<i>Trichloroethylene</i>	0.54	8	80000	8000	14800
Dichloroethene, c-1,2-	0.8	9.7	97000	9700	12100
<i>Vinylidene chloride</i>	0.82	6.5	65000	6500	7900
<i>Methyl mercaptan</i>	0.54	3.9	39000	3900	7200
<i>Tetraethyl lead (as Pb)</i>	0.3	1.8	18000	1800	6000
Methyl bromide	1.7	10	100000	10000	5900
Dimethyl disulfide	0.20	1.1	11000	1100	5500
<i>Trichlorobenzene, 1,2,4-</i>	0.46	2.5	25000	2500	5400
Methyl sulfide	0.44	2.2	22000	2200	5000
<i>Ethyl mercaptan</i>	0.56	2.8	28000	2800	5000
<i>Dichlorobenzene, o-</i>	0.47	2.2	22000	2200	4700
<i>Ethylamine</i>	0.8	3.5	35000	3500	4400
Ethyl sulfide	0.51	2.2	22000	2200	4300
Methylamine	1.2	4.9	49000	4900	4100
<i>Methylstyrene, alpha-</i>	0.50	1.9	19000	1900	3800
Hexamethyldisilazane, 1,1,1,3,3,3-	0.24	0.8	8000	800	3300
<i>Chlorobenzene</i>	0.40	1.3	13000	1300	3300
Bromopropane, 1-	1.5	4.6	46000	4600	3100
<i>Dimethylformamide, N,N-</i>	0.7	2.2	22000	2200	3100
3000 ppm Alarm ↑					
Toluidine, o-	0.50	1.5	15000	1500	3000
Mesitylene	0.35	1	10000	1000	2900
<i>Xylene, p-</i>	0.39	1.1	11000	1100	2800
<i>Aniline</i>	0.48	1.3	13000	1300	2700
<i>Pyridine</i>	0.68	1.8	18000	1800	2600
<i>Pinene, a-</i>	0.31	0.8	8000	800	2600
<i>Diacetone alcohol</i>	0.70	1.8	18000	1800	2600
<i>Dimethylhydrazine, 1,1-</i>	0.78	2	20000	2000	2600
<i>Xylene, m-</i>	0.44	1.1	11000	1100	2500
<i>Isoprene</i>	0.63	1.5	15000	1500	2400
<i>Butadiene</i>	0.85	2	20000	2000	2400
<i>Trimethylamine</i>	0.85	2	20000	2000	2400
<i>Turpentine</i>	0.35	0.8	8000	800	2300
<i>Furfural</i>	0.92	2.1	21000	2100	2300
<i>Acetone</i>	1.1	2.5	25000	2500	2300
<i>Benzene</i>	0.53	1.2	12000	1200	2300

Chemical Name	10.6 eV CF	LEL (Vol %)	LEL (ppm)	10% LEL (ppm)	10% LEL Response w/IBE Calibration
<i>Dimethyl acetamide, N,N-</i>	0.80	1.8	18000	1800	2300
<i>Styrene</i>	0.40	0.9	9000	900	2300
<i>Toluene</i>	0.50	1.1	11000	1100	2200
<i>Vinyl acetate</i>	1.2	2.6	26000	2600	2200
<i>Naphthalene</i>	0.42	0.9	9000	900	2100
<i>Monomethyl hydrazine</i>	1.2	2.5	25000	2500	2100
<i>Benzoyl chloride</i>	0.6	1.2	12000	1200	2000
<i>Xylene, o-</i>	0.46	0.9	9000	900	2000
Dichloro-1-propene, 2,3-	1.3	2.6	26000	2600	2000
Diethylenetriamine	1.0	2	20000	2000	2000
<i>Crotonaldehyde</i>	1.1	2.1	21000	2100	1900
<i>Ethanolamine</i>	1.6	3	30000	3000	1900
Methyl t-butyl ether	0.91	1.7	17000	1700	1900
<i>Dimethylamine</i>	1.5	2.8	28000	2800	1900
<i>Diethylamine</i>	0.97	1.8	18000	1800	1900
Xylenes (o-, m-, p-isomers)	0.49	0.9	9000	900	1800
<i>Benzyl chloride</i>	0.60	1.1	11000	1100	1800
Ethyl silicate	0.71	1.3	13000	1300	1800
<i>Dioxane, 1,4-</i>	1.1	2	20000	2000	1800
Isobutylene	1.0	1.8	18000	1800	1800
<i>Phenol</i>	1.0	1.8	18000	1800	1800
<i>Vinyl chloride</i>	2.0	3.6	36000	3600	1800
<i>Butene, 1-</i>	0.90	1.6	16000	1600	1800
<i>Isopropyl ether</i>	0.80	1.4	14000	1400	1750
<i>Vinyl-2-pyrrolidinone, 1-</i>	0.80	1.4	14000	1400	1750
<i>Diethyl ether</i>	1.1	1.9	19000	1900	1700
<i>Benzyl cyanide</i>	0.60	1	10000	1000	1700
Dicyclopentadiene	0.48	0.8	8000	800	1700
<i>Cumene</i>	0.54	0.9	9000	900	1700
<i>Gasoline #1</i>	0.85	1.4	14000	1400	1600
<i>Methyl ethyl ketone</i>	0.86	1.4	14000	1400	1600
Cyclohexene	0.80	1.3	13000	1300	1600
Methyl-2-pyrrolidinone, N-	0.80	1.3	13000	1300	1600
<i>Pentanone, 2- (Methyl propyl ketone)</i>	0.93	1.5	15000	1500	1600
<i>Propylene glycol monomethyl ether acetate (PGMEA)</i>	1.0	1.6	16000	1600	1600
Petroleum distillates	0.7	1.1	11000	1100	1600
<i>Ammonia</i>	9.7	15	150000	15000	1500
<i>Butylamine, n-</i>	1.1	1.7	17000	1700	1500
<i>Ethyl benzene</i>	0.52	0.8	8000	800	1500

Chemical Name	10.6 eV CF	LEL (Vol %)	LEL (ppm)	10% LEL (ppm)	10% LEL Response w/IBE Calibration
1500 ppm Alarm ↑					
Hexene, 1-	0.80	1.2	12000	1200	1500
Methyl isobutyl ketone	0.80	1.2	12000	1200	1500
<i>Diisopropylamine</i>	0.74	1.1	11000	1100	1500
Piperylene, isomer mix	0.69	1	10000	1000	1400
Picoline, 3-	0.90	1.3	13000	1300	1400
<i>Propene</i>	1.4	2	20000	2000	1400
Gasoline #2, 92 octane	1.0	1.4	14000	1400	1400
Dichloro-1-propene, 1,3-	0.96	1.3	13000	1300	1400
<i>Jet fuel JP-5</i>	0.6	0.8	8000	800	1300
<i>Jet fuel JP-8</i>	0.6	0.8	8000	800	1300
Methoxyethoxyethanol, 2-	1.2	1.6	16000	1600	1300
<i>Chloroprene, beta-</i>	3.0	4	40000	4000	1300
<i>Triethylamine</i>	0.90	1.2	12000	1200	1300
Ethoxyethanol, 2- (Cellosolve)	1.3	1.7	17000	1700	1300
<i>Jet fuel JP-4</i>	1.0	1.3	13000	1300	1300
Cyclohexylamine	1.2	1.5	15000	1500	1300
Methylcyclohexane	0.97	1.2	12000	1200	1200
<i>Cyclohexanone</i>	0.90	1.1	11000	1100	1200
<i>Hydrogen sulfide</i>	3.3	4	40000	4000	1200
<i>Diesel Fuel #2</i>	0.66	0.8	8000	800	1200
Propionaldehyde	1.9	2.3	23000	2300	1200
<i>Benzyl alcohol</i>	1.1	1.3	13000	1300	1200
<i>Tetrahydrofuran</i>	1.7	2	20000	2000	1200
<i>Kerosene (Jet Fuel)</i>	0.6	0.7	7000	700	1200
<i>Methyl isocyanate</i>	4.6	5.3	53000	5300	1200
<i>Propylene glycol monomethyl ether</i>	1.4	1.6	16000	1600	1100
<i>Methyl methacrylate</i>	1.5	1.7	17000	1700	1100
<i>Stoddard Solvent</i>	0.71	0.8	8000	800	1100
<i>Hydrazine</i>	2.6	2.9	29000	2900	1100
<i>Methyl ether</i>	3.1	3.4	34000	3400	1100
<i>Carbon disulfide</i>	1.2	1.3	13000	1300	1100
Diethylaminopropylamine, 3-	1.3	1.4	14000	1400	1100
Isopar M Solvent	0.66	0.7	7000	700	1100
<i>Allyl alcohol</i>	2.4	2.5	25000	2500	1000
<i>Nicotine</i>	0.70	0.7	7000	700	1000
Phenyl ether	0.70	0.7	7000	700	1000
1000 ppm Alarm ↑					
<i>Nitrobenzene</i>	1.9	1.8	18000	1800	950
Cyclohexane	1.4	1.3	13000	1300	930

Chemical Name	10.6 eV CF	LEL (Vol %)	LEL (ppm)	10% LEL (ppm)	10% LEL Response w/IBE Calibration
Butoxyethanol, 2-	1.2	1.1	11000	1100	920
Isooctane	1.2	1.1	11000	1100	920
<i>Dichloroethyl ether</i>	3.0	2.7	27000	2700	900
Benzonitrile	1.6	1.4	14000	1400	880
Diesel Fuel #1	0.93	0.8	8000	800	860
<i>Diphenyl (Biphenyl)</i>	0.70	0.6	6000	600	860
<i>Bromobenzene</i>	0.60	0.5	5000	500	830
<i>Butyl alcohol, tert-</i>	2.9	2.4	24000	2400	830
<i>Diethanolamine</i>	2.0	1.6	16000	1600	800
<i>Methyl acrylate</i>	3.7	2.8	28000	2800	760
Butyl acetate, tert-	2.0	1.5	15000	1500	750
Methoxyethanol, 2-	2.4	1.8	18000	1800	750
Ethyl hexyl acrylate, 2-	1.1	0.8	8000	800	730
<i>Acrolein</i>	3.9	2.8	28000	2800	720
Caprolactam	2.0	1.4	14000	1400	700
<i>Isopropyl acetate</i>	2.6	1.8	18000	1800	690
<i>Allyl chloride</i>	4.3	2.9	29000	2900	670
<i>Acetaldehyde</i>	6.0	4	40000	4000	670
<i>Butyl acetate, n-</i>	2.6	1.7	17000	1700	650
<i>Toluene-2, 4-diisocyanate (TDI)</i>	1.4	0.9	9000	900	640
<i>Ethyl acrylate</i>	2.4	1.4	14000	1400	580
Decane	1.4	0.8	8000	800	570
<i>Nonane</i>	1.4	0.8	8000	800	570
<i>Butyl acetate, sec-</i>	3.0	1.7	17000	1700	570
<i>Octane, n-</i>	1.8	1	10000	1000	560
<i>Isobutyl acetate</i>	2.6	1.3	13000	1300	500
500 ppm Alarm ↑					
<i>Propyl acetate, n-</i>	3.5	1.7	17000	1700	490
Hexanol, 1-	2.5	1.2	12000	1200	480
<i>Amyl acetate, n-</i>	2.3	1.1	11000	1100	480
<i>Isoamyl acetate</i>	2.1	1	10000	1000	480
<i>Propylene glycol</i>	5.5	2.6	26000	2600	470
<i>Methyl acetate</i>	6.6	3.1	31000	3100	470
Ethyl (S)-(-)-lactate	3.2	1.5	15000	1500	470
Phosphine	3.9	1.79	17900	1790	460
<i>Isobutyl alcohol</i>	3.8	1.7	17000	1700	450
<i>Epichlorohydrin</i>	8.5	3.8	38000	3800	450
<i>Acetic Anhydride</i>	6.1	2.7	27000	2700	440
<i>Propyl alcohol, n-</i>	5	2.2	22000	2200	440
<i>Amyl acetate, sec-</i>	2.3	1	10000	1000	440
<i>Ethyl acetate</i>	4.6	2	20000	2000	440

Chemical Name	10.6 eV CF	LEL (Vol %)	LEL (ppm)	10% LEL (ppm)	10% LEL Response w/IBE Calibration
<i>Butyl alcohol, sec-</i>	4.0	1.7	17000	1700	430
<i>Heptane, n-</i>	2.8	1.05	10500	1050	380
<i>Propylene oxide</i>	6.5	2.3	23000	2300	350
<i>Isopropyl Alcohol</i>	6.0	2	20000	2000	330
<i>Ethyl alcohol</i>	10	3.3	33000	3300	330
<i>Naphtha (Coal tar) {10% aromatics}</i>	2.8	0.9	9000	900	320
Undecane	2.0	0.6	6000	600	300
<i>Butyl alcohol, n-</i>	4.7	1.4	14000	1400	300
<i>Ethene</i>	9	2.7	27000	2700	300
<i>Hexane, n-</i>	4.3	1.1	11000	1100	260
250 ppm Alarm ↑					
<i>Amyl alcohol</i>	5.0	1.2	12000	1200	240
<i>Amyl alcohol, sec-</i>	5.0	1.2	12000	1200	240
<i>Ethylene oxide</i>	13	3	30000	3000	230
<i>Acrylic Acid</i>	12	2.4	24000	2400	200
<i>Ethylene glycol</i>	16	3.2	32000	3200	200
<i>Acetic Acid</i>	22	4	40000	4000	180
<i>Dimethyl sulfate</i>	20	3.6	36000	3600	180
<i>Pentane</i>	8.4	1.5	15000	1500	180
<i>Isopentane, & all isomers</i>	8.2	1.4	14000	1400	170
<i>Naphtha (Coal tar) {purely aliphatic}</i>	5.7	0.9	9000	900	160
100 ppm Alarm ↑					
Propylene carbonate	62	1.8	18000	1800	29
<i>Butane</i>	67	1.6	16000	1600	24
<i>Isobutane</i>	100	1.6	16000	1600	16

4.5 Dual Lamp Measurements for Enhanced Specificity in Variable Mixtures

In some cases of two-component mixtures whose component ratios may vary, it is possible to measure one component in the presence of another if they have different sensitivities on different lamps. The same principle applies to three-component mixtures using three lamps, although these will not be treated here because of their impracticality. The response to a mixture can be calculated as:

$$R_T^{9.8} = \frac{C_1}{CF_1^{9.8}} + \frac{C_2}{CF_2^{9.8}}$$

$$R_T^{10.6} = \frac{C_1}{CF_1^{10.6}} + \frac{C_2}{CF_2^{10.6}}$$

where R_T^n is the total response on lamp n in isobutylene equivalents and CF_X^n is the correction factor for compound X on lamp n . All the factors are known except for C_1 and C_2 , and therefore the concentrations can be determined using simple algebra for two equations in two unknowns. Examples of this calculation are given in Appendix 7 and below in Example 1.

Example 1. Measuring CS₂ in the Presence of H₂S.

Both CS₂ and H₂S respond on a 10.6 eV lamp with CFs of 1.2 and 3.3, respectively (See Appendix 3). The CS₂ can be measured selectively using a 9.8 eV lamp (CF = 4) without interference from the H₂S. Thus, if only the concentration of CS₂ is needed, measuring with a 9.8 eV lamp alone is sufficient. However, both components can be determined by using both 9.8 and 10.6 eV on the same gas sample.

For example, if the total response with the 9.8 eV lamp is 3 ppm IBE equivalents, and the response on the 10.6 eV lamp is 18 ppm IBE equivalents, then:

- The concentration of CS₂ is $3 \times CF_{9.8} = 3 \times 4 = 12$ ppm CS₂.
- The contribution by CS₂ on the 10.6 eV lamp response is:
 $12/CF_{10.6} = 12/1.2 = 10$ ppm IBE equivalents
- The response of the H₂S on the 10.6 eV lamp is the remainder:
 $18 - 10 = 8$ ppm IBE equivalents
- The concentration of H₂S is $8 \times CF_{10.6} = 8 \times 3.3 = 26.4$ ppm H₂S.

