

PIDS AS A HAZMAT RESPONSE TOOL

Photo Ionization Detectors (PID's) measure low levels (0-2000 ppm) of VOCs (Volatile Organic Compounds) and other toxic gases. Many HazMat (Hazardous Material) incidents are VOCs and the sensitivity of PID's to VOCs make them an invaluable tool for making HazMat decisions including:

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

While some HazMat teams have used PIDs, recent breakthroughs in PID technology increase their usefulness by making PIDs more rugged, more reliable and more affordable. Because of these developments, more HazMat responders may want to consider adding PIDs to their inventory of gas monitors.

What Are Some Common VOCs?

VOCs are the chemical compounds that keep industry going and include:

- ◆ Fuels
- ◆ Oils, Degreasers, Heat Transfer Fluids
- ◆ Solvents, Paints
- ◆ Plastics, Resins and their precursors

Why Not Use An LEL Monitor?

Many VOC's are flammable and may be detected by the LEL (Lower Explosive Limit) or combustible gas sensors found in virtually every multigas monitor. However, LEL sensors are not particularly useful in measuring toxicity because they do not have enough sensitivity.

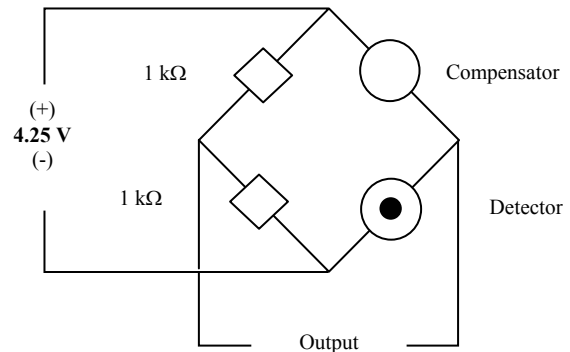
LEL Sensors Measure Explosivity, Not Toxicity

LEL sensors measure percent of LEL. For example, Gasoline has an LEL of 1.4%. Therefore, 100% of LEL is 14,000 ppm of gasoline, 10% of LEL is 1,400 ppm of gasoline and 1% of LEL is 140 ppm of gasoline. 140 ppm of gasoline is the lowest amount of vapor that the LEL monitor can "see." Gasoline has a TWA of 300 ppm and a STEL of 500 ppm; this does not make LEL sensors well suited for measuring gasoline vapors because they simply don't provide adequate resolution.

LEL sensors measure explosivity, not toxicity. Many Volatile Organic Compounds (VOCs) are potentially toxic at levels that are well below their explosive levels and below the sensitivity of the LEL sensors.

LEL Sensors Were Designed to Measure Methane

LEL sensors were originally designed to solve the problem of measuring methane levels in coal mines. Most LEL sensors use a Wheatstone bridge to measure the heat released when a flammable gas burns on a catalyst bead. The temperature rise causes a change in resistance, which is measured and converted to % LEL.



LEL Sensor Simplified

A Wheatstone Bridge sensor is simply a tiny electric stove with two burner elements. One element has a catalyst (such as platinum) and one doesn't. Both elements are heated to a temperature that normally would not support combustion.

However, the element with the catalyst "burns" gas at a low level and heats up relative to the element without the catalyst. The hotter element has more resistance and the

Wheatstone Bridge measures the difference in resistance between the two elements. Effectively, this sensor measures the temperature at which gas burns.



LEL Sensors Limitations

Two mechanisms affect the performance of Wheatstone bridge LEL sensors and reduce their effectiveness when applied to all but methane:

- **Gases burn with different heat**
Some gases burn hot and some burn relatively cool. These differing physical characteristics lead to difficulties when using LEL sensors. For example, 100% of LEL Methane (5% methane by volume) burns with twice the heat of 100% of LEL Propane (2.0 propane by volume).



- **“Heavier” hydrocarbon vapors have difficulty diffusing into the LEL sensor and limit LEL output**

Some “Heavier” hydrocarbon vapors have difficulty diffusing through the sintered metal flame arrestor on LEL sensors. This flame arrestor is necessary to prevent the sensor itself from starting a fire and does not prevent gases like methane, propane and ethane from reaching the Wheatstone bridge. However, hydrocarbons like gasoline, diesel, solvents, etc, diffuse through the flame arrestor slower so that less vapor reaches the Wheatstone bridge and the sensor gives less output.

Wheatstone Bridge LEL Sensor Sensitivity Relative to Methane

According to the following chart, gasoline produces less than half of the heat of methane on a Wheatstone bridge sensor.

Gas/Vapor	LEL (%vol)	Sensitivity (%)
Acetone	2.2	45
Benzene	1.2	40
Diesel	0.8	30
Gasoline	1.4	45
Methane	5.0	100
MEK	1.8	38
Propane	2.0	53
Toluene	1.2	40

So if an LEL monitor is calibrated on methane and then is used to measure gasoline vapors, the monitor will only display 45% of the true reading.

For example: After a calibration on methane, if a LEL sensor displays 45% of LEL in a mixture of Gasoline and air, the actual LEL is approximately 100% because Gasoline produces just 45% of the sensor output versus methane!

LEL readings can be corrected by choosing calibration gases that are more appropriate to the gas that you are measuring. The chart above shows that the LEL response of propane is much closer to common VOCs than methane. Some manufacturers calibrate their LEL sensors to propane for this reason. Correction factors (response factors) can also be used during calibration or electronically applied by the gas monitor to correct the reading to the correct target gas while still calibrating on methane. Methane calibration is preferred because it catches a failing sensor first. However, even with the appropriate correction factor, LEL sensors lack the sensitivity for measuring at the PPM levels necessary to protect workers from VOC toxicity.

