

USING PIDS TO ASSESS EXPOSURE RISK IN UNKNOWN ENVIRONMENTS

RISK DECISIONS BASED ON PIDS

Photoionization detectors (PIDs) can measure volatile organic compounds (VOCs) and other toxic gases at concentrations from parts per billion (ppb) to 10,000 parts per million (ppm). This sensitivity allows PIDs to be used to make accurate, instantaneous decisions as to the levels of ionizable chemicals to which workers are exposed. By simultaneously solving for human and PID meter sensitivity, a logical program of atmospheric risk reduction based upon PID response can be implemented in both known and unknown chemical environments.

Two Sensitivities Must Be Understood

In order to make an assessment of toxicity risk with a PID, two sensitivities must be understood:

1. The first is human sensitivity and is expressed in exposure limits defined by organizations such as OSHA (the US Occupational Safety and Health Administration), NIOSH (the US National Institute for Occupational Safety and Health) ACGIH (American Conference of Governmental Industrial Hygienists) or other such groups. These exposure limits are typically expressed in parts per million (ppm) of each individual chemical.
2. The second sensitivity is that of the PID. This sensitivity factor is called a Correction Factor (CF) or sometimes a Response Factor. The CF is a ratio of the PID sensitivity to a particular chemical referenced to the PID calibration gas of isobutylene. CFs are specific to a PID brand (for more information on CFs and how PIDs work, refer to RAE Systems' AP-000: PID Training Outline, and AP-211: PIDs For Continuous Monitoring of VOCs).

One can express this relationship as:

$$\text{PID sensitivity} + \text{Human Sensitivity} = \text{Decision}$$

Or

$$\text{CF} + \text{Exposure Limit} = \text{Decision}$$

Correction Factors are the Key

Correction Factors are the key to unlocking the power of a PID for assessing varying mixtures and unknown environments. They are a measure of PID sensitivity to a particular gas. CFs 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 are instrument and/or manufacturer specific, so it is important 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. 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.

THREE SCENARIOS ON HOW TO SET PID ALARMS:

In order to better understand making a decision that combines these two sensitivities we can look at three specific examples of applying a PID to make an exposure limit decision:

- Single gas/vapor
- Gas/vapor mixture with constant make-up
- Gas/vapor mixture with varying make-up

1. PID Alarms for a Single Gas/Vapor

It is comparatively easy to gain information on a single chemical:

- Identify the chemical.
- Set the PID correction factor to that chemical from the PID manufacturer's listing. This solves the equation for PID sensitivity.
- Find the Exposure limit(s) for the chemical (refer to ACGIH/NIOHS/OSHA). This solves the equation for human sensitivity.
- Set the PID alarms according to the exposure limits.

Most PIDs can automatically do the math involving CF, so, for example, all the user has to do is select “toluene” from the PID library, and the PID is measuring in “toluene” ppm. Then set the PID alarm to the appropriate value (100 ppm for OSHA), and the PID is able to accurately make “toluene” decisions. For example:

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

$$\text{Exposure Limit} = 100 \text{ ppm}_{toluene}$$

$$\text{Conclusion} = \text{Atmosphere is safe}$$

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

Often processes 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 contents of the mixture are identifiable, the individual chemicals and their concentrations should be easily determined through a contents label or MSDS. 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 (percent by volume) 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:

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

- 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 for styrene
- 0.85 is 85% xylene
- 0.6 is the CF for o-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, an actual concentration in mixture units was 67.2 ppm. This is under the calculated exposure limit of 87 ppm of mixture. If the reading were 178 ppm in isobutylene units, the actual concentration would be 100 ppm of the mixture, consisting of 15 ppm styrene and 85 ppm xylene. This mixture reading is over the exposure limit of 87, even though none of the components are over their individual exposure limits.

Note: An Excel format spreadsheet is available at the end of the online version of Technical Note TN-106 at www.raesystems.com. It allows calculations of CFs and alarm limits for complex mixtures.

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

Many times we can identify the chemicals present, but their relative concentrations vary throughout a process. Or, in situations like HazMat Response, one cannot predict the chemicals present or their relative concentrations. Therefore, we have to look at another way of using the PID to make decisions. Setting alarms in a varying or unknown mixture means that you have to simultaneously interpret both the human sensitivity (exposure limits) and PID sensitivity (Correction Factors) for all of the chemicals involved. 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 the entire mixture. The basic assumption is that if we are safe for the “worst” chemical in a mixture, we will be safe for all of the others.