In summary, the 12 ppm CS₂ plus 26.4 ppm H₂S give a response of 3 ppm on the 9.8 eV lamp and 18 ppm on the 10.6 eV lamp.

Note that it is not correct to simply subtract the response of the 9.8 eV lamp from that of the 10.6 eV lamp, even if both lamps were calibrated directly to CS₂, because H₂S has a different CF than CS₂ on both lamps.

4.6 Volatile Emissions from Paint

Paints are a special case of the mixtures described in previous sections, because they contain a large fraction of non-volatile materials, such as titania, silica, and organic polymers. These non-volatile components are the residues left behind on the painted surface that provide the protective and decorative coating. Typically a Material Safety Data Sheet (MSDS) for the paint will provide the percentage by weight of all the components, not just the volatile ones detectable by PID. In this section, we work through some examples of how to estimate correction factors and set alarm limits for paints based on the percentages provided on an MSDS.

In this analysis, it is often necessary to make some assumptions because the exact composition is often not defined in the MSDS.

Example 1 – Nonvolatile Paint Component

There is a spill of Part B of the topcoat Interthane 870, consisting of:

TABLE 4.6.1. Composition of Interthane 870 Part B

Component	MSDS Wt. %	Estimated Actual Weight % of Total	Weight % of Volatiles
Homopolymer of HMDI	50-100	70	-
Trimethylbenzene	10-25	15	50
Aromatic Hydrocarbons	10-25	10	33
Xylene	1-10	5	17
Total	72-160	100	100

TABLE 4.6.2. Conversion of Wt.% to Mole% for Part B volatiles

Component	Wt. %	m.w. (g/mol)	(Wt.%)/(m.w.) (mol/g liq)	mol %
Trimethylbenzene	50	120.2	0.416	47.9
Aromatic Hydrocarbons	33	~113	0.292	33.6
Xylene	17	106.2	0.16	18.4
Total	100	-	0.868	99.9

It is immediately clear that a number of assumptions need to be made. First, the isomers of trimethylbenzene and xylene are not specified. These have slightly different CFs and exposure limits and therefore an average or typical value must be assumed. Second, it is assumed that the aromatic hydrocarbons are different from trimethylbenzene and xylene, because they are listed separately. Third, in the absence of other information, it was assumed that the aromatics are other isomers of xylene and trimethylbenzene in approximately equal ratio, giving an average molecular weight between the two. Finally, it is assumed that the homopolymer of HMDI is completely non-volatile and thus can be ignored in the CF calculation. Using the mole percentages of the volatile components, one can then calculate the correction factor and alarm limits using the equations for mixtures from Chapter 3.1.6 (Table 4.6.3).

In this example, the painting operations are conducted using supplied air respirators; therefore, it is not necessary to meet OSHA TWA limits. Nevertheless, to avoid undue skin exposure, the factory regulations call for a shutdown of operations if the organic vapor levels reach 5 times the TWA for either ethylbenzene (100 ppm), xylene (100 ppm), or trimethylbenzene (25 ppm), or 500, 500 and 125 ppm, respectively. Table 4.6.3 shows that the overall CF for the mixture of volatiles is 0.40 with a 10.6 eV lamp and the action level is 205 ppm, or an equivalent PID response of 517 ppm when calibrated to isobutylene. In this calculation mesitylene (1,3,5-trimethylbenzene) was used to represent the MSDS “trimethylbenzene” and o-xylene was used to represent the MSDS “aromatics” because it has a slightly higher CF than other xylenes and therefore would tend to err on the conservative (safe) side.

TABLE 4.6.3. CF and action level alarm calculation for Part B volatiles

Compound	CF 9.8 eV	CF 10.6 eV	CF 11.7 eV	Mol. Fraction	Conc. (ppm)	Action Level (ppm)
Mesitylene	0.36	0.35	0.32	0.479	47.9	125
Xylene, o-	0.56	0.46	0.43	0.336	33.6	500
Xylene, m-	0.5	0.44	0.4	0.184	18.4	500
Mixture value:	0.43	0.40	0.36	1.00	100 ppm	205 ppm
Action alarm setpoint when calibrated to isobutylene:	472 ppm	517 ppm	562 ppm			

Example 2 – Formaldehyde in Paint Volatiles

A paint is applied containing the following VOCs and allowed to air-dry. The mole percentages were calculated from the weight percentages using the methods described above, and the mixture CF and alarm limits are calculated using the methods in Chapter 3.1.6.

TABLE 4.6.4. Composition of paint volatiles

Component	Mole % of Total	TWA
Formaldehyde	0.6	Ceiling 0.3
Toluene	1.5	50
PGMEA	1.5	~50
Isobutanol	14.6	50
p-Xylene	23.4	100
n-Butyl acetate	58.5	150

In this case, a TLV of 0.3 for formaldehyde was entered, which is actually the ceiling value, in the absence of a TWA value.

The CF and alarm limit calculation table is given in Appendix 4. With the above mixture one calculates an average CF of 1.1 for a 10.6 eV lamp, and 1.0 for 11.7. After calibration with isobutylene, the CF is set to 1.1, and the alarm to 33 ppm to equal the mixture TLV. This alarm setpoint is very sensitive to the TLV entered for formaldehyde. For example, if the formaldehyde TLV is doubled to 0.6 ppm, the CF remains at 1.1 while the alarm setpoint increases to 51 ppm for a 10.6 eV lamp. Even though the formaldehyde is not detected, the calculations account for its toxicity in the mixture. The other compounds act as a marker for CH₂O, while CH₂O dominates the toxicity. If the reading is less than 33 ppm total, one is assured that formaldehyde is <0.3 ppm, and the ceiling is not exceeded.

4.7 Ammonia Measurement by PID

Ammonia (NH₃) is a common alkaline gas, also referred to as anhydrous ammonia in the absence of water or in the gas phase. Lighter than air, it has a strong, distinctive smell and is highly corrosive. Its affinity for water causes it

to cauterize respiratory tracts, resulting in death at concentrations of 5,000 ppm. It has the following relatively low exposure limits (NIOSH, 1994):

- TWA 25 ppm
- STEL 35 ppm
- IDLH 300 ppm
- LEL 15 Vol%

As an alternative to ozone-depleting chlorofluorocarbon refrigerants, the use of ammonia as a refrigerant (R717) has increased substantially over the past few years. Large quantities of ammonia can also be found in:

- Fertilizer plants
- Resin production using urea
- Explosives/munitions plants
- Nylon production
- Semiconductor production
- Water & wastewater facilities
- Clandestine drug labs

Why Measure Ammonia?

While ammonia's distinctive smell makes it relatively easy to identify, the human nose is not calibrated to measure its concentration. Therefore, real-time monitors are necessary to allow continuous determination of the Personal Protective Equipment (PPE) necessary to provide proper protection from ammonia. According to the NIOSH pocket guide (NIOSH, 1994), protection from low levels of ammonia (up to 250 to 300 ppm) can be as little as a respirator with the appropriate ammonia cartridges. Entries into concentrations above 300 ppm or into unknown concentrations require positive-pressure supplied-air or SCBAs. Even higher concentrations require full encapsulation suits (Level A) because of the highly reactive alkaline nature of ammonia gas. At concentrations above 15% (150,000 ppm), the ammonia atmosphere is potentially explosive. Accurate, reliable, and continuous portable ammonia monitors are useful to make these decisions.

LEL and EC Sensors for Measuring Ammonia

Catalytic bead LEL sensors can measure ammonia in the low volume % range, but do not have the low-ppm sensitivity necessary to make decisions at TWA or STEL levels. Also, ammonia can deactivate LEL sensors. So while they provide good initial warnings of very high ammonia levels (~10,000 ppm) their life in these high concentrations are limited to minutes or hours, depending on the concentration of ammonia.

Electrochemical sensors are an inexpensive way of making selective ammonia measurements in the low ppm range. However, common electrochemical ammonia sensors suffer from long response times (two to three minutes) and rapid burnout at high ammonia exposures (because the cell uses a sacrificial iodine reagent).

Measuring Ammonia with a PID

Ammonia has an ionization energy of 10.16 eV and can be readily measured with a PID using a standard 10.6 eV lamp. The CF for ammonia is about 10 with a 10.6 eV lamp (Appendix 3). Therefore, the detection limit is about 1 ppm ammonia, for a PID with 0.1 ppm isobutylene detection limit. This detection limit is about the same as for an electrochemical sensor. The sensitivity can be improved by a factor of 3 using an 11.7 eV lamp. However, it is questionable whether the improved response is necessary or desirable in light of the higher maintenance and replacement costs of the 11.7 eV lamp. The 10.6 eV lamp provides enough sensitivity for most applications. Portable PIDs have considerable advantages for measuring ammonia in ranges above the TWA and STEL of ammonia (25 to 35 ppm):

- PIDs have a broader range (up to 15,000 ppm) than EC sensors and therefore can be used for all PPE decisions and for leak detection.
- PIDs are not damaged by over-ranging.
- PIDs have much faster response time of <5 seconds, compared to 150 seconds for ammonia sensors. The fast response makes it easier to assess changing conditions and detect leaks.
- Isobutylene calibration gas for the PID is less expensive and more stable than the ammonia gas required for electrochemical sensors.
- Lower operating cost than EC sensors because the lamp is changed less frequently and at lower price than an NH₃ sensor.

PID Specificity to Ammonia

A PID is not specific to ammonia and it responds to a variety of other compounds (see Appendix 3). However, a major ammonia leak can often be determined by its distinctive smell. Use of a selective technique, such as gas detection tubes, can provide an inexpensive verification of the presence of ammonia, while the continuous measurement capability of the PID can be used to monitor with much greater speed and flexibility.

4.8 Measurement of Phosphine (PH₃) by PID In the Food Storage Industry

Introduction

Phosphine (PH₃) is used as a pesticide in food-storage units, especially in the agriculture and marine shipping industries. To ensure adequate pest control, a few hundred ppm are typically applied and the concentration verified by measurement. PH₃ has a low exposure limit (8-hour TWA of 0.3 ppm) and, when entering the storage vessels, must be measured at low levels to ensure worker safety. PH₃ has an IE of 9.87 eV and can be measured by PID using different lamps:

TABLE 4.8.1. Phosphine correction factors and resolution for RAE PIDs

Lamp eV	9.8 eV	10.6 eV	11.7 eV
CF	28	3.9	1.1
Resolution	~3 ppm	~0.4 ppm	~0.2 ppm

In most cases, the 10.6 eV lamp is chosen because of its good sensitivity and durability. At high concentrations, the 9.8 eV lamp may be useful if cross-interferences are present.

Lamp Fogging Phenomenon

Phosphine is unique in its behavior with PIDs in that it reacts photochemically to form products that can coat the PID lamp. The products are surmised to be phosphorus oxides such as polyphosphates, although this has not been verified. This lamp coating occurs with all lamps and becomes more severe

as concentration and exposure time increase. The situation is most obvious at a few hundred ppm, but even 20 ppm can cause a noticeable response drop within minutes. Short, intermittent exposures help minimize the buildup of such coatings. The coatings are easily removed by cleaning the lamp crystal with anhydrous methanol. Near the TWA level, the coating deposits are negligible.

There is also some evidence that the sensor electrodes can become coated, again reducing response. Therefore, sensor cleanings may help reverse the problem.

Measurement Recommendations

1. Calibrate using isobutylene gas instead of a phosphine standard.
2. Use as short an exposure duration as possible (e.g., 10 seconds, with a PID having t_{90} response time of <5 seconds).
3. Expose to the lowest concentration possible, i.e., use a dilution system if available and still allows enough gas to measure accurately.
4. Use an old lamp or turn down the lamp drive, if possible (on a MiniRAE 2000, use 150).
5. Recalibrate frequently, possibly after every few measurements.
6. Clean the lamp frequently. For a MiniRAE 2000, leave the unit on the charger overnight to allow self-cleaning.
7. Leave the pump on between measurements to help flush out the coating.
8. Clean the sensor frequently.

Gas Detection Tube Combinations

It may be desirable to measure the high-end PH_3 concentrations using an alternate method such as colorimetric gas detection tubes, to avoid exposure of the PID lamps to high concentrations. The PID can be used more effectively at the low concentration range where the tubes lack sensitivity. Gas detection tubes for phosphine are readily available in the 500 to 1,000 ppm range often used for initial fumigation.

4.9 PIDs for EPA Method 21 Leak Detection

Introduction

EPA Method 21 (40 CFR, Ch.1, Pt. 60 Appendix A) is a standard for selecting and using monitors for leak detection and monitoring fugitive emissions. PIDs are listed among the common instruments appropriate for making the measurements. Method 21 does not define leak thresholds; these are defined in other regulations. Tougher requirements have resulted in better monitoring equipment for determining VOC leaks. Method 21 is designed primarily to limit emissions of hydrocarbons that result in tropospheric ozone generation in sunlight. For this purpose, the term VOC includes most organic compounds but excludes such non-ozone-generating compounds as methane, ethane, acetone, methyl acetate, methylene chloride, 1,1,1-trichloroethane, most Freon refrigerants (CFCs and HCFCs), and methylated siloxanes.

Calibration at 10,000 ppm?

It is a common misconception that Method 21 requires calibration at 10,000 ppm methane. It does not; it simply uses 10,000 ppm in an example of where a leak definition might be set. In the definitions, it states:

“For example, If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example the leak definition is 10,000 ppmv, and the reference compound is methane.”

The “leak definition” is defined in another regulation specific to the industry or application. The reference compound is “The VOC species selected as an instrument calibration basis for specification of the leak definition concentration.” It can be any compound appropriate for the type of instrument used.

What is the Recommended Calibration Gas Concentration?

Under the Definitions, the calibration gas is defined as:

“The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.”

This statement does not define the gas type or concentration. These are best defined by the regulation controlling the leak threshold. Under Title V, most leak definitions fell to 500 ppmv or less. For example, in Subpart VV – Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry (EPA 40 CFR Part 60), the calibration gas is defined as approximately 10,000 ppm methane or n-hexane, and the leak definition is 500 or 10,000 ppm, depending on the device being tested.

Can a Different Calibration Gas be Used?

Under Reagents and Standards, Method 21 states:

“Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.”

For example, if the leak definition is given in methane equivalents, then the PID response needs to be converted to methane equivalents to set the leak alarm on the PID. Clearly the PID cannot be calibrated directly with methane, because it does not respond to methane. In other words, compound A can be used to calibrate the instrument to measure the emission of compound B (the VOC) in equivalents of compound C (reference gas – usually methane or hexane equivalents).

Calibration on Isobutylene is Permitted if the CF is <10

The only limitation on the use of calibration gas different from the reference gas is that correction factors for the measurement VOCs are always less than 10. Thus, one could calibrate on isobutylene and measure toluene leaks (CF = 0.5) but not ethylene oxide leaks (CF = 13). However, one could use an 11.7 eV lamp, where the CF = 3.5, or use hexane or ethylene to calibrate and thus reduce the ethylene oxide CF to 3.0 or 1.3, respectively (see Chapter 3.1.4 to convert CFs).

PID Compliance with Method 21

Several other specifications are required to be met when selecting an instrument for use under Method 21. The following table shows how several PIDs comply to the specifications. (The data for MultiRAE assume that a PID is installed.)