Measuring in PPM: The Maturation of Gas Monitors

When confined space monitors first hit the safety market, the need was to stop killing people in confined spaces due to the acute (immediate) affects of toxic or explosive gases. Simply put, *LEL sensors made sure that workers*

got home at night. As our gas monitoring needs mature, safety, hygiene and HazMat professionals are becoming increasingly concerned with the chronic (long-term) affects of many gases and vapors. Measuring at these low levels requires gas measurement tools that measure in Parts Per Million (PPM). *Measuring in PPM lets workers enjoy retirement!* We can use the following methods to measure VOCs (Volatile Organic Compounds) at ppm levels:

- **Colorimetric Tubes:** Lack accuracy and have other shortcomings.
- **Metal Oxide Sensors (MOS):** Lack accuracy and sensitivity.
- **Portable Gas Chromatography/ Mass Spectrometry (GC/MS):** Selective and very accurate, but not continuous and very expensive.
- **FID (Flame Ionization Detector):** limited by large size, weight and the need to carry hydrogen.
- **PID:** Used properly, a PID is the best choice to provide responders with confidence in many HazMat environments.

Why Not Use Colorimetric Tubes

Colorimetric tubes (often referred to as “Drager” tubes) have been the foundation of HazMat response gas detection for years. They are an accepted and proven means of measuring many toxic gases and vapors at ppm levels. Colorimetric tubes are inexpensive, but have limitations:

- Tubes only provide “Snap-shots,” like a “Polaroid” camera. They cannot provide quality analysis or continuous monitoring with alarms. A tube cannot be put on personnel and be expected to alarm when conditions become dangerous.
- The “spot check” nature of tubes also makes them more prone to sample error. Continuous monitors, sampling at 100-500 cc/min, are less likely to be “fooled” by a false high or low reading due to small sample volume, air currents or bad sampling technique.
- Tubes are slow to respond. They give readings in minutes rather than seconds.
- Bellows type tube pumps provide 25% accuracy at best and piston/syringe style tubes provide 15% accuracy, so if the true concentration of a gas is 100 ppm a bellows-type tube can read between 75 and 125 ppm!
- Tube readings are subject to interpretation.
- Tubes generate glass splinters and chemical waste.
- A large stock of tubes is expensive.
- Tubes expire.
- There are a limited number of tube chemistries so tubes are not as specific as many would want to believe.

Why Not Use a MOS Sensor?

Semiconductor or Metal Oxide Sensors (MOS) are one of the oldest and least expensive measurement

technologies used in portable instruments. While MOS sensors can detect a very wide range of contaminants, they have number of shortcomings that limit their effective use in HazMat response.

- They have limited sensitivity, with detection limits usually in the 10's of ppm
- They produce a non-linear output so they are not particularly accurate, so MOS sensors are at best a gross indicator for toxic gases and vapors. Making go/no-go decisions based on their output can be dangerous because their non-linear output is like trying to measure paper with a rubber ruler.
- They are slow to react (relative to a PID)
- They respond positively to moisture and temperature
- They can be poisoned and dirtied and are not easily cleaned.
- MOS sensors are the first true "broad-band" sensor so they respond to a wide variety of compounds.

Portable GC/MS

Gas Chromatography/Mass Spectrometry (GC/MS) has the ability to be selective but not continuous. It can only take "snapshots" and is unable to provide continuous monitoring with alarms. The "spot check" nature of GS/MS also makes them prone to sample error.

Continuous monitors, sampling at 100-500 cc/min, are less likely to be "fooled" by a false high or low reading due to small sample volume, air currents or bad sampling technique. In addition, no GC/MS is portable or rugged enough to be worn continuously by a worker. Therefore, a GC/MS is also a reactive rather than a proactive form of protection. It can only report intermittently on what happened. A GC/MS can tell a story in snapshots rather than continuous, instantaneous video. Finally, GC/MS tends to be prohibitively expensive.

Flame Ionization Detectors (FIDs)

Flame Ionization Detectors (FIDs) respond to a broad-range of organic compounds but are non-selective.

While their linearity is excellent, their use is limited by their large size and weight, the need to carry a hydrogen cylinder. FIDs are relatively expensive and maintenance intensive and this limits their use in most industries.

PIDs and FIDs are often referred to generically as Organic Vapor Analyzers or OVAs. Many people want to know the difference between the two techniques and the difference is really one of preference. The difference between a FID and a PID is like the difference between a meter stick and a yardstick. They effectively measure the same things. However, because PIDs are smaller, easier to use and significantly less expensive, their usefulness in industry is potentially greater than FIDs.

Photo Ionization Detectors (PIDs)

A PID is essentially a Gas Chromatograph without its separation column and therefore, a PID can provide excellent accuracy. Some say that while the PID is clearly sensitive and accurate to many toxic gases and vapors at ppm levels, its lack of selectivity reduces its

usefulness. However, most of the other methods also have limited selectivity including colorimetric tubes, MOS and FIDs. The advantage of the PID is that while it is not selective, it is a small, continuous monitor that can provide instantaneous feedback to workers. This lets them take control of their actions and allows them to perform their job tasks with confidence that they are not being exposed to hazardous chemicals. Like a VCR, the PID measures continuously and its results can be datalogged and "played-back" instantly.

Why Are PIDs Not More Common?

In the 1970's PIDs moved from the laboratory to the field for surveying chemically contaminated sites. While often difficult to use, the ability of early PIDs to identify the presence of contaminants without costly and time-consuming laboratory testing made PIDs invaluable to many environmental clean-up firms. Because of their low-level detection capabilities, some HazMat teams also found PIDs useful. But shortcomings, such as high cost of purchase and maintenance, lack of durability, bulky size, heavy weight, sensitivity to humidity and radio interference (RFI) from "walkie-talkies," limited the application of early PIDs in demanding HazMat applications.

