VOCs and PID

VOCs are organic compounds characterized by a tendency to evaporate easily at room temperature with the potential of forming a toxic gas concentration. While some Volatile Organic Compounds (VOCs) are acutely toxic at low concentrations, the harmful effects of most VOCs are delayed. Negative effects may occur long after the primary exposure thus many people ignore the potential danger. Long-term effects can include leukemia, memory problems, loss of hand-eye coordination, cancer, and a range of other physiological affects. Many personnel throughout the world work every day unprotected from VOCs either because they are unaware of the toxic hazards, or because they are without a monitor that detects for these gas concentrations.

Most VOCs have surprisingly low occupational exposure limits. An increased awareness has resulted in several newly revised VOC exposure limits, including TLVs for diesel vapor, kerosene, and gasoline. Photoionization detectors (PIDs) are able to detect VOCs and large hydrocarbon molecules that are undetectable by catalytic and electrochemical sensors. The GasAlertMicro 5 PID is the industry's first portable *and* affordable PID gas detector capable of alerting users to combustible and toxic gas hazards including a large array of VOCs.

Substance	Ionization Energy	Detectable by
carbon monoxide	14.01	electrochemical sensor
hydrogen cyanide	13.60	electrochemical sensor
methane	12.98	combustible sensor
sulfur dioxide	12.32	electrochemical sensor
oxygen	12.08	O_2 sensor
chlorine	11.48	electrochemical sensor
chlorine dioxide	10.57	electrochemical sensor
hydrogen sulfide	10.46	electrochemical sensor
n-hexane	10.18	combustible sensor
ammonia	10.16	electrochemical sensor
hexane	10.13	combustible sensor
phosophine	9.87	electrochemical sensor
nitrogen dioxide	9.75	electrochemical sensor
acetone	9.69	
benzene	9.25	
butadiene	9.07	
toluene	8.82	

detectable by 10.6 PID

[illegible] instruments are generally the best choice for measurement of VOCs at exposure limit concentrations.

This table lists ten common VOCs, their LEL concentration and their exposure limits per the UK OEL, NIOSH REL and ACGIH TLV. The table also identifies those contaminants (highlighted in red) with toxic exposure limits lower than 5% LEL.

Contaminant	LEL (Vol%)	OSHA PEL	NIOSH REL	TLV	5% LEL in PPM
Acetone	2.5	1,000 PPM TWA	250 PPM TWA	500 PPM TWA 750 PPM STEL	1250 PPM
Diesel (No.2) vapor	0.6	None Listed	None Listed	15 PPM	300 PPM
Ethanol	3.3	1,000 PPM TWA	1000 PPM TWA	1000 PPM TWA	1,650 PPM
Gasoline	1.3	None Listed	None Listed	300 PPM TWA 500 PPM STEL	650 PPM
Hexane	1.1	500 PPM TWA	50 PPM TWA	50 PPM TWA	550 PPM
Isopropyl alcohol	2.0	400 PPM TWA	400 PPM TWA 500 PPM STEL	200 PPM TWA 400 PPM STEL	1000 PPM
Kerosene/Jet Fuels	0.7	None Listed	100 mg/M³ TWA (approx. 14.4 PPM)	200 mg/M³ TWA (approx. 29 PPM)	350 PPM
MEK	1.4	200 PPM TWA	200 PPM TWA 300 PPM STEL	200 PPM TWA 300 PPM STEL	700 PPM
Turpentine	0.8	100 PPM TWA	100 PPM TWA	20 PPM TWA	400 PPM
Xylenes (o, m & p isomers	0.9—1.1	100 PPM TWA	100 PPM TWA 150 PPM STEL	100 PPM TWA 150 PPM STEL	450—550 PPM

toxic limits that exceed LEL limits

"INNOVATORS IN GAS DETECTION"

BW Technologies

PID Applications

Confined Space Entry

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HAZMAT

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Chemical Processing

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Water and Wastewater Processing