TABLE 4.9.1 PID compliance with EPA Method 21

Method 21 Specification	MiniRAE 3000	ppbRAE 3000
Detects compound	Responds to a broad range of organic compounds	Responds to a broad range of organic compounds
Instrument Range Encompasses leak definition	0 to 15,000 ppm	0 to 10,000 ppm
Range w/Dilution Probe Encompasses leak definition	No dilution probe	No dilution probe
Instrument Resolution ±2.5 % of leak definition	0.1 ppm (0 to 999.9 ppm) 1 ppm (1,000 to 15,000 ppm)	1 ppb (1 to 9999 ppb) 10 ppb (10 to 99 ppm) 0.1 ppm (100 to 999.9 ppm) 1 ppm (1000 to 9999 ppm)
Pump Flow Rate 0.1 to 3.0 L/min	0.45 to 0.55 L/min	0.45 to 0.55 L/min
Probe Dimensions ≤1/4" O.D.	3/16" O.D.	3/16" O.D.
Intrinsic Safety for Chemical Vapors Class I, Division 1	Class I, Division 1 Approved	Class I, Division 1 Approved
Correction Factor available for measured compound	Over 350 compound CFs available for RAE PIDs	Over 350 compound CFs available for RAE PIDs
Response Factor Value <10	<10 for most compounds, using isobutylene cal. gas	<10 for most compounds, using isobutylene cal. gas
Response Factor for Test Compound Measurable or Available	Pre-programmed with 222 compounds Available for >350 compounds	Pre-programmed with 222 compounds Available for >350 compounds
Cal. Precision Test Freq. Initial and every 3 months	Simple daily calibration	Simple daily calibration
Calibration Precision ±10% of Cal. gas value	±2% of cal. gas value	±2% of cal. gas value
Response Time ≤30 seconds to 90%	≤3 seconds to 90%	≤3 seconds to 90%

Please refer to TN 122 on our website.

4.10 Natural Gas Leak Detection by PID

Natural gas consists primarily of methane, but may contain significant amounts of higher hydrocarbons, as listed in Table 4.10.1. PIDs cannot detect methane, but do respond to the minor components. Biogenic methane produced in anaerobic waters does not contain higher hydrocarbons. Therefore, a PID with 10.6 or 11.7 eV lamp can be used to distinguish a natural gas leak in an underground pipeline from background biogenic methane such as in groundwater or landfills. By contrast, an FID or LEL catalytic bead sensor could not make this distinction.

TABLE 4.10.1. Composition of a “rich” natural gas sample

Gas component	Mole %
CO ₂	1.181
Nitrogen	0.405
Methane	83.000
Ethane	7.754
Propane	4.250
Isobutane	0.858
n-Butane	1.776
Isopentane	0.332
n-Pentane	0.305
n-Hexane	0.101
Heptane & C ₇ +	0.038
H ₂ S	0.012
Total Mol %	100.000

PIDs for EPA Method 21 Natural Gas Leak Detection

Table 4.10.2 lists measurement parameters for various instruments for EPA Method 21 leak detection. Using the equations described in Chapter 3.1.6 Part 3, an isobutylene CF of 220 can be calculated for this mixture with a 10.6 eV lamp, and a CF of 15 with an 11.7 eV lamp. Accordingly, the detection limits for these lamps are about 22 and 3 ppm, respectively. Method 21 has a requirement that the instrument used be able to resolve at least down to 2.5% of the leak definition. Common leak definitions are 10,000 ppm and 500 ppm.

TABLE 4.10.2. EPA Method 21 criteria for various sensors

Sensor	% of Gas Detected	CF	Detection Limit (DL)	DL Required for 10,000 ppm Leak Definition	DL Required for 500 ppm Leak Definition
FID Cal to Methane	99%	1	1 ppm	250 ppm	12.5 ppm
PID 11.7 eV Cal to Ethane	7.70%	1	3 ppm	250 ppm	12.5 ppm
PID 10.6 eV Cal to IBE	0.80%	220	22 ppm	250 ppm	12.5 ppm
LEL Cal to Pentane	99%	2.3	1% LEL or 140 ppm	250 ppm	12.5 ppm
LEL Cal to Methane	99%	1	1% LEL or 500 ppm	250 ppm	12.5 ppm

Table 4.10.2 shows that the PID with 11.7 eV lamp and FID can both be used for either a 500 ppm or 10,000 ppm leak definition, because their detection limits are below the minimum requirements of 12.5 and 250 ppm, respectively. PIDs with either 10.6 or 11.7 eV lamps are more sensitive to natural gas than a catalytic bead LEL sensor, despite the fact that the LEL sensor responds to essentially all of the natural gas and the PID only responds to a small fraction. The standard LEL sensor calibrated to methane cannot meet the sensitivity criterion for either a 10,000 ppm or 500 ppm leak definition. It is barely acceptable for the 10,000 ppm leak definition if calibrated with pentane (the sensitivity changes because the display usually limits the detection limit when calibrating with methane).

Note that the PID with an 11.7 eV lamp is nearly as sensitive as a portable FID, but is much smaller and easier to operate. The operating cost may be a bit higher due to lamp-replacement needs, but the initial purchase price is lower and FIDs are often considered too complicated.

Another criterion in EPA Method 21 is that the CF for the measured gas compared to the calibration gas be less than or equal to 10. The PIDs have greater CFs when calibrated with isobutylene, but can pass the criterion by calibrating with another gas such as ethane (CF = 15) for the 11.7 eV lamp and butane (CF = 67) for the 10.6 eV lamp. The new factors are obtained by division (Chapter 3.1.4) and are 1.0 and 3.3, respectively. The detection limit does not change when calibrating to these different gases.

A further consideration for complying with Method 21 is that, in principle, methane and ethane are not considered ozone precursor VOCs and thus may not need to be taken into consideration in the leak definitions. In this case, the calculated correction factors and leak definitions would change and would likely favor the use of a PID with 10.6 eV lamp.

4.11 ppb Level Detection by PID

4.11.1 Indoor Air Quality

The advent of ppb-level PIDs at the turn of the millennium has opened a new range of applications that are just now being characterized. One of these is the measurement of indoor air quality (IAQ). Outdoor air generally contains a few tens of ppb or less of organic vapors (excluding methane). Indoor air can

contain tens to hundreds of ppb. Previously, these concentrations were in the noise level of most PIDs and often were canceled out during instrument zeroing. Current ppb-level PIDs have resolution down to a few ppb and can now distinguish the different levels of VOCs in indoor air.

General Indoor Air Quality (IAQ)

It has been shown that people in industrialized societies typically spend greater than 95% of the time indoors. The drive for HVAC (Heating, Ventilation and Air Conditioning) energy conservation has led to buildings with lower fresh air replacement rates and thus higher indoor contaminant concentrations (Godish, 1995). These two factors combined have led to a rise in “sick building syndrome” (SBS) complaints. According to the American Lung Association, the top five indoor air pollutants (in alphabetical order) are:

- Carbon monoxide
- Formaldehyde
- Microbial contaminants (mold, dust mites, etc.)
- Second-hand tobacco Smoke
- Volatile organic compounds (VOCs)

VOCs have a wide range of effects including, eye and respiratory tract irritation, headaches, dizziness, visual disorders and memory impairment. In addition to their negative health affects, high levels of indoor VOCs have even been blamed as a cause of increased computer failures in offices. VOCs in an indoor environment can come from a wide variety of sources. They can be found in or caused by, among others:

- Human occupancy (exhalation, smoking, perfumes, etc.)
- Carpets, fabrics, finishes and furniture
- Office equipment (copiers, printers, plastic materials)
- Cleaning and maintenance supplies
- Renovations (plasters, paints, etc.)
- Microbial activity
- Vocational Training shops and art rooms
- Pesticides

PIDs with ppb capability can detect most of the major indoor contaminants except CO and formaldehyde.

VOC Types

VOCs in indoor air include alkanes, aromatics, alcohols, aldehydes, esters, ketones, ethers, organic acids, and halogenated compounds. For example, a study by the Japanese Department of Health & Welfare (2000) identified the following VOCs:

Major Compounds Found	Average Conc.
Ethanol	~150 ppb
BTEX & Trimethylbenzenes	~50 ppb
p-Dichlorobenzene	~21 ppb
Acetone, Butyl acetate	~16 ppb
C ₈ – C ₁₂ Alkanes	~14 ppb
Limonene, α-Pinene	~7 ppb

Average Total ~280 ppb

Contaminated Building Total ~5,500 ppb

The average CF for the mixture above is calculated as 1.4, using the techniques described earlier. This CF suggests that an isobutylene calibration can be used to give an approximate measure of the total VOCs. Other indoor air mixtures have similar low estimated CFs, but not identical.

CO₂: An Indirect Measure of IAQ

ASHRAE (American Society of Heating, Refrigeration and Air Conditioning Engineers) standards historically use CO₂ levels as a marker for indoor air quality. Levels of CO₂ in excess of 700 ppm over outdoor levels (typically 350 ppm), or usually over 1,000 ppm total, are an indication of “poor” indoor air quality. Such levels of CO₂ can indicate that air is not being refreshed enough so that CO₂ is built up from the exhaled breath of the building occupants. At the levels typically found in IAQ investigations, CO₂ is not a toxicity concern (OSHA PEL = 5,000 ppm), only a gross indicator of possible contamination from one of the five sources listed above. If the building is ventilated enough to reduce CO₂ levels, it often solves the IAQ problem by dilution. PIDs complement CO₂ monitors by providing a direct measurement of VOCs and help locate their sources.

tVOCs Correlate With SBS but not CO₂

tVOC concentration has been found to correlate with the prevalence of sick build syndrome (SBS) symptoms (Norback et al., 1990). However, CO₂ levels do not correlate with total VOCs (tVOCs) in IAQ measurements. In an informal study at a wide variety of sites worldwide, including offices, conference rooms, hotel rooms, homes, etc., tVOCs, as measured by a ppbRAE calibrated on an Isobutylene scale did not significantly correlate ($r = 0.11$) with CO₂ readings taken with a gas detection tube. This result reflects the fact that tVOCs and CO₂ come from different sources. Although human breath contains measureable levels of acetone and other hydrocarbons, these apparently do not contribute significantly to the tVOCs in indoor air. It is clear that CO₂ as a survey tool for IAQ assessments can (and does) miss elevated VOC levels.

Options for Measuring VOCs

For Indoor Air Quality assessment, one can use the following methods to measure VOCs (Volatile Organic Compounds) at low levels:

- **Adsorbent Media (e.g., activated carbon) followed by GC/MS Lab Analysis:** Accurate, specific, and highly sensitive, but are expensive and lack real-time feedback (1 day to 2 weeks).
- **Metal Oxide Sensors (MOS):** Low cost, but have limited sensitivity, slow response (minutes), respond to moisture, CO₂ and temperature changes.
- **PID:** Rapid, broad-band, highly sensitive with intermediate cost, but having limited selectivity.

Laboratory analyses by GC/MS are expensive and can take days or weeks to return from the lab. By the time that the results are available, a minor Indoor Air Quality problem can grow into a major incident. PIDs provide rapid, direct measurement of VOCs so that problems can be quickly identified and fixed. They can be used for both portable IAQ surveys and permanent IAQ subsystems of a building HVAC system.

In a Japanese study, Hara (2000) found “significant correlation” between samples tested with a TenaxTA-thermal desorption-GC/MS and a ppbRAE PID (Figure 4.11.1).

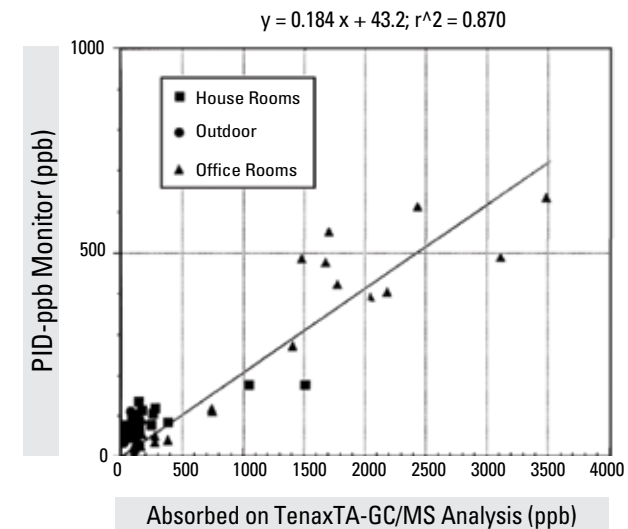


FIGURE 4.11.1. Correlation of ppbRAE response with laboratory GC/MS

tVOCs Concept

The urgency and complexity of the Sick Building Syndrome problem triggered a search for a practical (time/cost-effective) assessment method using tVOC levels as practical standards (Godish, 1995). Such a “total component” concept has already gained acceptance in other health related disciplines, such as TSP (Total Suspended Particles) and TdB (Total deciBel) as screening standards for particle and sound pollution, respectively. Pioneering work on using tVOC level as practical overall standard are not complete (Seifert, 1990; Molhave, 1991) and require further epidemiological research. Even so, tVOCs are emerging as a more direct approach of surveying indoor environments for contamination, and several organizations have recommended tVOC limits (Table 4.11.1).

TABLE 4.11.1 tVOC limit recommendations

Agency	Recommended Limit	
	$\mu\text{g}/\text{m}^3$	ppb
Scandinavian Construction Materials Assoc.	300-1300	~75-325
Japan Ministry of Health	400-1000	~100-250
ASHRAE/ACGIH	<1000	~200
Texas General Services Commission	500	~100
Australian National Health & MRC	500	~100
Finnish Society of IAQ & Climate	200-600	~50-150
German Guideline (Seifert, 1999)	300	~75
Denmark Institute of Hygiene	250	~50

Global consensus has resulted in the emergence of preliminary guidelines for tVOC standards for IAQ (Australian NHMRC, 1993; Finnish Society of IAQ, 1995; Seifert, 1999; Hong Kong EPA, 1999; Japan Ministry of Health, 2000). Depending on location (home, school, etc.), recommended levels range from 200 to 1300 $\mu\text{g}/\text{m}^3$, or about 50 to 325 ppb (toluene units) or approximately 100 to 650 ppb isobutylene units. By all accounts, the IAQ tVOC threshold for normal environments should not exceed 500 ppb (0.5 ppm) toluene units, which is equivalent to 1000 ppb (1 ppm) isobutylene equivalents. Field experience suggest the following guide for the use of PIDs to assess indoor environments:

- <100 ppb Isobutylene Units: normal outdoor air
- 100-400 ppb Isobutylene Units: normal indoor air
- 500+ ppb Isobutylene Units: indicates potential of IAQ contaminants

PIDs Identify Copier Odors

A school district had many older photocopiers in operation using liquid toner. The liquid toner had an exposure limit of 100 ppm. Heavy copier use released significant concentrations of toner vapor in the small copier rooms, where there was little ventilation. A PID was used to initially identify the problem and subsequently to help “tune” the new ventilation system to vent the copier odor away from workers.

Mold (mVOCs)

Molds release allergens, spores and mold particles that cause a variety of human health problems (Godish, 1995). A number of operators have reported that ppb-level PIDs can be used to indirectly determine the presence of molds and fungi on surfaces (Knobel, 2001; McGuinness, 2002). The major compounds released by molds can all be detected using a PID with a 10.6 eV lamp:

- Heptane, octane, nonane (CFs = 1 - 3)
- Benzene, toluene, styrene (CFs ~0.5)
- C₅ - C₁₀ Alcohols (CFs 2 - 5)
- Octenols (Major odor compound) (CF ~1)
- C₈ - C₉ Ketones, acetophenone (CFs 0.5-1)
- C₄ - C₈ Acetates (CFs 2 - 5)

These compounds are not primarily of direct toxic concern because of their low concentrations, but act as indicators of the mold toxins. Concentrations are usually below 1,000 ppb immediately adjacent to a living mold culture. PID detection works well for locating “hot spots” for further testing, by categorizing the culture as dead or alive.

Recent studies on chemistry of VOCs in Indoor Air (secondary emission and reactive species) and the human health effects of microbial VOCs (Wolkoff, 2000; Salthammer, 2000; Hess, 2001) call for need of further research. Until complete understanding is reached, researchers (Seifert, 1999; Salthammer, 2000; Hara 2000) are refining a tVOC approach as a practical screening method for exposure risk assessment to total VOCs in working and living environments.

4.11.2 Other ppb-PID Applications

Electronics Manufacturing Clean Rooms

Many electronic components such as silicon wafers and flat panel displays suffer from poor yields when organic vapors deposit on them. A common contaminant is di-octylphthalate and other phthalate esters used as plasticizers in many synthetic materials. Conventional methods such as contact angle determinations require hours to accumulate enough surface deposits for accurate measurement. Continuous PID detection in the ppb range can be of use to monitor the level of VOC contamination in the clean room or test bay, or to screen materials before entry. To date, attempts to correlate PID response to product yields have met with partial success.