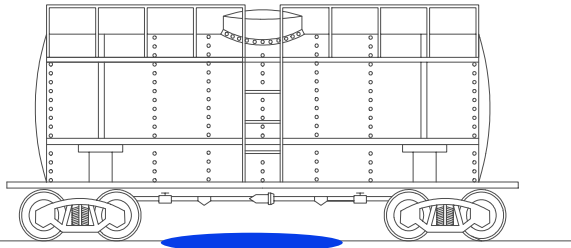
PIDs As a Powerful HazMat Tool!

Now PIDs measure 0-10,000 ppm (parts per million) with resolution as low as 1 ppb (parts per billion) and therefore are a very appropriate means of measuring gasoline (and other toxic gases and vapors) at the low levels leading to chronic toxicity. Breakthroughs in PID technology have addressed PID shortcomings and now provide HazMat teams with a powerful yet affordable measurement technology. The PIDs ability to provide accurate measurement in a wide range of situations makes it a powerful tool for the following HazMat uses:

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

Initial PPE Assessment

When approaching a potential HazMat incident the responder must make a PPE (Personal Protective Equipment) 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. ***No monitor will provide all the answers to a responder.*** But the PID is an excellent aid in this decision making process. For many incidents the PID lets the responder identify the presence or absence of potentially toxic gases or vapors.



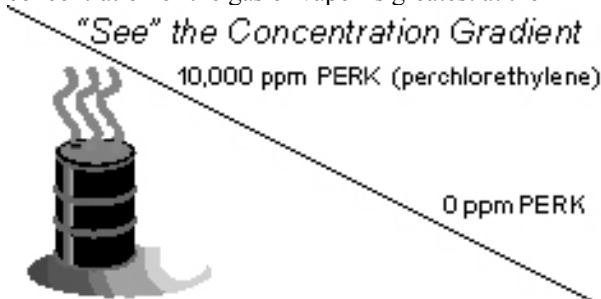
A HazMat contractor was called by a railroad to respond to a leaking tank car on a hot (95°F), humid (95%RH) summer day. According to the manifest, the tank car was loaded with benzene. Due to the carcinogenic nature of benzene (PEL of 1 ppm) the HazMat contractor chose to dress-out in Level A.

But, 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 ambient temperature combined with relative humidity above 95% produced a puddle of water not benzene.

Using a PID would have helped the contractor determine if there was an ionizable vapor present. Because the manifest identified the tank car contents as benzene, and benzene is readily ionizable, the contractor could have ruled out the presence of benzene vapors using a PID. This would reduce the cost of the response and prevent the potential of heat-stress injuries from dressing out in full Level A encapsulation.

Leak Detection with a PID

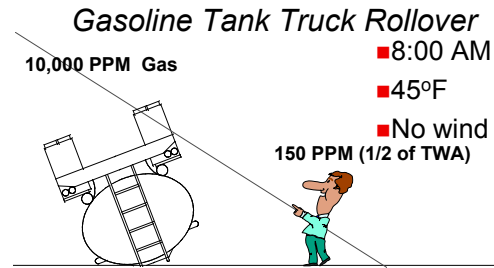
Often a leak is not readily apparent and it must first be located before it can be effectively stopped. Anytime that a gas or vapor is released into air it disperses outwards from the source of the leak. As the gas or vapor disperses it is diluted by ambient air until at some point the gas or vapor cannot be detected. This process establishes a concentration gradient where the concentration of the gas or vapor is greatest at the



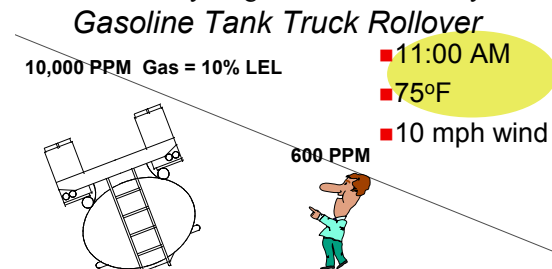
source of the leak and the concentration is effectively zero when the gas or vapor is fully dispersed. The PID allows us to measure and “see” concentration gradients for many gases and vapors that we would otherwise be unable to detect. We can use the PID like a “Geiger-Counter” to “see” the concentration gradient and follow the increasing concentration of gas or vapor to its source. The leak detection capability of the PID saves time and resources, allowing leaks to be quickly pinpointed.

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 people without a high degree of experience.

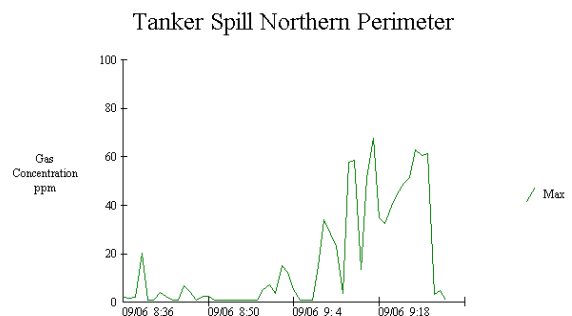


As conditions change, perimeters often are not adjusted because perimeter workers do not have the experience to recognize that the conditions have changed. The experienced HazMat technicians are typically focused upon the problem of dealing with complications of the original spill. Therefore, perimeter 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 can warn perimeter workers when to retreat from the incident for everything from ammonia to xylene.



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.



But most 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. Saving a “non-detect” can help to quickly establish 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. With all these liquids present, the PID provides an excellent tool for responders to zero in on spilled fuel rather than wasting time, and absorbent, on pavement that is only wet with water. A PID will respond positively to contaminated pavement and will not respond to pavement wet with water. This allows responders to quickly find the spill and reduce the money spent on absorbent.

PIDs can help separate the "Water" from the "Oil"



Limited Absorbent can be Efficiently used only on the Diesel Spill

Using a PID for Decon

Hazardous materials often get on responders. For ionizable compounds like fuels and other VOCs, a PID is a quick and effective means of determining if a responder requires decontamination, and if decontamination has been complete. This may make it easier for a HazMat team to make a decision to reuse an encapsulation suit because it was not contaminated. The PID is swept over areas of suspected contamination. It will respond positively to areas that are contaminated with ionizable compounds and it will not respond to clean or properly decontaminated areas.