First Responders

Petrochemical

General Industry

Arson Investigation

Homeland Security

Drug Labs

Perimeter Monitoring

VOC Leak Surveys

Fire Service

Food Packaging

Leak Detection

May 2005/5062-11

VOCs and other gases detected by PID

Acetaldehyde
Acetic anhydride
Acetone
Acrolein
Acrylamide
Allyl alcohol
Allyl chloride
Allyl glycidyl ether
Allyl propyl disulfide
Amino pyridine
Ammonia
Amyl acetate
Aniline
Aromatic hydrocarbons
Benzene
Benzyl chloride
Biphenyl
Bromoform
Butadiene
2-Butanone (MEK)
Butoxyethanol
Butyl acetate
Butyl alcohol
Butyl mercaptan
Butyl amine
Butyl glycidyl ether
Butyl toluene
Camphor vapor
Carbon disulfide
Chloroacetophenone
Chlorobenzene
Chloronitropropane
Chloroprene
Chrysene
Cresol
Crotonaldehyde
Cumene (isopropyl benzene)
Cyclohexane
Cyclohexanol
Cyclohexanone
Cyclohexene
Cyclopentadiene
Cyclopropane
Diazomethane
Dibutylphthalate
Dichlorobenzene
Dichlorvos
Diesel
Diethyl amine
Diethyl ether
Diethyl ketone
Diethyl sulfide
Diisopropylanmine
Dimethyl amine
Dimethylaniline
Dimethylformamide
Dimethylphthalate
Dinitro analine
Dioxane
Diphenyl
Dipropyl amine
Epichlorohydrin
Ethanol
Ethyl acetate
Ethyl acrylate
Ethyl amine
Ethyl amyl ketone
Ethyl benzene
Ethyl bromide
Ethyl disulfide
Ethyl isothiocyanate
Ethyl ether
Ethyl mercaptan
Ethyl propionate
Ethyl silicate
Ethylene dibromide
Ethylene diamine
Ethyleneimine
Ethynylbenzene
Fluorotoluenes
Furfural
Furfuryl alcohol
Gasoline vapors
Glycidol
Heptane
Hexane
Hexanone
Hexone
Hexylacetate
Hydrogen sulfide
Hydroquinone
Iodine
Isoamyl acetate
Isobutyl acetate
Isobutyl alcohol
Isophorone
Isopropyl acetate
Isopropyl alcohol
Isopropyl amine
Isopropyl ether
Jet fuels
Kerosene
Ketene
Mesitylene
Mesityl oxide
Methyl acetate
Methyl acetylene
Methyl acrylate
Methyl amyl ketone
Methyl amine
Methyl bromide
Methyl butyl ketone
Methyl cellosolve
Methyl ethyl ketone
Methyl hydrazine
Methyl iodide
Methyl isobutyl ketone
Methyl mercaptan
Methyl methacrylate
Methyl styrene
Methylcyclohexane
Monomethyl aniline
Monomethyl hydrazine
Morpholine
Naphthalene
Naphthylamine
Nitroaniline
Nitrobenzene
Nitrogen dioxide
Nitrotoluene
Octane
Pentaborane
Pentane
Pentanone
Perchloroethylene
Phenol
Phenyl ether
Phenylene diamine
Phenyl hydrazine
Phosphine
Propioaldehyde
Propyl acetate
Propyl alcohol
Propyl amine
Propyl benzene
Propyl ether
Propyl formate
Propylene
Propylene imine
Propylene oxide
Pyridine
Quinone
Stibine
Solvent vapors, various
Styrene
Terphenyls
Tetrahydrofuran
Toluene
Toluidine
Trichloroethene
Trichloroethylene
Triethyl amine
Trimethyl amine
Turpentine vapor
Vinyl chloride
Vinyl methyl ether
Vinyl toluene
Xylenes

Many other hazardous VOCs can be detected by PID that are not found on this list. Please contact the BW Regional Sales Manager in your area for specific chemicals or concerns.

Photoionization Detectors (PIDs)

For years, fire departments, law enforcement agents, HazMat teams, and now more than ever First Responders, have been concerned about detecting and identifying hazardous compounds in emergency situations. Several techniques and technologies are used such as:

- Catalytic sensors
- Electrochemical sensors
- Gas chromatography
- Flame ionization
- Photoionization
- Ion Mobility Spectrometry
- Surface Acoustic Wave
- Color-changing detectors

While each of the above technologies have their advantages, photoionization detectors offer the ideal combination of speed-of-response, ease-of-use and maintenance, size, ability to detect low levels (in the ppm range) of many hazardous compounds, and affordability. PIDs are capable of effectively detecting and monitoring several hundred, if not thousands, of hazardous substances for maximum benefits and safety to users.

What Does Ionization Mean?

When the gas being sampled absorbs the energy from the PID lamp, it becomes "excited" and its molecular content is altered. The compound loses an electron (e-) and becomes a positively charged ion. Once this happens, the substance is considered to be "ionized." This is what happens inside the PID.

Pictorially, we see photoionization at work in Figure 1.