IVF Facilities

In contrast to *in vivo* embryos, which are protected within the body, *in vitro* fertilization allows potential exposure of the gametes and embryos to the ambient air. Sudden loss of fertility rates has been attributed to exposure to ambient VOCs and other contaminants (Cohen, *et. al*, 2002). Studies are currently underway to assess the ability of ppb-level PID response to warn IVF facilities of potentially harmful VOC levels in the incubators.

4.12 Measuring PID Correction Factors

This chapter gives practical details on how to measure correction factors (CFs) for new compounds. Correction factors are used to allow measurement of a large variety of compounds while calibrating with only a single standard gas, commonly isobutylene.

In general, CFs are independent of the type of instrument as long as the lamp chemistry and crystal are qualitatively the same. Often it is easiest to use a PID with a built-in pump. In this case it is preferable to use the same type of gas supply to both calibrate the PID and measure the unknown (i.e., using a gas bag –such as one made of Tedlar – for both or a pressurized cylinder for both), in order to nullify the effects of pressure or flow variations.

The matrix of the gas has important effects on the PID response. CFs listed in Appendix 3 are measured in dry air and apply only to this condition. High humidity generally decreases the response by 30% to 50%, while measurements in pure nitrogen may give roughly a 10% to 30% increase in signal over dry air when an 11.7 eV lamp is used. Therefore it is important to measure the calibration gas and the sample gas in the same matrix. A correction factor measured with room air may be more representative of the actual use conditions, but is a less convenient reference point.

Correction Factor Definition

The correction factor is defined as the response of the isobutylene (IBE) calibrated PID to an equal concentration (ppmv) of the compound of interest (Gas Y):

$$CF = \frac{\text{Instrument's IBE Reading} * \text{Gas Y Concentration (ppmv)}}{\text{IBE Concentration (ppmv)} * \text{Gas Y Instrument Response}}$$

Thus, the higher the correction factor, the lower the sensitivity to the compound of interest. To account for any drift during the measurements, one can make isobutylene measurements before and after the sample measurements and take the average response to the isobutylene standard. With a standard PID having a measurement range of 0.1 to a few thousand ppm, it is preferable to use a gas standard of at least 50 to 100 ppmv in order to be well above the noise level of the instrument.

CF Measurement Using Gas Standards

If a cylinder of standard gas in dry air is available, simply calibrate the instrument with isobutylene and then measure the gas standard in the same way. Use the equation above to calculate the CF.

CF Measurement For Liquid Samples

If the gas standard is to be prepared from a liquid sample, proceed as follows:

- Obtain a large vessel such as a 5-gallon glass water jug or a 1-gallon glass bottle, and calibrate its volume. One simple way to do this is to fill the bottle with water and measure the difference in weight with an accurate balance. The volume equals the weight in grams of the water. Thoroughly dry the vessel before use. Alternately, use a Tedlar gas bag. A 3-L or 5-L gas bag is convenient if a 1 μ L syringe is available for liquid injections.
- If a glass jug is used, place some small inert objects (e.g., PTFE pieces) inside or use a magnetic stirrer to aid in mixing. Bore two holes in the cap to insert the instrument influent and effluent sample lines. Use PTFE tubing for these lines to minimize losses due to adsorption.
- Flush the sample vessel with dry air. If a gas bag is used, fill the bag to a known volume using a high-volume syringe (e.g., 1.5 L) or a mass flow controller system. Do not fill the gas bag completely, to allow for easier mixing in a subsequent step.
- Calibrate the instrument with isobutylene or other reference gas.
- Using a microliter syringe, inject a volume of liquid calculated to give the desired concentration:

$$\text{Concentration (ppmv)} = \frac{24.4 \text{ (L/mol)} * \text{Volume injected } (\mu\text{L}) * \text{Liquid density (g/mL)} * 106}{1000 \text{ (mg/g)} * \text{Molecular weight (g/mol)} * \text{Vessel volume (L)}}$$

- Allow time for the liquid to evaporate and mix. Assist mixing with magnetic stirring or agitation of the inert objects inside the closed vessel. If the compound is high-boiling, it may be necessary to apply heat (e.g., heat gun) to the vessel wall to speed evaporation. For a Tedlar bag, massage the bag gently to mix the air.
- Uncap the vessel and quickly insert the PID influent and effluent lines (recap or reseal it as quickly as possible), or attach the PID influent probe to the gas bag using a minimum of flexible tubing.
- Allow a minute or so for equilibration, record the sample measurement, and remove the sample lines. Calculate the CF using the equation above.
- Repeat a few more times at different concentrations to obtain a calibration curve and several CF values to average.

If desired, a known volume of liquid water can also be injected to achieve a desired relative humidity and CF under humid conditions. For such measurements it is important that the sensor be very clean, or else the readings may drift upward.

4.13 Dessicant Tubes for Removing Humidity During Continuous PID Measurements

Introduction

PID response can be reduced by high humidity (Figure 4.13.1). In addition, a false-positive reading can result if the sensor is dirty or if water condenses in the sample line and the sensor (Figure 4.13.2). For false positives, the preferred solution is good sensor cleanliness and instrument maintenance. The humidity filtering tubes described in this section address both types of humidity issues and allow more accurate measurements for many chemicals.

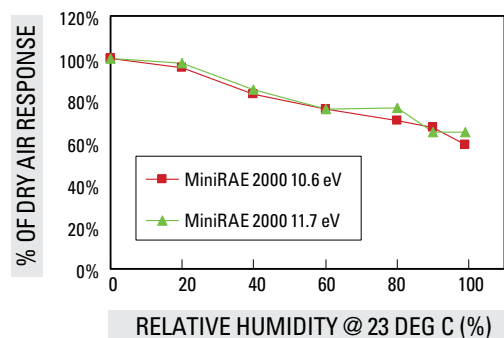


FIGURE 4.13.1. Response to test gas with clean sensor

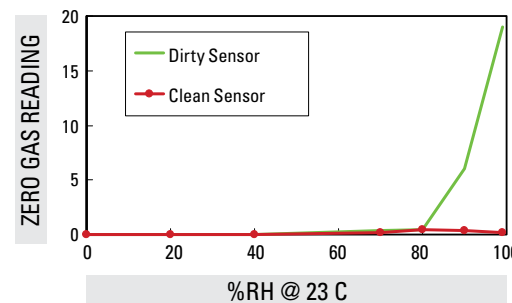


FIGURE 4.13.2. Response to zero gas vs. humidity on "dirty" vs "clean" sensor

High-humidity situations that can cause problems include:

- Soil vapor extraction systems
- Combustion stack gases
- Moving from a cool location to a hot, humid area, such as calibrating in an air-conditioned lab and moving outdoors.

Humidity Filtering II Tubes

The RAE Humidity Filtering II tube, attached to the inlet of a PID, can reduce humidity for the times listed in Table 4.13.1. The tube can be used while measuring organic vapors, with some precautions (see below).

TABLE 4.13.1. Run times for the Humidity Filtering II tubes.

T (°C)	T (°F)	RH (%)	10% RH Breakthrough time (min @ 500 mL/min)	20% RH Breakthrough time (min @ 500 mL/min)
45	113	100	12	14
		75	17	18
		50	35	>40
		25	>40	>40
40	104	100	18	20
		75	25	30
		50	40	>40
30	86	100	22	26
		75	28	32
		50	40	>40
20	68	100	23	~30
		75	34	>40
		50	40	>40

At extreme sample conditions such as 45°C (113°F), 100% RH and 500 mL/min flow rate, the humidity filtering tube can maintain <20% RH downstream for at least 14 minutes, as shown in Table 4.13.1. At this low RH, the effects shown in Figures 4.13.1 and 4.13.2 are almost completely removed. Under more typical conditions, the protection time can be expected to be much longer (see Table 4.13.1). A worst-case humidity breakthrough curve is shown in Figure 4.13.3.

The tubes are sealed and broken open immediately before use. They are intended for single use, but might be used for a few samples if within a short time or if the tube ends are capped. There is no color change in the tube, but a spent tube can be identified by a glassy gel formation on the solid absorbent. Caution: The tube contents may liquify after very long sampling or if a tube is left open in ambient air for several days. Dispose of tubes soon after use to avoid leakage or having liquid sucked into the instrument.

Break-through Characteristics of Humidity Filtering Tube

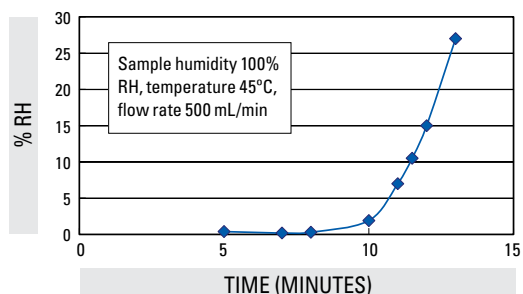


FIGURE 4.13.3. Worst-case breakthrough curve (Note: 45°C is higher than some instrument ratings)

Effect of Mist

Test of Humidity Filtering II Tube with H₂O Mist using ppbRAE

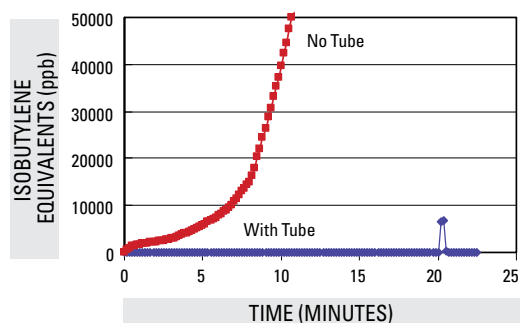


FIGURE 4.13.4. Test of humidity filtering II tube in the presence of water mist using a ppbRAE

The tubes can be used to measure VOCs in the presence of water mist. As shown in Figure 4.13.4, when mist is drawn into a PID with no tube, a false positive reading occurs similar to that in Figure 4.13.2. The Humidity Filtering II tube (diamonds on Fig. 4.13.4) prevents this and keeps the readings very close to ambient response for at least 20 minutes. The bump check at the end of the test with the tube with about 7 ppm (7,000 ppb) shows that the tube still responds to VOCs even when it is almost completely saturated with water.

Precautions

- Use the tube immediately after opening to avoid loss of absorption capacity.
- Use with caution when making PID measurements with the tube in place, as some compounds may be lost or exhibit delayed response (See Table 4.13.2). Contact manufacturer if the compound to be measured is not listed in Table 4.13.2 or the data sheet shipped with the tube.
- Use particular caution at low temperatures and low concentrations because adsorption losses can be relatively more severe. Extended sampling times may be required.
- If unexpectedly low readings are obtained, remove the tube and measure again to check for absorption losses. A rapid rise in a few seconds indicates VOC presence, while a slow rise suggests a false humidity response.
- Be sure that all connections are tight, or the sample gas will not be properly dried and may be diluted.
- The tube forms a gel and then liquid after excessive moisture has been drawn through. Remove the tube before such a gel fills the tube, or the liquid may be sucked into the PID, causing possible damage.
- It is still desirable to maintain a clean sensor to prevent drifting readings during measurements in high humidity.
- The contents of the tube are non-toxic and can be disposed of in a landfill. However, the tube may absorb some toxic compounds during use and become contaminated.

Effect on VOC Response

TABLE 4.13.2. Effect of Humidity Filtering II Tube on VOC response

Compound	Concentration (ppm)	T (°C)	t ₉₀ (sec)	HCF*
Isobutylene	100	22	3	1
Isobutylene	10	0	5	1.17
Cyclohexane	10	22	3	1
Octane	100	22	3	1
Undecane	100	22	60	1.1
Benzene	5	22	3	1
Toluene	10	22	3	1
Xylenes	100	22	10	1.05
Styrene	50	22	10	1
Gasoline	100	22	15	1.05
Gasoline	10	22	15	1
Gasoline	10	0	28	1.6
Jet Fuel JP-5	10	22	65	1
Diesel Fuel	100	22	110	1.3
Vinyl Chloride	10	22	3	1
Trichloroethylene	10	22	3	1
Trichloroethylene	10	0	5	1.2
Perchloroethylene	10	22	4	1
Glutaraldehyde	10	22	NR** (480)	NR** (1.05)
Ethanol	1000	22	3	1
Ethanol	100	22	40	1
Isopropanol	10	22	90	1.15
Acetone	1000	22	3	1
Acetone	100	22	20	1
Acetone	10	22	80	1
Acetone	10	0	115	1.17
PGMEA (propylene glycol methyl ether acetate)	10	22	240	1.1
Phenol	20	22	150	1
Methyl methacrylate	10	22	150	1.05
Dimethyl sulfide	10	22	3	1
Ethyl mercaptan	10	22	4	1.05
Butyl mercaptan	10	22	5	1.05
Hydrogen sulfide	7	22	3	1
Ethylamine	high	22	NR*	NR*
Ammonia	50	22	NR*	NR*

*HCF = Humidity Correction Factor. Multiply by reading to get true concentration to correct for some loss. If calibrating with isobutylene, must also multiply by the Correction Factor in Appendix 3 to get true concentration. *

**Not recommended because of severe losses.

Note: The data in Table 4.13.2 were generated in dry air at about 22°C (72°C). Tests showed that 50% RH does not affect the response time to isobutylene, benzene, PGMEA, dimethyl sulfide, phenol, acetone or ethanol, but causes total loss of ammonia. 80% RH does not affect the response time of isobutylene, benzene, or H₂S. The response time for polar compounds is not significantly different between a fresh tube and a partially used tube up to 20% humidity breakthrough.

Other compounds: Volatile ethers, esters, haloalkanes, and olefins should not be affected except for possible slower response. Glycols, aldehydes and alcoholamines are expected to have slower and/or lower response. Acids and bases maybe lost on the tube. Compounds that hydrolyze easily, such as acetic anhydride, isocyanates or hexamethyldisilazane may be lost.

The tubes can be used to measure a variety of volatile organic compounds (VOCs). The tubes have no effect on the response of nonpolar compounds such as isobutylene, hexane, benzene, and vinyl chloride but may affect the response time and efficiency of other compounds (see Table 4.13.2). Response time is faster at higher concentrations and higher temperature; therefore at low levels or low temperatures extra measurement time may be required.

Procedures

1. Insert the tip of the instrument probe into the smaller end of the tube adapter;
2. Break the two ends of a humidity filtering tube using the smaller side hole of the tube adapter;
3. Immediately insert one end (an arrow on the tube indicates the direction) of the open humidity filtering tube into the bigger end of the adapter;
4. Measure the sample gas;
5. Discard the used humidity filtering tube after the maximum time has elapsed as shown in Table 1, or when the tube becomes saturated as shown by a glassy gel formation.

If moving from a cool to a hot, humid environment:

- 4a. Run the instruments for at least 15 min with the humidity filtering in place to warm up the sample line and the instrument sensor. This is useful even if the sensor is clean and shows no humidity effect, in order to prevent liquid condensation.

4.14 Moisture Exchange Tubes for Humidity Control of Calibration and Test Gases

Introduction

As described earlier, many PIDs have a reduced response in humid air compared to the dry air that is often used for calibration. A convenient way to correct for this effect is to humidify the calibration gas to the same humidity as the air to be measured. Humidity corrections are usually negligible for PIDs below 40% RH at room temperature and for electrochemical sensors (although the latter may have transient responses to humidity changes).

Moisture Exchange Tube

Some PID manufacturers supply a 12" (30cm) or 24" (61cm) moisture exchange tube that can be connected directly between the calibration gas and instrument calibration cup or other connector. The tube consists of a membrane that allows moisture to pass, but retains organic vapors. Thus, moisture from ambient air enters the gas stream inside the tube without losing the organic compound. The tube works best for low-molecular-weight, nonpolar compounds like propane and isobutylene. Heavier compounds like toluene can be adsorbed onto the tube, and polar compounds such as alcohols, aldehydes, amines, and ketones can be lost by absorption into the moist pores of the tube.