Often a first responder to a fuel spill incident gets gasoline on his flame-retardant turnout clothing.

Absorbed gasoline will compromise the flame-retardant properties of turnout gear. The PID will quickly respond to contamination and identify 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 for arson investigation (Please reference RAE Systems publication AP-207: "PIDs as an Arson Investigation

Tool").

PIDs can help answer these questions:



- Is Worker Contaminated?
- Is Decon Complete?
- Can we reuse suit?
- Is my turn-out contaminated with Fuel Products?

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 in a sample headspace (Total Petroleum Hydrocarbons) 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 PID is one of the best-recognized tools for making such a determination for environmental officials and environmental contractors. HazMat responders now have an effective decision making tool that reduces guesswork as to whether a contractor should be called for further remediative action. This can allow responders to quickly reopen areas that were at first thought to be contaminated.

Because of variations in the weather and soil conditions it is best to do a headspace sample on suspect soil or water rather than just waving the PID probe over the suspicious area. This is because on a cold day, VOCs are less likely to evaporate and waving the probe over the area might miss contamination. Conversely, on a hot day, waving the probe over a contaminated area could overestimate contamination.

How To Do a Headspace Sample

1. Put contaminated soil or water in a container or even a plastic bag
2. Cover/seal the container and bring it up to room temperature (~15 min)
3. Put PID probe into container and sample
4. Generally <100 ppm is good (Caution: 100 ppm is a general guideline. Check your local regulations for specific rules).

What is a PID?

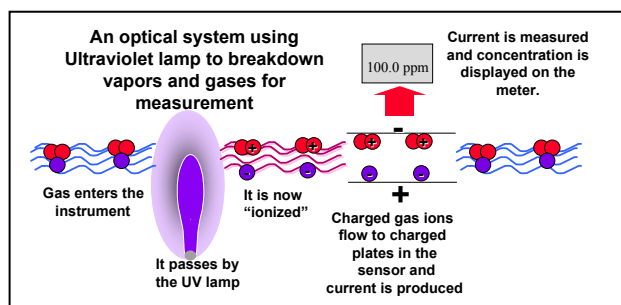
A Photo-Ionization Detector measures VOCs and other toxic gases in low concentrations from ppb (parts per billion) up to 10,000 ppm (parts per million or 1% by volume). A PID is a very sensitive broad-spectrum monitor, not unlike a “low-level LEL monitor.” If toxic gases and vapors could be considered alligators, the LEL monitor does not respond until the user is swimming with alligators, while the PID lets you know when your foot is wet!

How Does a PID Work?

A PID uses an ultraviolet (UV) light source (**Photo**=light) to break down chemicals to positive and negative ions (**Ionization**) that can easily be counted with a **Detector**. The detector measures the charge of the ionized gas and converts the signal into current. The current is then amplified and displayed on the meter as “ppm.” After measurement the ions reform the original gas or vapor. PIDs are non-destructive; they do not “burn” or permanently alter the sample gas, which allows them to be used for sample gathering.

Ionization Potential

All elements and chemicals can be ionized, but they differ in the amount of energy they require. The energy required to displace an electron and “ionize” a compound is called its **Ionization Potential (IP)**, measured in **electron volts (eV)**. The light energy



emitted by an UV lamp is also measured in eV. **If the IP of the sample gas is less than the eV output of the lamp, then the sample gas will be ionized.**

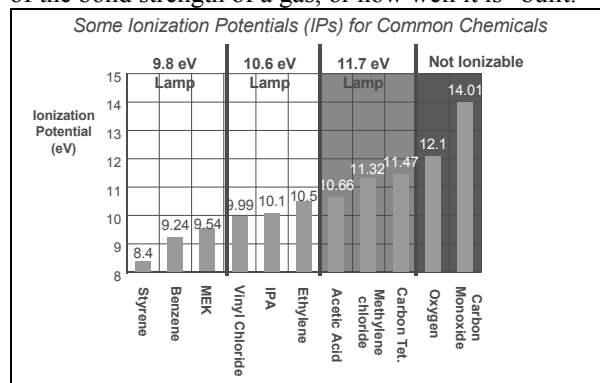
PID Operation Simplified

While this sounds complicated, it is very simply explained. A PID uses a lamp to break down gases and vapors.

- If the “wattage” of a gas or vapor is less than the “wattage” of the PID lamp, then the PID can “see” the gas or vapor.
- If the “wattage” of the gas or vapor is greater than that of the PID lamp the PID cannot “see” the vapor.

Therefore, a PID with a “75 watt” lamp could see a “50 watt” gas but could not “see” a “85 watt” gas. “Wattage” for PIDs is expressed in “Electron Volts” or eV and is known as the Ionization Potential (IP) for a particular gas or vapor. Ionization Potential is a measure

of the bond strength of a gas, or how well it is “built.”



Benzene has an IP of 9.24 eV and can be seen by a “standard” 10.6 eV lamp. Methylene Chloride has an IP of 11.32 eV and can only be seen by an 11.7 eV lamp. Carbon Monoxide has an IP of 14.01 eV and cannot be ionized by a PID lamp.

IPs can be found in the NIOSH Pocket Guide, PID manufacturer literature or in many chemical texts. RAE Systems uses a NIST (National Institute of Science & Technology) Database containing over 11,000 compounds to determine IPs of new compounds to be measured (please reference RAE Systems publication TN-106 “Correction Factors, Ionization Potentials and Calibration Characteristics”).

What Does a PID Measure?

