

## PIDS AS HAZMAT RESPONSE TOOLS

Photoionization detectors (PIDs) measure low levels (0 to 2000 ppm) of VOCs (volatile organic compounds) and other toxic gases. Many HazMat (Hazardous Material) incidents are VOCs and the sensitivity of PIDs to VOCs make them an invaluable tool for making HazMat decisions including:

- Initial PPE (personal protective equipment) 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 VOCs 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.

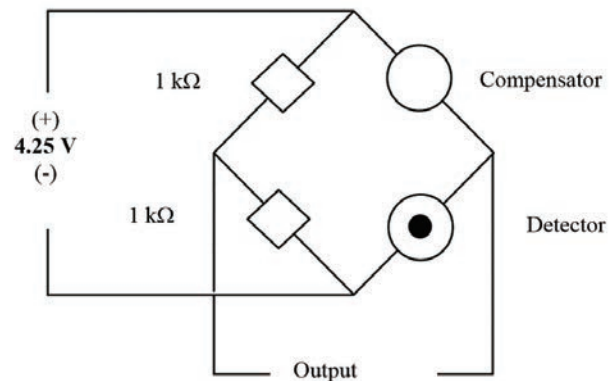
### LEL Sensors Measure Explosivity, Not Toxicity

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 (time-weighted average) of 300 ppm and a STEL (short-term exposure limit) 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 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 Sensors 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 Sensor 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% 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
<b>Methane</b>	<b>5.0</b>	<b>100</b>
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 intended 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 (parts per million) 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) effects 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) effects of many gases and vapors. Measuring at these low levels requires gas measurement tools that measure in ppm. 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 “Dräger” 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 snapshots, 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 among the oldest and least expensive measurement technologies used in portable instruments. While MOS sensors can detect a very wide range of contaminants, they have a number of shortcomings that limit their effective use in HazMat response:

- They have limited sensitivity, with detection limits usually in the tens of ppm
- They produce a non-linear output and 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 GC/MS also makes it 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, and they require carrying 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.

### Photoionization 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 PIDs Are Not More Common

In the 1970s PIDs moved from the laboratory to the field for surveying chemically contaminated sites. While often difficult to use, early PIDs were able to identify the presence of contaminants without costly and time-consuming laboratory testing. This 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-frequency 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 to 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 PID's ability to provide accurate measurement in a wide range of situations makes it a powerful tool for the following HazMat uses:

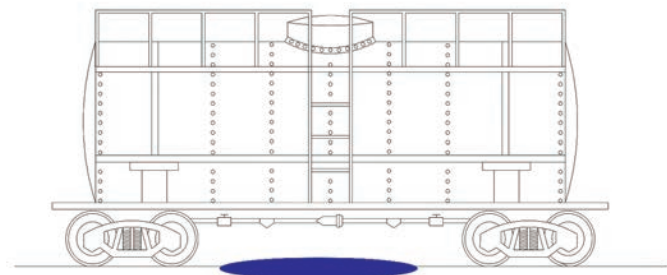
- Initial PPE assessment
- Leak detection
- Perimeter establishment and maintenance
- Spill delineation
- Decontamination
- Remediation

### Initial PPE Assessment

When approaching a potential HazMat incident the responder must make a PPE decision. Some potential incidents may not be "incidents" at all and may not require PPE. Some incidents may initially appear to have no contamination, yet require significant levels of PPE. No monitor can provide all the answers to a responder. However, 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, or permissible exposure level, of 1 ppm) the HazMat contractor chose to dress-out in Level A gear.

Because it was a hot summer day, though, 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.

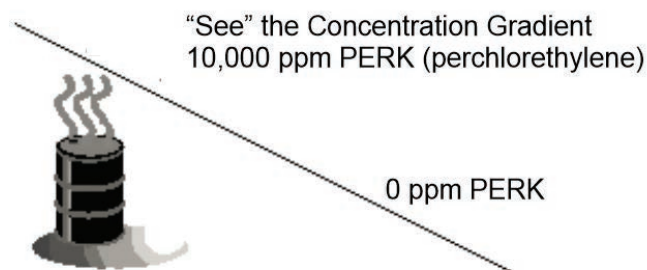
Using a PID would have helped the contractor determine if there was an ionizable vapor present. Because the manifest identified the tank car contents as benzene, and because benzene is readily ionizable, the contractor could have ruled out the presence of benzene vapors using a PID. This would reduce 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

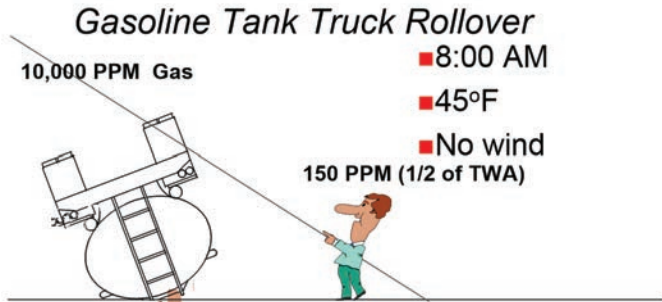
Often a leak is not readily apparent and it must first be located before it can be effectively stopped. Anytime that a gas or vapor is released into air it disperses outwards from the source of the leak. As the gas or vapor disperses, it is diluted by ambient air until at some point the gas or vapor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