In principle, the tube could also be used to dry a humid measurement stream, if the tube is jacketed with a dry air stream or other drying agent such as a silica gel pack. However, it is simpler to humidify the calibration gas than to dehumidify the measurement gas, because (1) the calibration gas can be selected to avoid adsorption losses on the tube, whereas the measurement gases may vary and unknown losses may occur, (2) the humidification needs to be performed only once during calibration, assuming the RH does not change significantly during measurement, and (3) large amounts of drying agents are typically required to provide drying capacity for more than a few minutes, creating handling and disposal complexity.

Operation

To operate the tube, first allow it to equilibrate for at least five minutes at the humidity desired for subsequent measurements. Then simply connect it between the calibration gas cylinder and the instrument inlet probe or calibration cup, and calibrate as usual (see Figure 4.14.1). The direction of flow through the tube is not important.

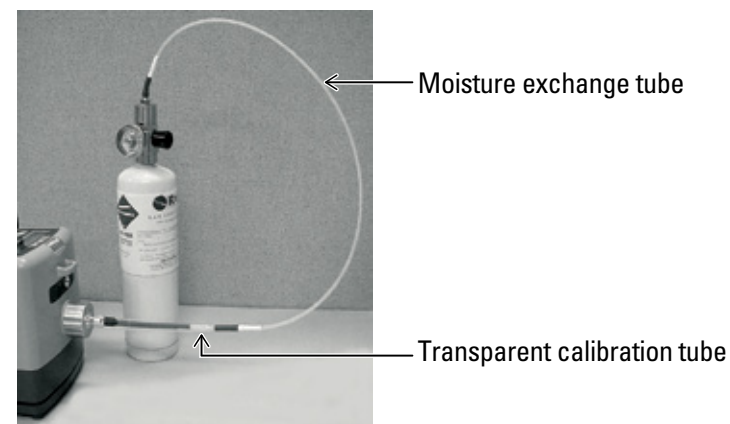


FIGURE 4.14.1. Connection of moisture exchange tube to gas cylinder and open calibration tube

Figure 4.14.2 shows the humidification efficiency as a function of gas flow rate. At 0.5 L/min., the tube is able to equilibrate a dry gas stream to ambient humidity for an extended period of at least 10 minutes. At 1.0 L/min., it is recommended that the calibration be completed within two minutes of starting the gas flow in order that the humidity not drop by more than 10% (by <5% RH at 50% RH).

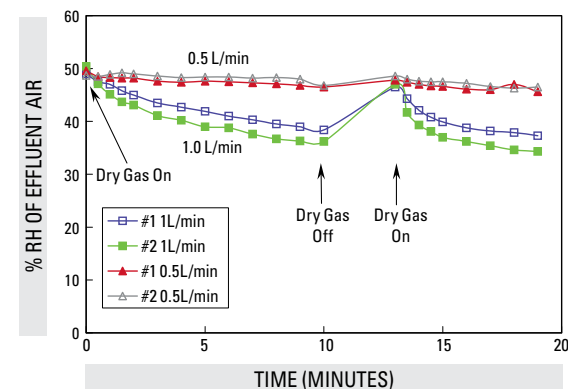


FIGURE 4.14.2. Humidification of dry air using a 24" moisture exchange tube

Figure 4.14.2 shows that when the dry gas is turned off, the tube recovers by absorbing moisture from the ambient air. The tube appears to have a reservoir of moisture in its pores that requires replenishment after being

used to humidify a dry gas sample. Therefore, if multiple calibrations are to be performed with a single tube at 1 L/min. or more, at least five minutes' humidity equilibration time should be allowed with the gas off between calibrations. The tube is rated for flows up to 2 L/min., but will show reduced performance at this higher flow rate.

Other Matrix Gas Effects

The Moisture Exchange Tube will not compensate for other matrix gas effects, such as the suppression of PID signals due to methane, because methane does not pass through the membrane.

4.15 Chemical Warfare Agent Detection by PID

Introduction

Many chemical warfare agents (CWAs, i.e., nerve agents and related compounds) can be detected by PID. Table 4.14.1 lists some common agents and several of their physical properties and PID correction factors (CF).

Nerve Agent Response on PIDs

All the listed compounds can be detected with a 10.6 eV lamp, except phosgene, which requires an 11.7 eV lamp, and HCN and ClCN, which cannot be detected by PID. VX has inherent sensitivity, but it is too heavy a compound to get to the PID sensor and thus cannot be reliably measured. The 8-hr TWAs and IDLHs are extremely low, and the PID cannot measure nerve agents at these levels, except in a few cases with a ppbRAE. However, it can locate sources and detect the agents at levels well below those that are lethal in one minute (see LCt50 in Table 4.15.1). Compounds with low vapor pressures tend to respond more slowly on the PID, in some cases requiring several minutes. In the case of VX, the lethal dose is above its vapor pressure at room temperature; therefore, the lethal one-minute dose can be attained only if the air is hot or the chemical is sprayed as an aerosol. At the maximum room temperature concentration of VX, more than one minute of exposure is required for lethal effects.

Table 4.15.2 shows that many of the common decomposition products of aged warfare agents can also be detected by PID. These are often more volatile than the agent itself (especially for VX), and thus the products serve as a more easily detectable surrogate than the original material.

TABLE 4.15.1. Properties of chemical warfare agents and simulants including detectability by PID

Compound	Structure	m.w.	Lamp (eV)	CF	8-hr TWA (mg/m ³ (WPL))	8-hr TWA (ppbv)	IDLH (ppbv)	LCt50 (ppmv-min)	Vapor Press. (ppmv)
Blood Agents									
Arsine (SA)	AsH ₃	78	10.6	1.9	0.16	0.05	3,000		Gas
Hydrogen Cyanide (AC)	HCN	27	ND**	ND**	11	10,000	50,000	270	Gas
Cyanogen Chloride (CK)	ClCN	61.5	ND**	ND**	0.6 Cξ	300 Cξ			Gas
Blister Agents									
Lewisite (L1)	ClCH=CHAsCl ₂	207	10.6	-1*	0.003	0.35	0.11	140	460
Mustard (H or HD)	S(EtCl) ₂	159	10.6	0.6	0.0004	0.061		>230	95
N Mustard (HN-1)	N(Et)(EtCl) ₂	172	10.6	-1*					320
HT	60% HD & 40% T (O(Et.S.EtCl) ₂)				See HD; T part is non-volatile and poses low				
Phosgene Oxime (CX)	HON=CCl ₂	114	11.7	-5*				685	15000
Choking Agent									
Phosgene (CG)	O=CCl ₂	99	11.7	8.5	0.4	100	2,000	790	Gas
Nerve Agents									
Sarin (GB)	O=PF(Me)(OPr)	140	10.6	-10	0.0001	0.017	17	12	3800
Soman (GD)	O=PF(Me)(OCH(Me)(tBu))	182	10.6	-3*	0.00003	0.004	6.7	9	530
Tabun (GA)	O=PC(N)(OEt)(NMe ₂)	162	10.6	0.8	0.0001	0.015	15	20	92
VX	O=PF(Me)(OEt)(S.Et.NiPr) ₂	267	10.6	-0.5*	0.00001	0.00091	0.27	2.7	0.92
GF	O=PF(Me)(O-Cyclohex)	180	10.6	-3*	0.00003	0.004	6.8		79
Simulants									
DMMP	O=PF(Me)(OMe) ₂	124	10.6	4.3					
Triethyl phosphate	O=P(OEt) ₃	182	10.6	3.1					
Methyl salicylate	2-(HO)C ₆ H ₄ CO ₂ Me	152	10.6	0.9					

* Estimated value. ** ND = Not Detectable by PID. ξC = ceiling value.

TABLE 4.15.2. Estimated response of warfare agent degradation products by PID

Agent & Products	CAS No.	IE* (eV)	CF Estimate 10.6 eV Lamp	CF Estimate 11.7 eV Lamp
<i>Lewisite (LI)</i>				
	541-25-3	?	~1	~1
2-Chlorovinyl arsenic oxide	123089-28-1	?	~1	~1
2-Chlorovinylarsonic acid	64038-44-4	?	~1	~1
Dihydroxy-2-chlorovinylarsine	85090-33-1	?	~1	~1
Sodium arsenite	11137-68-1		ND	ND
Acetylene	74-86-2	11.4	ND	2
Hydrogen chloride	7647-01-0	12.8	ND	ND
Arsenic trichloride		10.55	~10	~1
<i>Mustard (HD)</i>				
	505-60-2		0.6	~0.5
1,4-Dithiane	505-29-3	-8.5	-0.5	~0.4
1,4-Oxathiane	15980-15-1	~9	-0.5	~0.4
2-Chloroethyl vinyl sulfide	81142-02-1	~9	~1	~1
2-Chloroethyl vinyl sulfoxide	40709-82-8	~10	~1	~1
Bis-2(bis(2-hydroxyethyl)-sulfonium ethyl)		?	?	?
Bis (2-hydroxyethyl)-2-(2-chloroethylthio) ethyl sulfonium	64036-91-5	?	?	?
Divinyl sulfoxide	1115-15-7	~10	~1	~1
Hemi Mustard	693-30-1		~1	~1
Mustard sulfone	471-03-4	~10	~5	~1
Mustard sulfoxide	5819-08-9	~8.8	~1.5	~1
Thiodiglycol	111-48-8	<9	~1	~1

* IE = Ionization Energy, the minimum lamp energy needed to detect the compound by PID

Agent & Products	CAS No.	IE* (eV)	CF Estimate 10.6 eV Lamp	CF Estimate 11.7 eV Lamp
<i>Mustard (HD) (continued)</i>				
Dichloroethane	73-34-3	11.06	ND	0.6
1,1,2,2-Tetrachloroethane	79-34-5	11.1	ND	0.6
Tetrachloroethylene (PCE)	127-18-4	9.32	0.57	0.31
Trichloroethylene (TCE)	79-01-6	9.45	0.54	0.43
1,3-Butadiene	106-99-0	9.07	0.85	1.1
2-Butene	107-01-7	~9.6	~1	~1
Vinyl chloride	75-01-4	9.99	2	0.6
<i>Phosgene (CG)</i>				
	75-44-5	11.55	ND	8.5
Carbon dioxide	124-38-9	13.8	ND	ND
Hydrochloric acid	7647-01-0	12.8	ND	ND
<i>PhosgeneOxime(CX)</i>				
		~11.5	ND	~5
Carbon dioxide	124-38-9	13.8	ND	ND
Hydrochloric acid	7647-01-0	12.8	ND	ND
Hydroxylamine	7803-49-8	~10.0	~10	~3
<i>Sarin (GB)</i>				
	107-44-8	<10.6	3	~1
Diisopropyl methylphosphonate (DMIP)	1445-75-6	<10.6	~3	~1
Hydrogen fluoride	7664-39-3	16	ND	ND
Isopropanol (IPA)	67-63-0	10.12	6	2.7
Isopropyl fluoride	420-26-8	11.1	ND	~3

* IE = Ionization Energy, the minimum lamp energy needed to detect the compound by PID

Agent & Products	CAS No.	IE* (eV)	CF Estimate 10.6 eV Lamp	CF Estimate 11.7 eV Lamp
<i>Sarin (GB)</i>	Isopropyl methylphosphonic acid (IMPA)	?	?	?
	Methylphosphonofluoridic acid	?	?	?
	Methyl phosphonic acid	?	?	?
<i>Soman (GD)</i>	96-64-0	<10.6	~3	~1
	Methyl phosphonic acid	?	?	?
	Pinacolyl methylphosphonic acid	<10.6	~3	~1
<i>Tabun (GA)</i>	77-81-6	?	~0.8	~0.6
	Dimethylphosphoramidate	?	~2	~1
	Dimethyl phosphoramidocyanidate	?	~2	~1
	O-ethyl N,N-dimethylphosphoramidate	?	~2	~1
	O-ethyl phosphorocyanidate	?	?	?
VX	50782-69-9	?	~0.5	~0.4
	Bis(2-diisopropylaminoethyl) disulfide	?	~0.5	~0.4
	Bis(2-diisopropylaminoethyl) sulfide	?	~0.5	~0.4
	Diisopropylaminoethanol	?	~0.5	~0.4
	Diisopropylaminoethyl mercaptan	?	~0.5	~0.4
	Diisopropylaminoethyl methylphosphonic acid	?	~0.5	~0.4
	Ethyl methylphosphonoethioic acid isopropyl	?	?	?
	Methyl phosphonic acid	?	?	?
	S-(Diisopropylaminoethyl) methylphosphonothioate	?	~0.5	~0.4
	73207-98-4	?	~0.5	~0.4

*IE = Ionization Energy, the minimum lamp energy needed to detect the compound by PID

4.16 Heat Transfer Fluids by PID

Introduction

Heat transfer fluids are used in many processing applications to carry heat to or from a source, such as a boiler, or a target process, such as a chemical-processing vessel. While hardly volatile at room temperature, some heat transfer fluids contain highly toxic substances that can become volatile when heated. Heat transfer fluids typically are contained in a closed-loop system so that they do not come in contact with personnel or the process. However, leaks can and do occur. Because of the high toxicity of some heat transfer fluids, it is desirable to measure them for leak detection and to assure that levels are low enough to allow workers to operate safely. PIDs are very sensitive to the compounds that make up many heat transfer fluids and offer an effective means of providing real-time measurement for worker health and safety and for leak detection.

Example 1 – DowTherm® A

DowTherm® A, commonly referred to as DowTherm® or Therminol®*, is made up of 73% Diphenyl Oxide (Phenyl Ether) and 27% Diphenyl (Biphenyl). Both of these constituents have relatively low exposure limits:

TABLE 4.16.1. Dowtherm® A toxicity

Threshold	Diphenyl Oxide	Biphenyl	DowTherm® A (total)
Odor	0.001-0.01 ppm	0.0095 ppm	<0.001 ppm
PEL (OSHA)	1 ppm (7 mg/m ³)	0.2 ppm (1 mg/m ³)	0.48 ppm
IDLH	100 ppm	20 ppm (100 mg/m ³)	48 ppm

The TLV for the DowTherm® A mixture is calculated by the formula given in Chapter 3.1.6:

$$TLV_{mix} = 1 / (X_1/TLV_1 + X_2/TLV_2)$$

where X_i, TLV_i, are the mole fraction (percentage) of total VOCs, TLVs, of the individual components, respectively.

Therefore, the calculated limits for DowTherm® A are:

$$\text{TLV} = 1 / (0.73/1 + 0.27/0.2) = 0.48$$

$$\text{IDLH} = 1 / (0.73/100 + 0.27/20) = 48$$

DowTherm® A has a characteristic “sweet” odor. It can be readily detected by smell well below its exposure limit but cannot be quantitated this way. Grab samples and lab analysis provide accuracy, but they take too long for the results. PIDs provide rapid measurements of DowTherm® A that allow workers to immediately make PPE decisions.

Measuring at Lower Temperatures

DowTherm® A's high boiling temperature of 495°F (257°C) and vapor pressure of 0.025 mm Hg at 25°C means that at normal ambient temperatures, few DowTherm® A vapors are produced. For example, sampling the vapors above a bucket of DowTherm® A well below room temperature (41°F, 5°C) should produce little or no reading on a PID. At room temperature (68°F, 20°C) the saturated air space above a bucket of DowTherm® A could be expected to contain 33 ppm. However, because DowTherm® A is used as a heat transfer fluid, it is often used at elevated temperatures that can produce significant vapors.

Calibrating a PID to DowTherm®

Because DowTherm® A has a high boiling point, it is impossible to make a compressed gas standard for it, and a surrogate calibration with isobutylene is recommended. Because the TLV is low, a 10 ppm isobutylene calibration is preferred over 100 ppm. A CF of 0.4 is often appropriate for a 10.6 eV lamp (check with manufacturer).