The largest group of compounds measured by a PID are the Organics: compounds containing Carbon (C) atoms. These include:

- **Aromatics** - compounds containing a benzene ring including: benzene, toluene, ethyl benzene and xylene.
 - **Ketones & Aldehydes** - compounds with a C=O bond including: acetone, methyl ethyl ketone (MEK) and acetaldehyde.
 - **Amines & Amides** - Carbon compounds containing nitrogen, like diethylamine.
 - **Chlorinated hydrocarbons** - trichloroethylene (TCE), perchloroethylene (PERC)
 - **Sulfur compounds** – mercaptans, sulfides
 - **Unsaturated hydrocarbons** – like butadiene and isobutylene
 - **Alcohol’s**- like isopropanol (IPA) and ethanol
 - **Saturated hydrocarbons** - like butane and octane
- In addition to organic compounds, PIDs can be used to measure some Inorganics. These are compounds without carbon and include:
- Ammonia
 - Semiconductor gases: Arsine, Phosphine
 - Hydrogen sulfide
 - Nitric Oxide
 - Bromine and Iodine

What PIDs Do Not Measure

- Radiation

- Air (N₂, O₂, CO₂, H₂O)
- Common Toxics (CO, HCN, SO₂)
- Natural Gas (Methane, Ethane)
- Acid Gases (HCl, HF, HNO₃)
- Others- Freons, Ozone (O₃), Hydrogen peroxide
- Non-volatiles: PCBs, Greases

PID Lamps, 9.8& 10.6 eV versus 11.7 eV

At first glance, it may appear that to measure the broadest range of gases with a PID an 11.7eV lamp should be used instead of a 10.6eV lamp. However, the following must be considered:

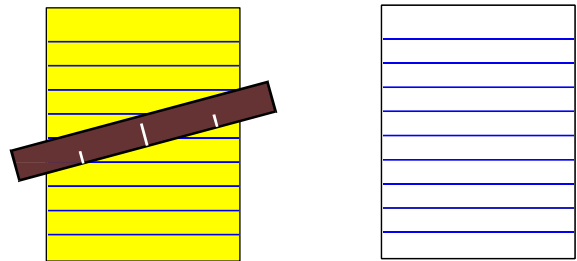
- 9.8 and 10.6 are more specific
- 9.8 and 10.6 last 12-24 months (about the same as a CO sensor)
- 9.8 and 10.6 costs about the same as a CO sensor
- 9.8 and 10.6 are more accurate
- 11.7 have a shorter life than 9.8 or 10.6. All 11.7 eV lamps have a window made of Lithium Fluoride to transmit the high energy UV light. Lithium Fluoride is harder to seal to the lamp glass, is very hygroscopic and readily absorbs water from air even when not in use. This causes the window to swell and decreases the amount of light transmitted through the window. Lithium Fluoride also is degraded by UV light, the more the instrument is used the greater the damage. These factors contribute to a shortened lamp life.
- 11.7 eV bulbs should only be used when compounds with IPs over 10.6 eV are expected (eg: methylene chloride, chloroform, and formaldehyde).
- 11.7 costs more

As a solution to the problem of short lifetime for 11.7 lamps, RAE offers them packaged in sealed glass ampoules. The gas in the ampoule is the same as in the lamp. The ampoule effectively packages a new lamp in a lamp. When the 11.7 lamp is required, the ampoule is broken, the lamp removed and inserted into the PID. 11.7eV lamp life can be extended if the lamp is stored in a desiccant environment (in or out of the PID) between uses. This can simply be a container containing “silica gel” drying packs like those that ship with electronic and camera equipment. It is not recommended to store MultiRAEs in a desiccant environment because this will decrease the life of its electrochemical sensors.

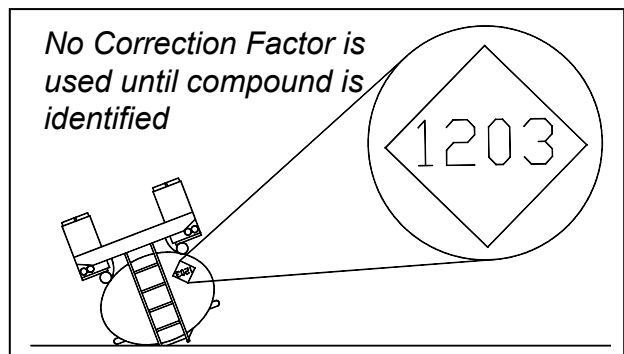
Selectivity & Sensitivity

A PID is a very *sensitive* monitor that can accurately measure gases and vapors in low ppm or even ppb levels. However, the PID is not a *selective* monitor. It has very little ability to differentiate between chemicals. To visualize this, let’s compare the PID to a ruler. A ruler is a sensitive and accurate means of measuring the width of a sheet of paper. But it cannot tell the difference between gray and white paper. Therefore, if one wants to know the width of the gray sheet of paper, that person must first select the proper sheet of paper

before measuring with the ruler. *We use our head to determine which sheet of paper is gray.*



The PID is similar to the ruler. It can tell us how much of a gas or vapor is present, but we must use our head to determine the exact gas or vapor present. When approaching an unknown chemical release, the PID is set to its calibration gas of isobutylene. Once the chemical is identified by means of placard, manifest, waybill or other means, the PID sensitivity can be adjusted to that chemical so that it reads in an accurate scale. For example, if we calibrate on isobutylene and happen to measure a toluene leak of 1 ppm the PID will display 2 ppm because it is twice as sensitive to toluene as it is to isobutylene. Once we have identified the leak as toluene, then the PID scale can be set to a toluene Correction Factor and the PID will accurately read 1 ppm if exposed to 1 ppm of toluene.



Remember that we use our head for “selectivity” and the PID “sensitivity.” No Correction Factor is used until a compound is identified.

What’s a Correction Factor?