- Express all exposure limits in equivalent units.
- Look for the compound with the lowest exposure limits in equivalent units.
- Set the PID for that setpoint, and you are safe for all of the chemicals in the mixture.

Table 1:

Chemical Name	Exposure Limit
Ethanol	1000
Toluene	100
Acetone	750

Table 1 is a simple example where ethanol appears to be the safest compound and toluene appears to be the most toxic. This is because most people are accustomed to making decisions solely on human sensitivity. Users of meters rarely take into account that, like humans, meters have varying sensitivities to different chemicals. Therefore, Table 1 only provides half of the decision-making equation. The exposure limit is expressed in units of different chemicals. When trying to use a PID to make a decision regarding which is the “worst” chemical, one might be comparing 1000 apples to 100 pineapples. What is required is to express the exposure limits in a common unit of measurement. Because PIDs are calibrated to isobutylene, and Correction Factors are expressions of PID sensitivity to a chemical relative to isobutylene this is very easy to do. First let’s look at this theoretically:

EL_{Chemical} : Exposure Limit in chemical units (ppm).

Unless otherwise indicated the EL is typically an 8-hour TWA.

$$CF = \frac{\text{PID Isobutylene Response} \times \text{Concentration of gas (ppmv)}}{\text{Conc. of isobutylene (ppmv)} \times \text{Response of gas on PID}}$$

$$EL_{\text{Isobutylene}} = \frac{EL_{\text{Chemical}} (\text{ppmv})}{CF_{\text{Chemical}}}$$

So to get the exposure limit in units of isobutylene we divide the exposure limit in chemical units by the ratio of chemical units to isobutylene units.

Table 2:

Chemical Name	10.6eV CF	EL_{Chemical}	$EL_{\text{Isobutylene}}$
Ethanol	12	1000	83
Toluene	0.50	100	200
Acetone	1.1	750	682

In Table 2, the far right column expresses all of the exposure limits in equivalent units of isobutylene. Now the chemicals can be compared on equal footing. One can compare apples to apples. While humans are not as sensitive to ethanol as they are to toluene, the low PID sensitivity to ethanol combined with the highest exposure limit in the table makes ethanol the “controlling compound” when the exposure limits are expressed in equivalent isobutylene units. In this example, the PID is left on an isobutylene

measurement scale and the alarm is set to 83 ppm. As long as the PID does not alarm, then no respiratory protection is required.

Important: In the rest of this discussion, exposure limits in “Isobutylene Units” calculated by

$$EL_{\text{Isobutylene}} = \frac{EL_{\text{Chemical}} (\text{ppmv})}{CF_{\text{Chemical}}}$$

will be called RAE Units (RU) because their calculation involves a RAE Systems PID Correction Factor which should only be applied to RAE Systems PIDs. Similar calculations can be done for any other PID brand that has a published list of correction factors.

Note: Setting alarm limits this way is the most conservative, restrictive approach, required by the limited information. When compound ratios are known better, the methods in Section 2 always allow higher alarm settings and fewer work restrictions.

UTILIZING RAE UNIT LOGIC TO HELP CHARACTERIZE UNKNOWN ENVIRONMENTS

RAE Units provide people who need to characterize unknown environments (HazMat technicians, health and safety professionals, indoor air quality consultants) with an important tool. It allows them to gauge the risk to themselves and others. The higher the chemical’s RU, the less risk. If the RU (isobutylene equivalent) is below the threshold for a particular chemical, it does not pose a threat. For example, if the PID reads 45 ppm isobutylene in an area with toluene (RU=400), styrene (RU=250) and cumene (RU=92) vapors, we are safe because the RU for all three of these chemicals is well above 45 ppm (refer to Table 3).

Acceptable levels of exposure can change with the circumstances. In a “normal” HazMat response (like a truck rollover), a 50 ppm RU alarm might be the most appropriate for going to respiratory protection because the typical threat is hydrocarbons from fuel products and a RU alarm of 50 is very conservative for all hydrocarbon fuels. However, in a potential terrorist chemical agent attack, a RU of 1.00 ppm might be more appropriate because it is below the LCT50 (Lethal Concentration) for mustard (LCT50 RU=385), Sarin (LCT50 RU=2.61) and Tabun (LCT50 RU=25). RAE Units are only one gauge of the threat level in any circumstance. The PID user must use all of the clues present to reach a decision. In the preceding example, we would also look to see if victims were affected. If not, we might have a hoax on our hands. If victims were showing the telltale signs of chemical exposure, more monitoring assets would be required to make a determination as to the type of chemical agent (Reference AP-216: Using PIDs in Terrorist Chemical Attacks).