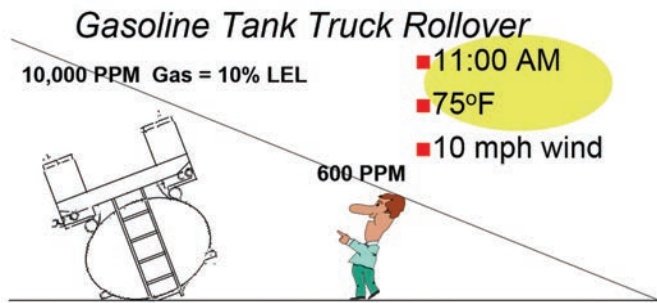
HazMat technicians assess the incident and set a perimeter based upon the toxicity of the gas or vapor, the temperature, wind direction



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. Experienced HazMat technicians are typically focused upon the problem of dealing with complications of the original spill. Therefore,



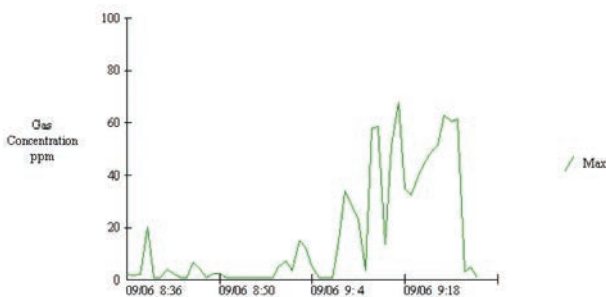
perimeter workers are often unprotected from changing conditions that may require movement of a perimeter away from the spill site. For many HazMat incidents, a PID allows those manning a perimeter line to adjust the line in response to changing conditions. PIDs can provide instantaneous alarms that warn perimeter workers when to retreat from an 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 have been chemical releases. But most only datalog those incidents when the datalog shows 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.

Tanker Spill Northern Perimeter



**PIDS FOR SPILL DELINEATION**

In the course of a HazMat incident, many liquids can be present, including 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.

**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 responds positively to areas that are contaminated with ionizable compounds, but does not respond to clean or properly decontaminated areas.

First responders to a fuel spill incident often get gasoline on their flame-retardant turnout clothing. Absorbed gasoline compromises the flame-retardant properties of turnout gear. The 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 for arson investigation. (Refer to RAE Systems publication AP-207: “PIDs as an Arson Investigation Tool.”)

**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.

*PIDs can help answer these questions:*



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

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 photoionization 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!

**Note:** Refer to Application Note AP-000: RAE Systems PID Training Outline for a detailed description of how PIDs work.

### 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 (e.g., RAE Systems Correction Factors).

**IMPORTANT!** 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 (refer to 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

HazMat incidents do not often 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:

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

“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, let’s 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:

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

- 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:

$$CF_{\text{mix}} = 1/(0.15/0.4 + 0.85/.6) = 0.56$$

- 0.15 is 15% styrene
- 0.4 is the CF for 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 measurement 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.

#### Shortcut 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	10.6 eV 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 Systems 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. The RAE Systems MultiRAE Plus 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 require 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 are guidelines to help you determine when a PID requires cleaning:

- When a display creeps upwards after good zero.
- When a PID responds to moisture.
- When movement of the PID results in response on a display.

### How to Clean

1. Use anhydrous methanol (lamp-cleaning solution).
2. Clean the sample probe and replace or clean filters. If the PID holds a stable zero after this step, then further cleaning may not be necessary.
3. Clean the lamp face with lens tissue.
4. Clean the sensor by immersion in cleaning solution (an ultrasonic cleaner speeds cleaning).

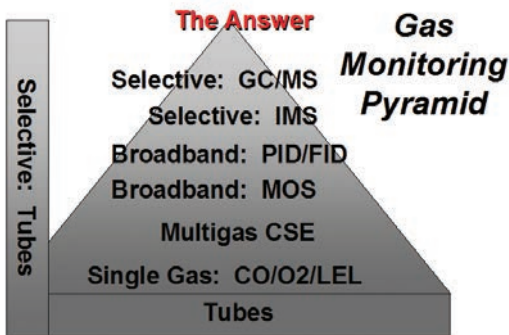
### Drying the PID

1. Let it air dry overnight.
2. Warm air (not hot) speeds drying.



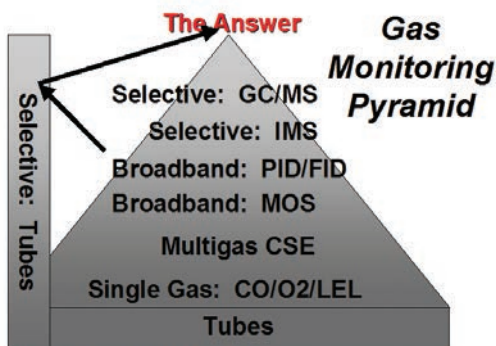
## WHERE DO PIDS FIT INTO A TOTAL GAS MONITORING PROGRAM?

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. It then builds to single-gas monitors (like CO monitors) and then progresses to multi-gas confined space monitors. From there, a gas-monitoring pyramid can add broadband monitoring of chemicals (via PIDs). At the top of the pyramid are specific techniques from colorimetric tubes to IMS (ion mobility spectroscopy) and GC/MS (gas chromatography/mass spectroscopy).



Selectivity Increases as you move up the Pyramid

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 who 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 ("Dräger") tube as can be seen in the next diagram.



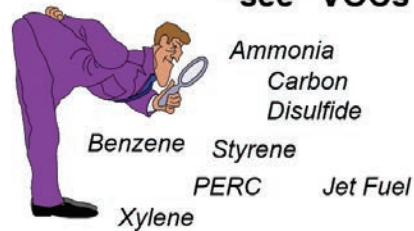
PID + Tubes Approximates the selectivity of GC/MS w/o the cost

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: EXCELLENT DETECTIVE TOOLS

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.

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



### Identify then Quantify!

With the increasing concerns of the effects 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.

## REFERENCES

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