Correction Factors (CF, also known as Response Factors) are a powerful tool in the use of PIDs. They are a measure of PID sensitivity to a particular gas. CF’s permit calibration on one gas while directly reading the concentration of another, eliminating the need for multiple calibration gases. PID manufacturers determine Correction Factors by measuring a PID’s response to a known concentration of target gas. Correction Factors tend to be instrument and/or manufacturer specific so it is best to use the CFs from the manufacturer of the PID. Therefore, it may be best to choose a PID manufacturer with the largest listing of CFs.

CF Measures Sensitivity

Correction Factors are scaling factors used to adjust the sensitivity of the PID to directly measure a particular gas compared to the calibration gas. The lower the Correction Factor (CF), the more sensitive the PID is a

gas or vapor. The following example uses CFs from a RAE Systems 10.6eV lamp:

- Toluene's CF is 0.5 so the PID is very sensitive to Toluene
- Ammonia's CF is 9.7 so PID is less sensitive to Ammonia

The PID is approximately 19 times more sensitive to Toluene as it is to Ammonia ($9.7/0.5=19.4$).

Guidelines for using Correction Factors

1. If a chemical is very toxic then if the PID is going to be used to measure it the PID should be very sensitive to that chemical. Therefore, if the chemical has an **exposure limit of 10 ppm** or less, a PID is an appropriate tool for personal safety decisions if the chemical's **CF is less than 1.0**. (eg: Benzene has an exposure limit of 1 ppm and a CF of 0.5)
2. If a chemical is not extremely toxic, then the PID doesn't need to be as sensitive to it. Therefore, if the chemical has an **exposure limit of over 10 ppm**, a PID is an appropriate tool for personal safety decisions if the chemical's **CF is less than 10**. (eg: ammonia has an exposure limit of 25 ppm and a CF of 9.7)
3. If the chemical's **CF is greater than 10** PIDs are still appropriate as gross leak detectors (eg: ethylene oxide has a CF of 13 with a 10.6 lamp) and are only appropriate for personal safety decisions for chemicals with very high exposure limits.

PID manufacturers publish CF lists and some integrate this information into the microprocessor of the PID. Microprocessor PIDs, like the MiniRAE 2000, can automatically store and apply over 100 CFs.

CF Example: Toluene

- If PID reads 100 ppm of isobutylene units in a Toluene atmosphere
- Then the actual concentration is 50 ppm Toluene units

$$0.5_{CF} \times 100 \text{ ppm}_{iso} = 50 \text{ ppm}_{toluene}$$

CF Example: Ammonia

- If PID reads 100 ppm of isobutylene units in an Ammonia atmosphere
- Then the actual concentration is 970 ppm Ammonia units

$$9.7_{CF} \times 100 \text{ ppm}_{iso} = 970 \text{ ppm}_{ammonia}$$

How to Determine if a PID can Measure a Particular Gas

1. Is the IP of the gas less than the eV output of the lamp?
 - **Yes:** go to step 2.
 - **No:** Select a higher energy lamp. If none available, then the PID cannot measure that gas.
 - **Don't Know:** Most PID manufacturers can help
2. Is the CF less than 10?
 - **Yes:** a PID is an appropriate way of measuring that gas.
 - **No:** a PID is not an accurate means of measuring that gas, but it could still be a good way of gross measurement like leak detection.

Don't Know: Most PID manufacturers can help

Making a Decision with a PID: Setting PID Alarms

Two bits of information are required to make a decision with a PID:

- **Human Toxicity:** as defined by ACGIH, NIOSH, OSHA or corporate guidelines
- **PID Sensitivity:** as defined through testing by the manufacturer of your PID (RAE CF)

ONLY USE A CORRECTION FACTOR FROM THE MANUFACTURER OF YOUR PID!

Three Scenarios On Setting PID alarms:

1. Single Gas/Vapor
2. Gas/Vapor mixture with Constant make-up
3. Gas/Vapor mixture with Varying make-up

1) PID Alarms for a Single Gas/Vapor

Single chemicals are easy:

- Identify the chemical
- Set the PID correction factor to that chemical from the PID manufacturer's listing
- **Find the Exposure limit(s) for the chemical (ref ACGIH/NIOHS/OSHA)**
- Set the PID alarms according to the exposure limits
The "Real World" is rarely this easy!

2) PID Alarms for a Gas/Vapor Mixture with Constant Make-up

Often HazMat incidents do not involve a single chemical, but may involve a compound that is a mixture of toxic chemicals. This "witches brew" of toxic

compounds requires greater care in determining alarm setpoints. If the mixture is identifiable, then the individual chemicals and their concentrations should be easily determined through a contents label or MSDS. If the chemical contents are identifiable then the following equation can be used to determine the toxicity of the mixture:

$$EL_{mix} = \frac{1}{(X_1/EL_1 + X_2/EL_2 + X_3/EL_3 + \dots X_i/EL_i)}$$

Where “EL” is the Exposure Limit and X is the mole fraction of each volatile chemical. Similarly, the Correction factor for the mixture can be calculated using the following equation:

$$CF_{mix} = \frac{1}{(X_1/CF_1 + X_2/CF_2 + X_3/CF_3 + \dots X_i/CF_i)}$$

To clarify the usage of these equations lets take an example. Suppose that you have a complaint of paint odors and upon investigating you find that the paint contains 15% styrene and 85% xylene. Then the exposure limit is calculated as follows:

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

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

In a similar manner the Correction Factor is calculated:

$$CF_{mix} = 1/(0.15/0.4 + 0.85/0.6) = 0.56$$

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

The reading in the area with the paint odors was 120 on the PID in Isobutylene units. Multiplying this reading by the correction factor of 0.56 the real reading for the mixture was 67.2 ppm. This is under the calculated exposure limit of 87 ppm for the mixture. However, styrene has an olfactory threshold of less than 2 ppm so even at safe levels the paint vapors have a distinct smell.