RAE Units and OSHA's Z-Listed Chemicals

There are approximately 436 chemical compounds on OSHA's Z-List. The approximate breakdown is as follows:

- Ionizable or potentially ionizable compounds: 270
- Non-ionizable vapors with Ionization Potentials (IP) above 11.7 eV: 37
- Non-ionizable solids or dusts: 131

Of the 270 compounds that are or may be ionizable, RAE Systems currently has Correction Factors (CF) for 121 compounds using the 10.6eV lamp (the most common PID lamp). These 121 compounds account for 45% of the potentially ionizable compounds on the Z list.

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. Table 3 is a list of 174 chemicals combining OSHA-Z, NIOSH, AGCIH and other exposure limits. Because they are enforceable by law, OSHA exposure limit, take precedence in Table 3 when there is a difference in exposure limits between OSHA, NIOSH and AGCIH. A RAE Systems PID with a 10.6eV lamp (the most common PID lamp) set to the following alarms and not beeping provides protection from:

- **44 chemicals at a 100 ppm alarm**, includes major solvents like xylene, toluene, MEK, MPK, acetone.
- **65 chemicals at a 50 ppm alarm**, from sec-amyl acetate to acetone.
- **81 chemicals at a 25 ppm alarm**, from Diethylamine to Acetone.
- **105 chemicals at a 10 ppm alarm**, from toluidine to acetone.
- **140 chemicals at a 1 ppm alarm**, from diethylenetriamine to acetone. (**Note:** A ppbRAE is highly recommended when using the 1.0 ppm RU alarm).

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 Systems MultiRAE Plus and ToxiRAE PIDs are factory set with a low alarm at 50 ppm on an isobutylene scale. 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 50 ppm alarm in isobutylene units and the PID is not beeping,

users don't have to worry about more than 50 (65, exactly) common chemicals. Hence, this is known as the RAE Systems "50/50 Rule."

Table 3: RAE Unit Alarms Points for a 10.6eV Lamp

Note: OSHA Z-Listed Chemicals are in bold Italics

Chemical Name	CF	EX	RU-10.6
Acetone	1.10	1000.000	909.09
Kerosene	0.60	500.000	833.33
Petroleum distillates	0.71	500.000	704.23
Stoddard Solvent	0.71	500.000	704.23
Isopropyl ether	0.80	500.000	625.00
Methylcyclohexane	0.97	500.000	515.46
Dichloroethene, t-1,2-	0.45	200.000	444.44
Toluene	0.50	200.000	400.00
Mustard, Distilled (LCT50)	0.6	231.000	385.00
Cyclohexene	0.80	300.000	375.00
Diethyl ether	1.10	400.000	363.64
Gasoline #1	0.85	300.000	352.94
Pinene, a-	0.31	100.000	322.58
Gasoline #2, 92 octane	1.00	300.000	300.000
Turpentine	0.35	100.000	285.71
Octane, n-	1.80	500.000	277.78
Pinene, b-	0.37	100.000	270.27
Dichloroethene, c-1,2-	0.80	200.000	250.00
Styrene	0.40	100.000	250.00
Methyl ethyl ketone	0.86	200.000	232.56
Xylene, m-	0.43	100.000	232.56
Xylene, p-	0.45	100.000	222.22
Pentanone(2-) (Methyl propyl ketone)	0.93	200.000	215.05
Cyclohexane	1.40	300.000	214.29
Xylenes (o-, m-, p-isomers)	0.49	100.000	204.08
Methyl styrene(alpha-)	0.50	100.000	200.00
Ethyl benzene	0.52	100.000	192.31
Chlorobenzene	0.40	75.000	187.50
Heptane, n-	2.80	500.000	178.50
Xylene, o-	0.59	100.000	169.49
Ethoxyethanol (2-), (Cellosolve)	1.30	200.000	153.85
Diesel Fuel #2	0.66	100.000	151.52
Piperylene, isomer mix	0.69	100.000	144.93
Nonane	1.40	200.000	142.86
Ethyl silicate	0.71	100.000	140.85
Hexone (Methyl isobutyl ketone)	0.80	100.000	125.00