Unusual Characteristics of DowTherm® A

DowTherm® A has a high boiling point and tends to adsorb to surfaces and be absorbed by some materials. Therefore, when using a PID to sample for leaks, it is recommended that the probe be extended by slipping a drinking straw over it. If liquid DowTherm® A comes into contact with the straw, the straw can be thrown away. If DowTherm® A comes into contact with the sample probe of a PID, it must be thoroughly solvent cleaned before further sampling.

Never Use Tygon® Tubing with DowTherm® A

Because Tygon® sample tubing quickly absorbs heat transfer fluids, it should never be used when sampling for them. Long sample lines can cause heat transfer fluid vapors to condense; therefore, it is recommended that all sampling be conducted without additional sampling hose. In-line filters can also promote condensation of heat transfer fluid, so they should be eliminated or reduced.

Sampling High Concentrations of DowTherm® A

When DowTherm® A can be seen in plumes, this is an indication that high concentrations (25 to 100 ppm) are present, which can lead to condensation in the sampling train. If the PID does not clear with five minutes' exposure to fresh air, then clean the components of the PID using a methanol wash in the following order:

1. Sample probe
2. Filters (replace them if they cannot be cleaned)
3. Sensor and PID lamp

* **Note:** Therminol® is a registered Trademark of Solutia, Inc.

4.17 Additional Portable PID Applications

Introduction

Many other PID applications are known. A few key ones are described below.

Aircraft Wing Tank Entry

Aircraft maintenance requires workers to enter confined spaces that contain jet fuel vapors, which need to be monitored for both explosive and toxic levels. LEL sensors used in conventional confined space monitors have poor sensitivity to jet fuel vapors. Workers can often see or smell jet fuel when in a wing tank, without the meter detecting it. The LEL of jet fuels is on the order of 0.8 vol.% (8000 ppm), and therefore it can easily be detected by PID even at the 10% LEL level (800 ppm). Unlike LEL sensors, PIDs are not poisoned by chemicals commonly used in aircraft maintenance, including low-ppm levels of silicon compounds found in lubricants, adhesives, silicone rubbers (including caulking and sealant compounds), and others. Chlorinated hydrocarbons are another common group of chemicals that degrade LEL sensor performance. They are frequently found in solvents, including degreasing and cleaning agents used in and around aircraft.

Turpentine in Pulp Mills

The pulping process produces two major products: (1) paper and (2) chemicals for applications as diverse as paints and foods. Turpentine is one of these chemicals; it has a low LEL of 0.8% by volume (8000 ppm) and an OSHA PEL of 100 ppm. Because of its relatively high molecular weight, turpentine's vapors are difficult to measure with a conventional LEL sensor in the combustible range, and are undetectable in the PEL range. PIDs provide a simple way to measure both PEL and LEL levels. In addition, PIDs are not subject to the poisoning by sulfur compounds often present, as catalytic bead LEL sensors are. Turpentine is especially sensitive, having a CF of only 0.3 on a 10.6 eV lamp.

Marine Applications

A variety of instruments are needed aboard ships, depending on the tank and vessel type. The three main considerations are usually to monitor for enough oxygen, explosive vapors, and toxic gases based on the hygiene limits. Oxygen and explosive vapors are done with standard electrochemical and LEL sensors. The instrument for toxic gases depends of the tank and vessel type.

Cargo tanks can carry a wide variety of liquids, depending on the vessel's IMO (International Marine Organization) classification. There are three levels of IMO classification. IMO class 1 covers the least corrosive or toxic liquids while IMO class 3 covers the most corrosive or toxic liquids.

IMO 1 – Transport of vegetable oils
– LEL and O₂ sensors recommended

IMO 2 – Transport of crude oil and oil products
– LEL, O₂, and H₂S sensors recommended

IMO 3 – Transport of various chemicals (BTEX to MTBE)
– Colorimetric detection tubes are often used for entry into these spaces, but a portable PID monitor is often more cost efficient and provides greater safety in the form of continuous monitoring.

Slup Tanks are normally used for carrying water to clean the cargo tanks. Entry into these spaces requires at least an O₂ sensor. Slup tanks are sometimes also approved for use as additional cargo tanks.

Fuels Tanks for the transport of fuel. Entry into these tanks requires a gas monitor with at least LEL and O₂ sensors.

Ballast Tanks use seawater to aid navigation. The seawater is drawn from the harbor and is usually full of plants, mussels, and even fish that start to rot inside the tank. LEL, O₂, and H₂S sensors are standard for entry into these spaces.

Container Vessels account for more than 3,000 of the marine industry's vessels. These vessels require the standard LEL and O₂ sensors to clean, repair, and inspect the fuel and ballast tanks. There are fumigants (methyl bromide), coolants (ammonia), and many additional applications on container vessels that require a monitor capable of monitoring both the basics (LEL, O₂, and H₂S) and a broad range of chemicals (PID).

Seaport Inspections often require detecting VOC levels before unloading is allowed, or loading new materials in cleaned tanks is permitted.

4.18 Common Fixed PID Applications

Introduction

Fixed-system PIDs can be used to monitor VOCs on a continuous, 24-hour basis. Continuous measurement can be useful for both industrial hygiene monitoring of VOCs and for process control to increase productivity and efficiency. Typically, such PIDs must be hard-wired to a power supply to allow intrinsically safe (from causing explosion) operation. Portable instruments can be used for the same function, but lose their intrinsically safe rating when plugged into a charger, as is necessary for long-term operation. Therefore, when a portable PID is used in a fixed application where intrinsic safety is required, it must either be contained in an explosion-proof housing or used remotely from the hazardous area with extension tubing reaching to the sampling location.

Fixed PIDs are best suited for operation with long-life lamps such as 9.8 eV and 10.6 eV lamps. Because of their relatively short life, 11.7 eV lamps are generally not recommended for continuous operation. In-line filters are recommended to extend the calibration intervals.

Paint Booths

Paints may contain a variety of solvents including methyl ethyl ketone (MEK) and simple hydrocarbons, which are easily detected with a PID. During spray painting and paint drying, these solvents are emitted to the air. Large operations such as in the automobile and aviation industries may require one monitor for each paint booth.

Printing Processes

Printing and silkscreening processes use solvents like toluene to dissolve and apply inks. These solvents are then emitted to the atmosphere during drying. Fixed PIDs have been successfully installed in the effluent ducting to determine the drying process' completion.

Degreasing Operations

Vapor degreasers employ large amounts of solvents such as perchloroethylene (PCE) to remove cutting oils and greases used in machining and assembling metal parts. Major applications include automobile and aviation industries.

Indoor Air Quality Monitoring

PIDs can be used for continuous indoor air quality (IAQ) monitoring, including non-manufacturing facilities. VOC sources include those from newly installed carpets or painted surfaces or where air intakes are located near potential outside sources. One example is an airport in which the incoming air is potentially contaminated with jet fuels. In some cases, the PID is packaged with other IAQ monitors to provide complete IAQ monitoring systems.

Air Treatment System Performance

Many fixed PIDs have been successfully installed to monitor the performance of treatment systems, such as activated carbon or thermal oxidation. Contaminated air streams arise from manufacturing operations and environmental clean-up activities, such as soil vapor extraction. Common treatment systems include activated carbon adsorption systems, catalytic oxidizers, and liquid scrubbers. In some cases, a PID is placed both before and after the treatment system to determine treatment effectiveness. PIDs can also be used to measure VOC emissions from incinerators, if the gases are allowed to cool below 60°C before entering the unit.

Refrigeration

Ammonia is frequently used as a refrigerant, especially in the food industry. Ammonia can be measured with a PID, which has advantages over electrochemical sensors in that the response is much faster and there are no overload concerns. Some of the newer Freon replacements are simple hydrocarbons that may also be measurable with a PID.

4.19 Pre-filter Applications

Silazanes

Semiconductor manufacturers often use hexamethyldisilazane and similar compounds as coating surfaces. When a PID is used, silicate deposits may form on the lamp and sensor, reducing sensitivity to other target vapors such as photoresists. Because of its highly reactive nature, hexamethyldisilazane can be removed selectively using cellulose filters. Such filtering has proved useful in at least one semiconductor plant even for long-term monitoring using a fixed PID.

UltraRAE

The UltraRAE uses an absorbent filter tube to remove interferences before PID measurement. Filter tubes are available to detect benzene in gasoline, butadiene in polymer manufacturing processes, and halocarbons such as methylene chloride in mixtures with common organic solvents. Readings are not continuous, as the co-present vapors consume the filter media. Time for one sample is on the order of 30 to 90 seconds.

The UltraRAE can also be operated in VOC mode for continuous measurements. Thus, it is a powerful tool for continuously monitoring general VOCs until a significant concentration is reached, followed by specific determination of a particularly toxic component of the mixture. Figure 4.19.1 shows the apparent response to low levels of butadiene in the presence of 100 ppm n-hexane using an UltraRAE.

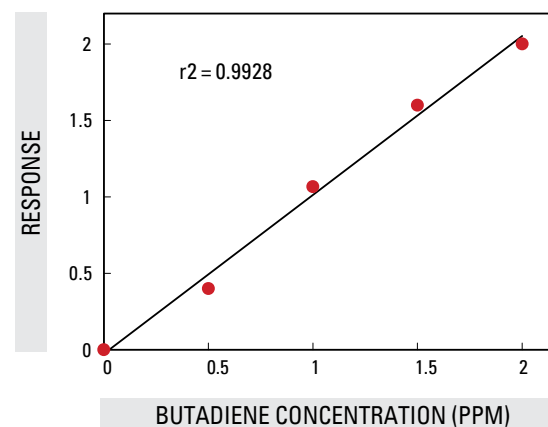


FIGURE 4.19.1. UltraRAE butadiene response in the presence of 100 ppm hexane using a RAE-Sep butadiene tube and 9.8 eV lamp

Table 4.19.1 lists the apparent response to a variety of compounds that may interfere in benzene measurements. Thus, appropriate filtering can provide selective measurements in the presence of large excesses of other responding compounds in certain applications.

TABLE 4.19.1. UltraRAE response to potential benzene interferences using RAE-Sep benzene tube with 9.8 Ev lamp

Compound	Test Concentration (ppmv)*	Apparent Benzene Response
Toluene	400	0.1
p-Xylene	200	0.0
Ethylbenzene	200	0.0
Styrene	100	0.0
Nitrobenzene	100	0.0
Phenol	100#	0.0
Chlorobenzene	20	2.5
Dichlorobenzene	50	0.1
Hydrogen Sulfide	150	0.0
Methane	25,000**	0.0
Propane	1000	0.0
Isobutane	100	0.0
Isobutylene	500	0.0
n-Pentane	1,500	0.0
1,3-Butadiene	300	0.0
n-Hexane	100#	0.0
Cyclohexane	10	0.4
n-Octane	300	0.1
β-Pinene	50	0.0
Ethanol	50	0.0
Isopropanol	100	0.0
Acetone	100	0.0
Cyclohexanone	200	0.0
Tetrahydrofuran	100	0.0
Ethyl acetate	100	0.0
Acrylonitrile	100	0.0
Epichlorohydrin	100	0.0
Trichloroethylene	100	66
Perchloroethylene	50	38

*Not necessarily the maximum allowable concentration.

**No effect on tube capacity. Propane and higher hydrocarbons do affect capacity.

#Higher concentrations may cause a reduced benzene response.

5. APPENDICES

5.1 Appendix 1: References

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5.2 Appendix 2. Glossary

ACGIH: American Conference of Governmental Industrial Hygienists. A non-regulatory professional society of hygienists that provides recommendations for human exposure limits, among other things.

Aldehydes: Compounds that contain a carbon bonded to a hydrogen, another carbon, and double bonded to an oxygen atom.

Aliphatics: Compounds containing only carbon and hydrogen and no double or triple bonds.

Alkanes: see Aliphatics.

Alkyl Halides: Aliphatics containing halogens.

Amines: Compounds with an $-NH_2$ group with alkalinity and corrosivity similar to ammonia.

Aromatics: Cyclic compounds that contain double bonds and have special stability, and sensitivity to PIDs. A common example is benzene, comprising 6 carbons and 6 hydrogens, but may contain nitrogen, oxygen, or other heteroatoms.

BTEX: Benzene, toluene, ethylbenzene, and xylenes. Aromatic hydrocarbons, usually as part of a fuel mixture.

CF: Correction Factor. This value is multiplied by the observed reading when the PID is calibrated to a surrogate gas (e.g., isobutylene), to obtain the true concentration of the compound measured. Higher values mean lower sensitivity of the compound.

Ceiling: Worker exposure concentration that should not be exceeded during any part of the working period.

CFC: Chlorofluorocarbon containing no hydrogen atoms. Condensable gas compounds commonly used as refrigerants, but causing potential damage to the ozone layer.

EC Sensor: Electrochemical sensor.

Ethers: Organic compounds containing an oxygen atom bonded to two carbon atoms.

FID: Flame Ionization Detector. Responds to a broad range of combustible compounds including methane, but not CO or CO₂.

GC: Gas Chromatography.

GAC: Granular Activated Carbon. Used as an adsorbent to collect vapor components for subsequent analysis.

Halogens: Compounds containing fluorine, chlorine, bromine or iodine.

HVAC: Heating, Ventilation and Air Conditioning.

HCFC: Hydrogen-containing chlorofluorocarbon. Condensable gas compounds commonly used as refrigerants, causing less potential damage to the stratospheric ozone layer than CFCs.

$h\nu$ Symbol for a photon of unspecified energy. The photon energy is the product of Planck's constant h (6.63×10^{-34} joule-seconds) and the frequency ν in cycles per second.

Hydrocarbons: Compounds containing carbon and hydrogen.

IAQ: Indoor Air Quality.

IBE: Isobutylene, a common calibration gas for PIDs.

IDLH: Immediately Dangerous to Life and Health.

IE or IP: Ionization Energy or Ionization Potential. More correctly termed ionization energy and commonly given in units of electron-volts (eV). This is the lowest photon energy capable of ejecting an electron from a target molecule.

Inorganics: Compounds that contain fewer than two carbon atoms.

ISEA: International Safety Equipment Association.

Ketones: Organic compounds containing a carbon bonded to two other carbons and a double-bonded oxygen.

LC50: The concentration of a gas or vapor that causes a 50% chance of death within a defined exposure time (used herein as 1 minute).

LED: Light-emitting diode. Commonly used for PID alarms.

LEL or LFL: Lower Explosive Limit or Lower Flammability Limit. The lowest vapor concentration that will sustain a flame when ignited in air.

Li-ion: Lithium ion battery. High power density batteries not subject to memory effects.

MAK: Exposure limits defined by the Federal Republic of Germany.

MDI: 4,4'-Methylenebis(phenyl isocyanate), an agent used in polymer manufacturing.

MEK: Methyl ethyl ketone (i.e., 2-butanone).

MIBK: Methyl isobutyl ketone.

MSDS: Material Safety Data Sheet.

NFPA: National Fire Protection Association.

NiCd: Nickel-Cadmium battery. Medium power density batteries that exhibit a memory effect when recharged before complete discharge.

NiMH: Nickel-Metal Hydride battery.

NIOSH: National Institute for Occupational Safety and Health. A U.S. government agency making non-enforceable exposure limit recommendations (RELs).

Olefins: Hydrocarbons containing double bonds.

Organics: Compounds containing more than one carbon atom and typically containing hydrogen.

OSHA: Occupational Safety and Health Administration, a U.S. government agency defining enforceable exposure limits (PELs).

PAH: Polycyclic Aromatic Hydrocarbons. Carcinogenic compounds formed in combustion processes, especially on fly-ash.

PC: Personal computer.

PEL: An OSHA-defined permissible exposure limit, legally enforceable.

PFA: A derivative of Teflon having perfluoroalkoxy copolymer blocks and similar chemical properties.

PGME: Propylene glycol monomethyl ether.

PGMEA: Propylene glycol methyl ether acetate.

PID: Photoionization Detector.

ppb or ppbv: Parts-per-billion or parts-per-billion by volume (used synonymously in this work).