Alarm Shortcuts for Constant Mixtures

Setpoints can often be based on the concentration of the most prevalent or most toxic compound. Many times this determination is as simple as reading the MSDS.

Shortcut for the most Prevalent Compound

- Find the average make-up of the mixture
- Determine the most prevalent VOC
- Base setpoints on the most prevalent VOC

Let’s take a look at the same paint odor example, but instead of doing the math we look at as the most prevalent chemical: xylene. The reading in the area with the paint odors was 120 on the PID in Isobutylene units. Multiplying it by the xylene correction factor of 0.59 the real reading for the reading in xylene units is 70.8 ppm which is under xylene’s exposure limit of 100 ppm. This shortcut can save time, but it is not without

its pitfalls, when a very toxic chemical is present in a mixture it can drastically change the mixture setpoints.

Short cut for the most Toxic Compound

For example, while the typical TWA for gasoline is 300 ppm and the STEL is 500 ppm, we can set alarms based upon the relative concentration of chemicals in gasoline. Gasoline is a mixture of hydrocarbons including benzene, ethyl benzene, toluene and xylene. These are all readily ionizable by a PID so we will measure a total of all these compounds. But benzene is by far the most toxic of these chemicals so we will first focus on it. Most Gasoline (and other fuel products) contains approximately 1% benzene. Benzene’s permissible limit is only 1 ppm due to its potentially carcinogenic properties. Therefore, in a “worst case” scenario where gasoline has 1% benzene, 100 ppm of gas means that you are exposed to as much as 1 ppm of benzene! 50 ppm of gasoline contains approximately 0.5 ppm of benzene and would be an appropriate level to go from “bareface” to respiratory protection like SCBAs. While this example ignores differing vapor pressures, this logic is used by some petroleum plants to determine worker respiratory protection requirements.

- “Gas” contains as much as 1% Benzene
- Benzene is carcinogenic (PEL = 1 PPM)
- 100 PPM of Gasoline contains as much as 1 PPM Benzene
- Set High Alarm at 100 PPM Gas < 1.0 PPM Benzene
- Set Low Alarm at 50 PPM Gas < 0.5 PPM Benzene

3) Setting PID Alarms for a Gas/Vapor Mixture with Varying Make-up: The “Controlling Compound”

Setting alarms in a varying mixture means that you have to simultaneously interpret both the toxicities of the gases/vapors on humans and their relative sensitivities (Correction Factor) on the PID. Fortunately this is easier than it sounds. Every mixture has a compound that is the most toxic and “controls” the setpoint for the whole mixture. Determine that chemical and you can determine a conservative setpoint for that mixture.

1. Express all Exposure Limits in equivalent units
2. Look for the compound with the lowest Exposure Limits in equivalent units
3. Set the PID for that setpoint and you are safe for all of the chemicals in the mixture

Chemical Name	IP (eV)	Exposure Limit
Ethanol	10.47	1000
Toluene	8.82	100
Acetone	9.71	750

- Ethanol “appears” to be the safest compound
- Toluene “appears” to be the most toxic

Chemical Name	10.6eV CF	IP (eV)	Exposure Limit	10.6 Lamp RAE Units
Ethanol	12	10.47	1000	83.33
Toluene	0.50	8.82	100	200.00
Acetone	1.1	9.71	750	681.82

But its lower sensitivity on the PID makes Ethanol the “controlling compound” when the Exposure Limits are expressed in equivalent isobutylene units or “RAE Units” (**IMPORTANT:** these are called RAE Units because their calculation involves a RAE PID Correction Factor which should only be applied to RAE Systems PIDs. Similar calculations can be done for any other PID brand). “RAE Units” are determined by dividing the Exposure Limit by the Correction Factor (CF) to provide us with a number that combines human toxicity with PID sensitivity. 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 concentration of the chemicals might be.

The 50/50 Rule

Using the RAE Unit logic allows one to use the PID to help determine Standard Operating Procedures (SOPs) because one can know exactly what chemicals the PID will provide protection from given a particular reading in isobutylene units. ***A RAE PID with a 10.6eV lamp set to the following alarms and not beeping provides protection from:***

- **37 chemicals at a 100 ppm alarm**, includes major solvents like Xylene, Toluene, MEK, MPK, Acetone
- **56 chemicals at a 50 ppm alarm**, from Cyclohexanone to Acetone.
- **68 chemicals at a 25 ppm alarm**, from Diethylamine to Acetone.
- **Over 107 chemicals at a 5 ppm alarm**, from Toluidine to Acetone.

Of course setting an alarm to 1 ppm would provide the highest level of protection, but it would also provide the most alarms. Too many alarms would be like “the boy who cried wolf” and would reduce user confidence in the PID. An alarm point of 1 ppm would be similar to always wearing a Level A suit! The RAE MultiRAE and ToxiRAE PIDs are set with a low alarm at 50 ppm; this alarm point provides protection from some of the most common chemicals in industry and is a good balance point between too many and too few alarms. ***One way of looking at this is with an alarm in isobutylene units set to 50 ppm and the PID is not beeping, responders don’t have to worry about 56 common chemicals or the RAE Systems “50/50 Rule.”*** Reference “RAE PIDs and OSHA Z-Listed Chemicals” and “RAE Unit Alarm Points” for further information on how to set alarms.

Never Use Tygon Sample Tubing in HazMat

Because tygon sample tubing quickly absorbs many chemical vapors, it should **NEVER** be used in HazMat operations. Tygon tubing will reduce the PID readout when measuring many chemicals and may cause “false positives” when chemicals do not exist due to the “outgasing” of old chemicals from the tygon tubing.

Tygon tubing is typically found as the remote sampling tubing supplied with most confined space monitors. Only Teflon, Teflon lined tygon or similar non-reactive tubing should be used in HazMat operations. Teflon tubing will not absorb chemicals but it can get coated. Clean contaminated teflon tubing with anhydrous methanol (lamp cleaning solution) if it gets coated with chemical.