Chemical Name	CF	EX	RU-10.6
Pentane	8.40	1000.000	119.05
Tetrahydrofuran	1.70	200.000	117.65
Hexane, n-	4.30	500.000	116.28
Diesel Fuel #1	0.93	100.000	107.53
Dichlorobenzene (o-)	0.47	50.000	106.38
Butyl acetate, (tert-)	2.00	200.000	100.00
Chlorotoluene, o-	0.50	50.000	100.00
Propylene glycol monomethyl ether acetate	1.00	100.000	100.00
100 ppm Alarm			
Isopropyl acetate	2.60	250.000	96.15
Cumene	0.54	50.000	92.59
Trichloroethylene	0.54	50.000	92.59
Dioxane, 1,4-	1.10	100.000	90.91
Ethyl acetate	4.60	400.000	86.96
Jet fuel JP-5	0.60	50.000	83.33
Jet fuel JP-8	0.60	50.000	83.33
Ethyl alcohol	12.00	1000.000	83.33
Isopentane, & all pentane isomers	8.20	600.000	73.17
Diacetone alcohol	0.70	50.000	71.43
Mesitylene	0.35	25.000	71.43
Propylene glycol monomethyl ether	1.40	100.000	71.43
Butyl acetate, (sec-)	3.00	200.000	66.67
Isopropyl Alcohol	6.00	400.000	66.67
Methyl methacrylate	1.50	100.000	66.67
Butyl acetate, (n-)	2.60	150.000	57.69
Isobutyl acetate	2.60	150.000	57.69
Propyl acetate, n-	3.50	200.000	57.14
Cyclohexanone	0.90	50.000	55.56
Amyl acetate (sec-)	2.30	125.000	54.35
Jet fuel JP-4	1.00	50.000	50.00
50 ppm Alarm			
Isoamyl acetate	2.10	100.000	47.62
Methyl t-butyl ether	0.91	40.000	43.96
Perchloroethene	0.57	25.000	43.86
Amyl acetate (n-)	2.30	100.000	43.48
Butoxyethanol, 2-	1.20	50.000	41.67
Butyl alcohol (sec-)	4.00	150.000	37.50
Hexene, 1-	0.80	30.000	37.50
Naphtha (Coal tar) {10% aromatics-RAE}	2.80	100.000	35.71

Chemical Name	CF	EX	RU-10.6
Butyl alcohol (tert-)	2.90	100.000	34.48
Acetaldehyde	6.00	200.000	33.33
Propyl alcohol (n-)	6.00	200.000	33.33
Methyl acetate	6.60	200.000	30.30
Triethylamine	0.90	25.000	27.78
Isobutyl alcohol	3.80	100.000	26.32
Diethylamine	0.97	25.000	25.77
25 ppm Alarm			
Tabun (LCT50)	0.8	20.000	25.00
Naphthalene	0.42	10.000	23.81
Methyl iodide	0.22	5.000	22.73
Butyl alcohol (n-)	4.70	100.000	21.28
Hexamethyldisilazane, 1,1,1,3,3,3-	0.24	5.000	20.83
Naphtha (Coal tar) {purely aliphatic -RAE}	5.70	100.000	17.54
Butyl mercaptan	0.60	10.000	16.67
Carbon disulfide	1.20	20.000	16.67
Ethyl mercaptan	0.60	10.000	16.67
Methyl mercaptan	0.60	10.000	16.67
Propylene oxide	6.50	100.000	15.38
Dimethyl acetamide, N,N-	0.80	10.000	12.50
Dimethylformamide, N,N-	0.80	10.000	12.50
Ethylamine	0.80	10.000	12.50
Vinyl bromide	0.40	5.000	12.50
Butane	67.00	800.000	11.94
Dibromoethane, 1,2-	1.70	20.000	11.76
Methyl bromide	1.70	20.000	11.76
Trimethylamine	0.85	10.000	11.76
Trichlorobenzene (1,2,4-)	0.46	5.000	10.87
Aniline	0.48	5.000	10.42
Dicyclopentadiene	0.48	5.000	10.42
Ethyl acrylate	2.40	25.000	10.42
Methoxyethanol, 2-	2.40	25.000	10.42
Toluidine, o-	0.50	5.000	10.00
10 PPM Alarm			
Chloroprene (beta-)	3.00	25.000	8.33
Cyclohexylamine	1.20	10.000	8.33
Methylamine	1.20	10.000	8.33
Vinyl acetate	1.20	10.000	8.33
Isobutane	100.00	800.000	8.00
Pyridine	0.68	5.000	7.35
Diisopropylamine	0.74	5.000	6.76