PPE: Personal Protective Equipment

ppm or ppmv: Parts-per-million or parts-per-million by volume (used synonymously in this work).

PTFE: Teflon or polytetrafluoroethane, a chemically inert polymer.

REL: Recommended Exposure Limit as suggested by NIOSH.

RF: Response Factor. The reading is divided by the RF to obtain the true concentration. Inverse of the CF.

SCBA: Self-Contained Breathing Apparatus.

SBS: Sick Building Syndrome. Used to describe a variety of indoor-related symptoms of which the cause is not clearly identified.

STEL: Short Term Exposure Limit. The maximum allowable exposure concentration averaged over a 15-minute period for at most 4 times per 8-hour day separated by at least one hour exposure below the TWA.

Sulfides: Organic compounds containing a sulfur atom bonded to two carbon atoms.

TLV: Threshold Limit Value. An ACGIH-recommended exposure limit (not legally enforceable).

TVOCs: Total VOCs, typically used as an IAQ parameter.

TWA: Time Weighted Average. A cumulative exposure dose, generally over an 8-hour period. TWA is calculated as the average concentration times the fraction of the (8-hr) time period elapsed.

VOC: Volatile Organic Compound. In general use this acronym refers to all organic compounds that have significant vapor pressure. The US EPA also defines VOCs according to their tropospheric ozone-forming potential and includes most carbon-hydrogen containing compounds but excludes such compounds as methane, ethane, acetone, methyl acetate, methylene chloride, and most CFCs and HCFCs.

VOC*: VOC in a short-lived, excited electronic state.

VOC+: Ionized VOC with a positive charge.

5.3 Appendix 3: Correction Factors, Ionization Energies and Exposure Limits

See Table at www.raesystems.com: Technical Note TN-106

5.4 Appendix 4: Sample Calculation for Gas Mixture CFs

Examples of Automatic Calculation of Correction Factors, TLVs and Alarm Limits for Mixtures

(Calculations performed using Excel version of this database, available on request)

Example 1: Solvent Mixture

Compound	CF 9.8 eV	CF 10.6 eV	CF 11.7eV	Mole Fraction	Conc. ppm	TLV-TWA ppm	STEL ppm
Benzene	0.55	0.53	0.6	0.01	1	0.5	2.5
Toluene	0.54	0.5	0.51	0.06	10	50	150
Hexane, n-	300	4.3	0.54	0.06	10	50	150
Heptane, n-	45	2.8	0.6	0.28	50	400	500
Styrene	0.45	0.4	0.42	0.06	10	20	40
Acetone	1.2	1.1	1.4	0.28	50	750	1000
Isopropanol	500	6	2.7	0.28	50	400	500
None	1	1	1	0	0	1	
Mixture value:	2.1	1.5	0.89	1	181 ppm	56 ppm	172 ppm

TLV alarm setpoint when calibrated to isobutylene:	26 ppm	37 ppm	62 ppm				
STEL alarm setpoint, when calibrated to isobutylene:	86 ppm	115 ppm	193 ppm				

Example 2: Paint Solvents

Compound	CF 10.6 eV	CF 11.7eV	Mole Fraction	Conc. ppm	TLV-TWA ppm
Formaldehyde	NR	1.6	0.006	0.5	~0.3
Toluene	0.50	0.50	0.015	1.25	50
PGMEA	1.0	0.82	0.015	1.25	~50
Isobutanol	3.8	1.5	0.14	12.5	50
Xylene, p-	0.39	0.38	0.23	20	100
Butyl acetate, n-	2.6	-1.5	0.59	50	150
Mixture value:	1.1	0.87	1.00	86 ppm	36 ppm
TLV alarm setpoint when calibrated to isobutylene:	33 ppm	42 ppm			

5.5 Appendix 5: Mixture Alarm Limits

Note: OSHA Z-listed chemicals are in italics.

Compound	CF@10.6 eV	OSHA PEL (ppm)	IBE-Equiv. Alarm
<i>Acetone</i>	1.1	1000	909
<i>Petroleum distillates</i>	0.71	500	704
<i>Stoddard Solvent</i>	0.71	500	704
<i>Isopropyl ether</i>	0.80	500	625
<i>Methylcyclohexane</i>	0.97	500	515
Dichloroethene, t-1,2-	0.45	200	444
<i>Toluene</i>	0.50	200	400
<i>Cyclohexene</i>	0.80	300	375
<i>Diethyl ether</i>	1.1	400	364
Gasoline #1	0.85	300	353
Pinene, α -	0.31	100	323
Gasoline #2, 92 octane	1.0	300	300
<i>Turpentine</i>	0.35	100	286
<i>Octane, n-</i>	1.8	500	278
Pinene, β -	0.37	100	270
<i>Xylene, p-</i>	0.39	100	256
Dichloroethene, c-1,2-	0.8	200	250
<i>Styrene</i>	0.40	100	250
<i>Methyl ethyl ketone</i>	0.86	200	233
<i>Xylene, m-</i>	0.44	100	227
<i>Xylene, o-</i>	0.46	100	217
<i>Methyl propyl ketone</i>	0.93	200	215
<i>Cyclohexane</i>	1.4	300	214
<i>Xylenes (o-, m-, p-)</i>	0.49	100	204
<i>Methyl styrene (alpha-)</i>	0.50	100	200
<i>Ethyl benzene</i>	0.52	100	192
<i>Chlorobenzene</i>	0.40	75	187
<i>Heptane, n-</i>	2.8	500	179
<i>Ethoxyethanol (2-)</i>	1.3	200	154
Piperylene, isomer mix	0.69	100	145
Nonane	1.4	200	143
<i>Ethyl silicate</i>	0.71	100	141
<i>Methyl isobutyl ketone</i>	0.80	100	125
<i>Pentane</i>	8.4	1000	119
<i>Tetrahydrofuran</i>	1.7	200	118

Compound	CF@10.6 eV	OSHA PEL (ppm)	IBE-Equiv. Alarm
<i>Hexane, n-</i>	4.3	500	116
<i>Dichlorobenzene (o-)</i>	0.47	50	106
<i>Butyl acetate, (tert-)</i>	2.0	200	100
<i>Ethyl alcohol</i>	10	1000	100
Chlorotoluene, o-	0.50	50	100
Propylene glycol methyl ether acetate	1.0	100	100
100 PPM Alarm \uparrow			
<i>Isopropyl acetate</i>	2.6	250	96
<i>Cumene</i>	0.54	50	93
<i>Trichloroethylene</i>	0.54	50	93
<i>Dioxane, 1,4-</i>	1.1	100	91
<i>Ethyl acetate</i>	4.6	400	87
Isopentane, & isomers	8.2	600	73
<i>Diacetone alcohol</i>	0.70	50	71
Mesitylene	0.35	25	71
Propylene glycol monomethyl ether	1.4	100	71
Butyl acetate, (sec-)	3.0	200	67
<i>Isopropyl Alcohol</i>	6.0	400	67
<i>Methyl methacrylate</i>	1.5	100	67
<i>Butyl acetate, (n-)</i>	2.6	150	58
<i>Isobutyl acetate</i>	2.6	150	58
<i>Propyl acetate, n-</i>	3.5	200	57
<i>Cyclohexanone</i>	0.90	50	56
<i>Amyl acetate (sec-)</i>	2.3	125	54
Kerosene	0.6	30	50
Jet fuel JP-8	0.6	30	50
50 PPM Alarm \uparrow			
Jet fuel JP-5	0.6	29	48
<i>Isoamyl acetate</i>	2.1	100	48
Methyl t-butyl ether	0.91	40	44
<i>Perchloroethene</i>	0.57	25	44
<i>Amyl acetate (n-)</i>	2.3	100	43
<i>Butoxyethanol, 2-</i>	1.2	50	42
<i>Butyl alcohol (sec-)</i>	4.0	150	38
Hexene, 1-	0.80	30	38
<i>Naphtha (Coal tar) {10% aromatics}</i>	2.8	100	36
<i>Butyl alcohol (tert-)</i>	2.9	100	34
<i>Acetaldehyde</i>	6.0	200	33

Compound	CF @10.6 eV	OSHA PEL (ppm)	IBE-Equiv. Alarm
<i>Propyl alcohol (n-)</i>	6.0	200	33
Jet fuel JP-4	1.0	30	30
<i>Methyl acetate</i>	6.6	200	30
<i>Triethylamine</i>	0.90	25	28
<i>Isobutyl alcohol</i>	3.8	100	26
<i>Diethylamine</i>	0.97	25	26
25 ppm Alarm ↑			
<i>Naphthalene</i>	0.42	10	24
<i>Methyl iodide</i>	0.22	5	23
<i>Butyl alcohol (n-)</i>	4.7	100	21
Hexamethyldisilazane, 1,1,1,3,3,3-	0.24	5	21
<i>Naphtha (Coal tar) {purely aliphatic}</i>	5.7	100	18
<i>Butyl mercaptan</i>	0.60	10	17
<i>Carbon disulfide</i>	1.2	20	17
<i>Ethyl mercaptan</i>	0.60	10	17
<i>Methyl mercaptan</i>	0.60	10	17
Diesel Fuel #2 (Automotive)	0.66	11	17
<i>Propylene oxide</i>	6.5	100	15
<i>Dimethyl acetamide, N,N-</i>	0.80	10	13
<i>Dimethylformamide, N,N-</i>	0.80	10	13
<i>Ethylamine</i>	0.80	10	13
Vinyl bromide	0.40	5	13
Butane	67	800	12
<i>Dibromoethane, 1,2-</i>	1.7	20	12
<i>Methyl bromide</i>	1.7	20	12
Diesel Fuel #1	0.93	11	12
Trimethylamine	0.85	10	12
Trichlorobenzene (1,2,4-)	0.46	5	11
<i>Aniline</i>	0.48	5	10
Dicyclopentadiene	0.48	5	10
<i>Ethyl acrylate</i>	2.4	25	10
<i>Methoxyethanol, 2-</i>	2.4	25	10
<i>Toluidine, o-</i>	0.50	5	10
10 PPM Alarm ↑			
<i>Chloroprene (beta-)</i>	3.0	25	8.3
Cyclohexylamine	1.2	10	8.3
<i>Methylamine</i>	1.2	10	8.3
Vinyl acetate	1.2	10	8.3

Compound	CF @10.6 eV	OSHA PEL (ppm)	IBE-Equiv. Alarm
Isobutane	100	800	8.0
<i>Pyridine</i>	0.68	5	7.4
<i>Diisopropylamine</i>	0.74	5	6.7
<i>Allyl glycidyl ether</i>	1.5	10	6.7
<i>Dimethylamine</i>	1.5	10	6.7
Butyl acrylate, n-	1.6	10	6.3
<i>Furfural</i>	0.92	5	5.4
<i>Ammonia</i>	9.7	50	5.2
<i>Dichloroethyl ether</i>	3.0	15	5.0
Formamide	4.0	20	5.0
<i>Phenol</i>	1.0	5	5.0
<i>Nitric oxide</i>	5.2	25	4.8
<i>Butylamine, n-</i>	1.1	5	4.6
Benzaldehyde	0.50	2	4.0
Ethylene glycol	16	50	3.1
<i>Hydrogen sulfide</i>	3.3	10	3.0
Dimethylethylamine	1.0	3	3.0
<i>Methyl acrylate</i>	3.7	10	2.7
Caprolactam	2.0	5	2.5
<i>Phenyl ether</i>	0.40	1	2.5
<i>Benzene</i>	0.53	1	1.9
<i>Ethanolamine</i>	1.6	3	1.9
<i>Crotonaldehyde</i>	1.1	2	1.8
Benzyl cyanide	0.60	1.04	1.7
<i>Benzyl chloride</i>	0.60	1	1.7
<i>Propylene imine</i>	1.3	2	1.5
Diethanolamine	2.0	3	1.5
Bromobenzene	0.60	0.78	1.3
Vinyl-2-pyrrolidinone, 1-	0.80	1	1.3
<i>Butadiene</i>	0.85	1	1.2
Dichloro-1-propene, 1,3-	0.96	1	1.0
Diethylenetriamine	1.0	1	1.0
<i>Iodine</i>	0.10	0.1	1.0
1 PPM Alarm ↑			
Acrylic Acid	12	10	0.8
<i>Allyl alcohol</i>	2.4	2	0.8
Benzoyl chloride	0.6	0.5	0.8
<i>Acetic Anhydride</i>	6.1	5	0.8

Compound	CF @10.6 eV	OSHA PEL (ppm)	IBE-Equiv. Alarm
<i>Dimethylhydrazine, 1,1-</i>	0.78	0.5	0.6
Butyl hydroperoxide, t-	1.6	1	0.6
Glutaraldehyde	0.80	0.5	0.6
<i>Epichlorohydrin</i>	8.5	5	0.6
<i>Nitrobenzene</i>	1.9	1	0.5
<i>Vinyl chloride</i>	2.0	1	0.5
<i>Acetic Acid</i>	22	10	0.5
<i>Diphenyl (Biphenyl)</i>	0.40	0.2	0.5
Methyl ethyl ketone peroxide	2	0.7	0.4
<i>Hydrazine</i>	3.0	1	0.3
<i>Nitrogen dioxide</i>	16	5	0.3
Diketene	2.0	0.5	0.3
<i>Allyl chloride</i>	4.3	1.0	0.2
<i>Bromoform</i>	2.5	0.5	0.2
<i>Methyl hydrazine (Monomethyl hydrazine)</i>	1.2	0.2	0.2
<i>Phosphorus trichloride</i>	4.0	0.5	0.1
<i>Nicotine</i>	0.70	0.075	0.1
<i>Bromine</i>	1.3	0.1	0.08
<i>Ethylene oxide</i>	13	1	0.08
<i>Phosphine</i>	3.9	0.3	0.08
Below Common Air Background Values of 0.05 ppm (50 ppb)			
<i>Dimethyl sulfate</i>	20	1	0.05
<i>Tetraethyl lead (as Pb)</i>	0.30	0.008	0.03
<i>Acrolein</i>	3.9	0.1	0.03
<i>Toluene-2,4-diisocyanate (TDI)</i>	1.4	0.02	0.01
Mustard, Distilled (TWA) (LC50)*	0.6	0.00046 >230	0.0008 >385
Tabun (TWA) (LC50)*	0.8	0.000015 20	0.00002 25
Sarin (TWA) (LC50)*	3	0.000017 12	0.000006 4

* LCt50 = Lethal concentration for 50% chance of death in a one minute exposure

5.6 Appendix 6: PID to FID Conversion

TABLE 5.6.1. PID to FID correction factors for methane equivalents

Compound	C's	PID CF (10.6 eV)	Lab FID RF	PID-FID CF (Meas.)	PID-FID CF (C Atom Calc)
Acetaldehyde	2	6			12
Acetic acid	2	22			44
Acetone	3	1.1	1.8	2.0	3.3
Acetonitrile	2	NR		NR	NR
Acetylene	2	NR		NR	NR
Acrolein	3	3.9			11.7
Acrylonitrile	3	NR		NR	NR
Allyl alcohol	3	2.4			7.2
Allyl chloride	3	~4			~12
Aniline	6	3.0			18
Benzene	6	0.53	4.3	2.3	3.2
Benzyl chloride	7	0.6			4.2
Bromoethane	2	~1.6			~3.2
Bromoform	1	2.5			2.5
Bromopropane, 1-	3	1.5			4.5
Butadiene, 1,3-	4	0.85			3.4
Butane, iso-	4	~100			~400
Butane, n-	4	NR		NR	NR
Butanol, n-	4	4.7			18.8
Butanol, iso-	4	3.8			15.2
Butyl mercaptan	4	0.52			2.1
Carbon tetrachloride	1	NR	0.40	NR	NR
Chlorobenzene	6	0.40	4.0	1.6	2.4
Chloroethane	2	NR		NR	NR
Chloroform	1	NR	0.49	NR	NR
Cumene	9	0.54			4.9
Cyclohexane	6	1.4			8.4
Dichlorobenzene, 1,2-	6	0.47			2.8
Dichlorobenzene, 1,4-	6	~0.5			~3
Dichloroethylene, 1,1-	2	~0.9	1.9		~1.8
Dichloroethylene,c-1,2-	2	~0.8			~1.6
Dichloroethylene, t-1,2-	2	0.45			0.9
Dichloropropane, 1,2-	3	NR		NR	NR
Dimethylformamide, N,N-	3	~0.8			~2.4