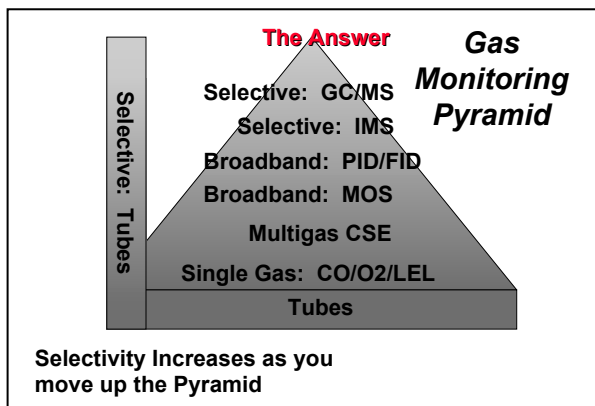
When to Clean a PID

From time to time a PID lamp and sensor requires cleaning. Historically, some PID users cleaned their lamps daily, often neglecting the sensor and sample components before the sensor. Typically frequent cleaning is not necessary and can lead to inadvertent damage to the PID lamp and sensor. The following is a guideline on when a PID requires cleaning:

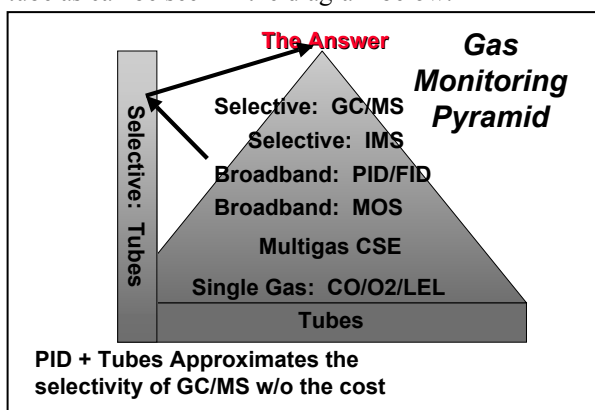
- ***Clean PID Lamp & Sensor***
 1. When display creeps upwards after good zero
 2. When PID responds to moisture
 3. When movement of PID results in response on display
- ***How to Clean***
 1. Use anhydrous methanol (Lamp cleaning solution)
 2. Clean sample probe and replace or clean filters. If PID holds a stable zero after this step then further cleaning may not be necessary
 3. Clean lamp face with lens tissue
 4. Clean sensor by immersion in cleaning solution (an ultrasonic cleaner will speed cleaning)
- ***Drying the PID***
 1. Let air dry overnight
 2. Warm air (not hot) will speed drying

Where Do PIDs Fit Into a Total Gas Monitoring Program?

PIDs are an important part of a gas monitoring program. However, a gas monitoring program must contain a variety of options that build towards specificity and sensitivity. A gas-monitoring program can be represented by a pyramid that builds upon techniques that increase in cost and sophistication until the answer is reached at the top of the pyramid. At its foundation are colorimetric tubes then it builds to single gas monitors (like CO monitors) and then progresses to multigas Confined Space Monitors. From there, a gas-monitoring pyramid can add broadband monitoring of chemicals (via PIDs) and finally move on to the top of the pyramid with specific techniques from colorimetric tubes to IMS (Ion Mobility Spectroscopy) and GC/MS (Gas Chromatography/Mass Spectroscopy).



However, it is dangerous to jump to the top of the gas-monitoring pyramid if one has not established a proper foundation. For example, if one's entire budget is spent on an expensive GC/MS, then little or none might be left for important broadband scanning devices. For those that don't have the budget or the demand for costly specific monitors like GC/MS or IMS the same ground can be covered with a continuous monitoring PID and a simple specific detector like a colorimetric ("Draeger") tube as can be seen in the diagram below.



Broadband scanning devices like PIDs are important, because they are simpler and can be fielded in greater quantities to provide more widespread protection. In addition, broadband detectors like PIDs can provide clues that a more specific measurement technique like GC/MS or even colorimetric tubes may be needed. In this case PIDs act as "scouts" or "survey" instruments for the more specific and complicated detectors.

PIDs: An Excellent Detective Tool

A PID is a sensitive and accurate detective tool for HazMat Responders. Like a criminologist's magnifying lens helps to identify fingerprints; PIDs allows HazMat "detectives" to identify the presence of gases and vapors and then quantify them. A magnifying lens does not identify fingerprints. But good detective work quickly can identify them. The same holds for toxic vapors. While a PID cannot identify toxic gases and vapors, good detective work can quickly provide identities and the PID can then provide the most accurate form of field measurement short of a Gas Chromatograph (GC). With

A Magnifying glass lets a detective see fingerprints; a PID lets us "see" VOCs

Ammonia
 Carbon Disulfide
 Benzene Styrene
 PERC Jet Fuel
 Xylene

Identify then Quantify!

the increasing concerns of the affects of even low levels of chemical releases, PIDs offer responders an excellent aid in their detective work. Properly used, PIDs can help identify and measure the potential toxic VOCs that make up the majority of HazMat incidents.

About the Author

A graduate of Cornell University, Christopher Wrenn is the Eastern Sales Manager for RAE Systems. Just prior to RAE Systems, Mr. Wrenn was Northeastern Regional Manager for CairnsAir, a division of Cairns & Brothers. Previously, as Product Manager for Biomarine (Manufacturer of BioPak SCBAs), Mr. Wrenn was responsible for training military personnel responsible for the clean-up of chemical weapons on the use of long duration closed-circuit SCBAs (rebreathers). Mr. Wrenn's past experience in gas monitoring came as Director of Marketing for Neutronics, Inc., a manufacturer of fixed gas monitoring for the chemical processing industry.

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