Chemical Name	CF	EX	RU-10.6
<i>Allyl glycidyl ether</i>	1.50	10.000	6.67
<i>Dimethylamine</i>	1.50	10.000	6.67
Butyl acrylate, n-	1.60	10.000	6.25
<i>Furfural</i>	0.92	5.000	5.43
<i>Ammonia</i>	9.70	50.000	5.15
<i>Dichloroethyl ether</i>	3.00	15.000	5.00
Formamide	4.00	20.000	5.00
<i>Phenol</i>	1.00	5.000	5.00
<i>Nitric oxide</i>	5.20	25.000	4.81
<i>Butylamine, n-</i>	1.10	5.000	4.55
Benzaldehyde	0.50	2.000	4.00
Ethylene glycol	16.00	50.000	3.13
<i>Hydrogen sulfide</i>	3.30	10.000	3.03
Dimethylethylamine	1.00	3.000	3.00
Methyl acrylate	3.70	10.000	2.70
Sarin (LCT50)	4.6	12.000	2.61
Caprolactam	2.00	5.000	2.50
<i>Benzene</i>	0.53	1.000	1.89
<i>Crotonaldehyde</i>	1.10	2.000	1.82
Benzyl cyanide	0.60	1.040	1.73
<i>Benzyl chloride</i>	0.60	1.000	1.67
<i>Propylene imine</i>	1.25	2.000	1.60
Diethanolamine	2.00	3.000	1.50
<i>Phenyl ether, vapor</i>	0.70	1.000	1.43
Bromobenzene	0.60	0.780	1.30
Vinyl-2-pyrrolidinone, 1-	0.80	1.000	1.25
<i>Butadiene</i>	0.85	1.000	1.18
Dichloro-1-propene, 1,3-	0.96	1.000	1.04
Diethylenetriamine	1.00	1.000	1.00
<i>Iodine</i>	0.10	0.100	1.00
1 PPM Alarm			
Acrylic Acid	12.00	10.000	0.83
<i>Allyl alcohol</i>	2.40	2.000	0.83
Benzoyl chloride	0.6	0.500	0.83
<i>Acetic Anhydride</i>	6.10	5.000	0.82
<i>Ethanolamine (Not Recommended)</i>	4.00	3.000	0.75
<i>Dimethylhydrazine, 1,1-</i>	0.78	0.500	0.64
Dimethylhydrazine, 1,1-	0.78	0.500	0.64
Butyl hydroperoxide, t-	1.6	1.000	0.63
Glutaraldehyde	0.80	0.500	0.63
<i>Epichlorohydrin</i>	8.50	5.000	0.59

Chemical Name	CF	EX	RU-10.6
<i>Nitrobenzene</i>	1.90	1.000	0.53
<i>Vinyl chloride</i>	2.00	1.000	0.50
<i>Acetic Acid</i>	22.00	10.000	0.45
Methyl ethyl ketone peroxide	2	0.700	0.35
<i>Hydrazine</i>	3.00	1.000	0.33
<i>Nitrogen dioxide</i>	16.00	5.000	0.31
<i>Diphenyl (Biphenyl)</i>	0.70	0.200	0.29
Diketene	2.00	0.500	0.25
<i>Allyl chloride</i>	4.30	1.000	0.23
<i>Bromoform</i>	2.50	0.500	0.20
<i>Methyl hydrazine (Monomethyl hydrazine)</i>	1.20	0.200	0.17
<i>Phosphorus trichloride</i>	4.00	0.500	0.13
<i>Nicotene</i>	0.70	0.075	0.11
<i>Bromine</i>	1.30	0.100	0.08
<i>Ethylene oxide</i>	13.00	1.000	0.08
<i>Phosphine</i>	3.90	0.300	0.08
Below Normal Outside Air Background Values of 0.05 ppm (50 ppb)			
<i>Dimethyl sulfate</i>	20.00	1.000	0.05
Tabun (TWA)	0.8	0.030	0.04
<i>Tetraethyl lead (as Pb)</i>	0.30	0.008	0.03
<i>Acrolein</i>	3.90	0.100	0.03
<i>Toluene-2, 4-diisocyanate (TDI)</i>	1.40	0.020	0.01
Sarin (TWA)	4.6	0.030	0.01

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