Compound	C's	PID CF (10.6 eV)	Lab FID RF	PID-FID CF (Meas.)	PID-FID CF (C Atom Calc)
Dioxane, 1,4-	4	~1.3			~5.2
Epichlorohydrin	2	8.5			17.0
Ethane	2	NR		NR	NR
Ethanol	2	12			24.0
Ethoxyethanol, 2- (Ethyl cellosolve)	4	~1.3			~5.2
Ethyl acetate	4	4.6	2.0	9.0	18.4
Ethyl acrylate	5	2.4			12.0
Ethylbenzene	8	0.52			4.2
Ethylene dibromide (1,2-Dibromoethane)	2	1.7			3.4
Ethylene dichloride (1,2-Dichloroethane)	2	NR	1.5	NR	NR
Gasoline	8	~1			~8
Heptane, n-	7	2.6			18.2
Hexane, n-	6	4.3	4.7	20.2	25.8
Isobutylene	4	1.0			4.0
Isoprene	5	0.6			3.2
Isopropanol	3	6.0	1.6	9.9	18.0
Methane	1	NR	1.0	NR	NR
Methanol	1	NR	0.58	NR	NR
Methoxyethanol, 2- (Methyl cellosolve)	3	2.4			7.2
Methyl bromide	1	1.7			1.7
Methyl chloride	1	NR		NR	NR
Methyl ethyl ketone	4	0.86	2.2	1.9	3.4
Methyl isobutyl ketone	6	0.8			4.8
Methyl methacrylate	5	1.5			7.5
Methyl t-butyl ether	5	0.9	3.2	2.8	4.5
Methylene chloride	1	NR	0.94	NR	NR
Nonane, n-	9	~1.4			~13
Octane (mix)	8	1.8			14.4
Pentane, n-	5	8.4			42.0
Perchloroethylene	2	0.57	1.3	0.8	1.1
Propane	3	NR		NR	NR
Propionaldehyde	3	~1.9			~5.7
Propylene oxide	3	6.5			19.5

Compound	C's	PID CF (10.6 eV)	Lab FID RF	PID-FID CF (Meas.)	PID-FID CF (C Atom Calc)
Styrene	8	0.4			3.2
Tetrachloroethane, 1,1,2,2-	2	NR		NR	NR
Tetrahydrofuran	4	1.7	2.5	4.2	6.8
Toluene	7	0.5	5.1	2.6	3.5
Trichloroethane, 1,1,1-	2	NR	1.6	NR	NR
Trichloroethane, 1,1,2-	2	NR		NR	NR
Trichloroethylene	2	0.5			1.0
Triethylamine	3	0.9			2.7
Vinyl acetate	4	1.2			4.8
Vinyl bromide	2	0.4			0.8
Vinyl chloride	2	2.0	2.0	4.0	4.0
Xylene, o-	8	0.59	3.6	2.1	4.7
Xylene, m-	8	0.43			3.4
Xylene, p-	8	0.45			3.6

TABLE 5.6.2. PID to FID correction factors for hexane equivalents

Compound	C's	PID CF (10.6 eV)	Lab FID RF	PID-FID CF (Meas.)	PID-FID CF (C Atom Calc)
Acetaldehyde	2	6			2.0
Acetic acid	2	22			7.3
Acetone	3	1.1	0.39	0.42	0.55
Acetonitrile	2	NR		NR	NR
Acetylene	2	NR		NR	NR
Acrolein	3	3.9			2.0
Acrylonitrile	3	NR		NR	NR
Allyl alcohol	3	2.4			1.2
Allyl chloride	3	~4			~2
Aniline	6	3.0			3.0
Benzene	6	0.53	0.92	0.49	0.53
Benzyl chloride	7	0.6			0.7
Bromoethane	2	~1.6			~0.5
Bromoform	1	2.5			0.42
Bromopropane, 1-	3	1.5			0.75
Butadiene, 1,3-	4	0.85			0.57
Butane, iso-	4	~100			~67
Butane, n-	4	NR		NR	NR

Compound	C's	PID CF (10.6 eV)	Lab FID RF	PID-FID CF (Meas.)	PID-FID CF (C Atom Calc)
Butanol, n-	4	4.7			3.1
Butanol, iso-	4	3.8			2.5
Butyl mercaptan	4	0.52			0.35
Carbon tetrachloride	1	NR	0.08	NR	NR
Chlorobenzene	6	0.40	0.86	0.34	0.40
Chloroethane	2	NR		NR	NR
Chloroform	1	NR	0.10	NR	NR
Cumene	9	0.54			0.81
Cyclohexane	6	1.4			1.4
Dichlorobenzene, 1,2-	6	0.47			0.47
Dichlorobenzene, 1,4-	6	~0.5			~0.5
Dichloroethylene, 1,1-	2	~0.9	0.40		~0.3
Dichloroethylene, c-1,2-	2	~0.8			~0.3
Dichloroethylene, t-1,2-	2	0.45			0.15
Dichloropropane, 1,2-	3	NR		NR	NR
Dimethylformamide, N,N-	3	~0.8			~0.4
Dioxane, 1,4-	4	~1.3			~0.9
Epichlorohydrin	2	8.5			2.8
Ethane	2	NR		NR	NR
Ethanol	2	12			4.0
Ethoxyethanol, 2- (Ethyl cellosolve)	4	~1.3			~0.9
Ethyl acetate	4	4.6	0.42	1.9	3.1
Ethyl acrylate	5	2.4			2.0
Ethylbenzene	8	0.52			0.69
Ethylene dibromide (1,2-Dibromoethane)	2	1.7			0.57
Ethylene dichloride (1,2-Dichloroethane)	2	NR	0.32	NR	NR
Gasoline	8	~1			~1.3
Heptane, n-	7	2.6			3.0
Hexane, n-	6	4.3	1.00	4.3	4.3
Isobutylene	4	1.0			0.67
Isoprene	5	0.6			0.53
Methoxyethanol, 2- (Methyl cellosolve)	3	2.4			1.2
Methyl bromide	1	1.7			0.28
Methyl chloride	1	NR		NR	NR

Compound	C's	PID CF (10.6 eV)	Lab FID RF	PID-FID CF (Meas.)	PID-FID CF (C Atom Calc)
Methyl ethyl ketone	4	0.86	0.48	0.41	0.57
Methyl isobutyl ketone	6	0.8			0.80
Methyl methacrylate	5	1.5			1.3
Methyl t-butyl ether	5	0.9	0.67	0.61	0.75
Methylene chloride	1	NR	0.20	NR	NR
Nonane, n-	9	~1.4			~2
Octane (mix)	8	1.8			2.4
Pentane, n-	5	8.4			7.0
Perchloroethylene	2	0.57	0.29	0.16	0.19
Propane	3	NR		NR	NR
Propionaldehyde	3	~1.9			~0.95
Propylene oxide	3	6.5			3.3
Styrene	8	0.4			0.53
Tetrachloroethane, 1,1,2,2-	2	NR		NR	NR
Tetrahydrofuran	4	1.7	0.53	0.90	1.1
Toluene	7	0.5	1.1	0.55	0.58
Trichloroethane, 1,1,1-	2	NR	0.35	NR	NR
Trichloroethane, 1,1,2-	2	NR		NR	NR
Trichloroethylene	2	0.5			0.17
Trimethylbenzene, 1,2,4-	6	~0.35	0.22	~0.08	~0.35
Triethylamine	3	0.9			0.45
Vinyl acetate	4	1.2			0.80
Vinyl bromide	2	0.4			0.13
Vinyl chloride	2	2.0	0.43	0.86	0.67
Xylene, o-	8	0.59	0.76	0.45	0.79
Xylene, m-	8	0.43			0.57
Xylene, p-	8	0.45			0.60

5.7 Appendix 7: Calculation of CS₂ and H₂S Concentrations in a Dual 9.8/10.6 eV Lamp PID System

Definitions:

[H₂S] = H₂S concentration in ppm

[CS₂] = CS₂ concentration in ppm

R_{9.8} = Reading with a 9.8 eV lamp in isobutylene equivalent ppm

R_{10.6} = Reading with a 10.6 eV lamp in isobutylene equivalent ppm

CF_{9.8-CS₂} = Correction factor for CS₂ with a 9.8 eV lamp

CF_{10.6-CS₂} = Correction factor for CS₂ with a 10.6 eV lamp

CF_{10.6-H₂S} = Correction factor for H₂S with a 10.6 eV lamp

The response to the 9.8 eV lamp is only due to CS₂. Therefore,

$$R_{9.8} = \frac{[CS_2]}{CF_{9.8-CS_2}} = \frac{[CS_2]}{4}$$

$$\therefore [CS_2] = 4R_{9.8}$$

The response to the 10.6 eV lamp is due to both CS₂ and H₂S. Therefore,

$$R_{10.6} = \frac{[CS_2]}{CF_{10.6-CS_2}} + \frac{[H_2S]}{CF_{10.6-H_2S}} = \frac{[CS_2]}{1.2} + \frac{[H_2S]}{3.3}$$

$$\therefore [H_2S] = 3.3 \left(R_{10.6} - \frac{[CS_2]}{1.2} \right)$$

For example, if the total response on the 9.8 eV lamp is 2 ppm isobutylene equivalents, and the total response on the 10.6 eV lamp is 10 ppm isobutylene equivalents, then

$$[CS_2] = 4R_{9.8} = 4 \times 2 = 8 \text{ ppm}$$

and

$$[H_2S] = 3.3 \left(R_{10.6} - \frac{[CS_2]}{1.2} \right) = 3.3 \left(10 - \frac{8}{1.2} \right) = 11 \text{ ppm}$$

5.8 Appendix 8: RAE PID Lamp Traits

This appendix gives an example of recommendations for selection and care of PID lamps.

PID Lamp Selection

RAE Systems photoionization detectors (PIDs) offer lamps with three different photon energies: 9.8 eV, 10.6 eV and 11.7 eV. A special high-intensity version of the 10.6 eV lamp is also available. Instruments are shipped with the standard 10.6 eV lamp unless otherwise specified. Because the 11.7 eV lamp has a shorter life (see Table 5.9.1) and is more expensive, use of the 9.8 or 10.6 eV lamps is recommended whenever possible.

Lamp Output and Resolution

The larger (1/2") lamps used in the MiniRAE, ppbRAE and UltraRAE series have greater output than the smaller (1/4") lamps used in the ToxiRAE, MultiRAE and AreaRAE series. 10.6 eV lamps also have significantly stronger output than 11.7 eV lamps, and slightly stronger than 9.8 eV lamps. Higher output translates to better resolution and lower detection limits. The resolution also depends on the type of compound measured; generic values for isobutylene are listed below. The "super-bright" 10.6 eV lamps are required for ppb-level detection, and the ppbRAE cannot use 11.7 eV lamps. These stronger lamps are not recommended for other PIDs because they may saturate the sensor at high VOC concentrations.

Lamps Stored in Glass Ampoules

Because lamps gradually lose power even when not in use, the warranty periods listed below apply even if the lamp is not turned on. New 1/4" 11.7 eV lamps shipped in sealed ampoules are warranted for storage of 3 months. The one-month operating warranty begins at the earlier of the three-month storage period or when the when the gas-tight container is opened. In order to maintain the warranty, it is important that these dates be recorded.

Lamp Care

Store lamps under dry conditions to minimize attack on the lamp window. Keep the lamps clean using dry methanol or isopropanol; never use acetone on 11.7 eV lamps.

Lamp Replacement

RAE Systems PID lamps do not burn out suddenly because they have no filament. Thus, because of the shorter life, we recommend purchasing 11.7 eV lamps as close as possible to the date of use. The strength of the lamp and thus its expected life can be determined using the special Diagnostic Mode (See RAE Systems Technical Note TN-123).

TABLE 5.9.1. PID lamp characteristics

Lamp Energy	Lamp Diameter	Typical Resolution	Warranty Period	Typical Life
9.8 eV	1/2 inch	0.1 ppm	6 months	1 year
9.8 eV	1/4 inch	0.2 ppm	6 months	1 year
10.6 eV*	1/2 inch	0.1 ppm	1 year (3 yrs)*	2 - 3 years
10.6 eV super bright	1/2 inch	0.002 ppm	1 year	1 year
10.6 eV	1/4 inch	0.1-0.2 ppm	1 year	1 year
11.7 eV	1/2 inch	0.1-0.2 ppm	1 month	1 - 2 months
11.7 eV in ampule	1/4 inch	1.0 ppm	1 month	4 mo. in ampule 1 - 3 mo. in use

*10.6 eV lamps used in MiniRAE 3000 instruments are warranted for three years under normal operating conditions are used.

5.9 Appendix 9: Conversion Factors for Gas Concentrations

To convert from the units on the left to the units on top, multiply by:

To: from:	Vol. %	ppmv	ppbv	mg/m ³	mg/L
vol. %	-	10 ⁴	10 ⁷	$\frac{10^4(\text{mw}\cdot\text{P})}{\text{MV}}$	$\frac{10(\text{mw}\cdot\text{P})}{\text{MV}}$
ppmv	10 ⁻⁴	-	10 ³	$\frac{(\text{mw}\cdot\text{P})}{\text{MV}}$	$\frac{10^{-3}(\text{mw}\cdot\text{P})}{\text{MV}}$
ppbv	10 ⁻⁷	10 ⁻³	-	$\frac{10^{-3}(\text{mw}\cdot\text{P})}{\text{MV}}$	$\frac{10^{-6}(\text{mw}\cdot\text{P})}{\text{MV}}$
mg/m ³	$\frac{10^{-4}\text{MV}}{(\text{mw}\cdot\text{P})}$	$\frac{\text{MV}}{(\text{mw}\cdot\text{P})}$	$\frac{10^3\text{MV}}{(\text{mw}\cdot\text{P})}$	-	10 ⁻³
mg/L	$\frac{0.1\text{MV}}{(\text{mw}\cdot\text{P})}$	$\frac{10^3\text{MV}}{(\text{mw}\cdot\text{P})}$	$\frac{10^6\text{MV}}{(\text{mw}\cdot\text{P})}$	10 ³	-

Key: P = pressure in atmospheres
 MV = molar volume of gas (for air see table below)
 mw = molecular weight of compound in g/mole

1 Atmosphere Equivalents
1013 hPa
101.3 kPa
1.013 bar
1013 mbar
760 mmHg
29.9 in. Hg
33.9 ft. H ₂ O
14.7 psia

Temp. (°C)	Temp. (°F)	Air Molar Volume (MV)
-10	14	21.59
-5	23	22.00
0	32	22.41
5	41	22.82
10	50	23.23
15	59	23.64
20	68	24.05
25	77	24.46
30	86	24.87
35	95	25.28
40	104	25.69
45	113	26.10
50	122	26.51

5.10 Appendix 10: RAE Systems Gas Detection Products

RAE Systems offers a broad array of products used to detect and monitor many different compounds. For the most up-to-date list of RAE Systems products, as well as technical notes, application notes, and other material, visit RAE Systems' website at: **www.raesystems.com**.

THE PID HANDBOOK

Theory and Applications of Direct-Reading Photoionization Detectors

Third Edition

The PID Handbook from RAE Systems by Honeywell combines the theory, performance and applications of direct-reading photoionization detectors (PIDs). This book is ideal for chemists, industrial hygienists, toxicologists, safety engineers, emergency responders and others responsible for assessing chemical threats from volatile compounds. *The PID Handbook* illuminates the history and techniques used with this technology, and showcases PID use in a variety of applications in industrial, environmental, energy exploration and refining, and hazardous-materials-spill monitoring.



Real-time gas detection
For real-time decisions