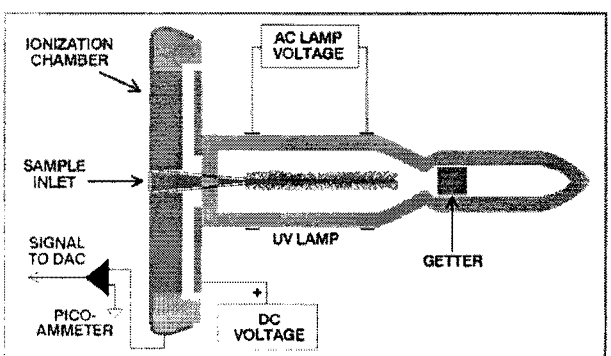

Figure 1. Block diagram of photoionization at work.

Theory of Operation

PIDs rely on ionization as the basis of detection. Most substances can be ionized; some more easily than others. The ability of a substance to be ionized is measured on an eV (electron volt) energy scale. The scale generally runs from a value of 7 to a value of approximately 16. Substances with an eV rating of 7 are very easy to ionize. Substances with an eV rating between 12 and 16 are extremely difficult to ionize. The eV ratings of some common substances include:

Substance	eV	Substance	eV
Benzene	9.24	Methyl ethyl ketone (MEK)	9.53
Hexane	10.18	Chlorine Dioxide	10.36
Toluene	8.82	Phosphine	9.87
Styrene	8.41	Ammonia	10.18

When chemicals being monitored have been ionized inside the instrument, a current is produced and the concentration of the compound is displayed as parts-per-million on the meter. PIDs utilize an ultraviolet (UV) lamp to ionize the compound to be monitored. The lamp, often the size of a common flashlight bulb, emits enough ultraviolet energy to ionize the compound.

There are different lamps available for PIDs. Two examples follow:

A 9.8 eV lamp puts out enough energy to ionize any compound whose eV rating is less than 9.6:

- Toluene ....8.82 eV
- Benzene ....9.25 eV
- Propylamine ....8.78 eV
- Styrene ....8.40 eV
- Vinyl acetate ....9.19 eV

A 10.6 eV lamp puts out enough energy to ionize any compound that a 9.8 eV lamp can detect, plus any compound whose eV rating is less than 10.6.

- Propy alcohol ....10.22 eV
- Phosphine ....9.96 eV
- Vinyl chloride ....10.00 eV
- Acetaldehyde ....10.22 eV

Substances that PIDs Can Detect

PIDs measure organic compounds such as benzene, toluene, and xylene, and also certain inorganics such as ammonia and hydrogen sulfide. As a general rule, if the compounds being measured or detected contain a carbon (C) atom, a PID can be used. However, this is not always the case, as methane (CH_4) and carbon monoxide (CO) cannot be detected with a PID.

Following are some of the common substances that a PID can detect and monitor:

- Benzene
- Toluene
- Vinyl chloride
- Hexane
- Ammonia
- Isobutylene
- Jet A fuel
- Styrene
- Allyl alcohol
- Mercaptans
- Trichloroethylene
- Perchloroethylene
- Propylene oxide
- Phosphine

Substances that PIDs Cannot Detect

PIDs cannot be used to measure the following common substances:

- Oxygen
- Nitrogen
- Carbon dioxide
- Sulfur dioxide
- Carbon monoxide
- Methane
- Hydrogen fluoride
- Hydrogen chloride
- Fluorine
- Sulfur hexafluoride
- Ozone

Response Factors

The optimal way to calibrate a PID to different compounds is by using a standard of the gas of interest. However, this is not always practical as it requires that a number of different and sometimes hazardous gases be kept on hand for this purpose. To address this issue, response factors are used. A response factor is a measure of the sensitivity of a PID to a particular gas. With response factors, a user can measure a large number of compounds using a single calibration gas – typically isobutylene. The user simply multiplies the instrument reading (calibrated for isobutylene) by the response factor to get the corrected value for the compound of interest.

The instruction manuals for most PIDs list the response factors. Some PIDs have response factors for common gases programmed into the software of the unit so that all response factor calculations are performed automatically. If the compound at a test site is known, the instrument can be set to indicate a direct reading for the target compound.

Threshold Limit Values (TLVs) and Permissible Exposure Limits (PELs)

The default low and high alarm values are set for isobutylene. If the user wants to monitor a different gas, they must determine the TLVs for the gas and then change the instrument's alarm level accordingly. The instrument manual should be referenced to ensure correct instructions are followed. Chemical limit values can be found by referencing ACGIH, NIOSH, or OSHA.

Indicator Versus Analyzer

A common misconception about PIDs is that they are analyzers. Many expect that a PID will tell them exactly what the vapor is at a spill site. This is not true. While PIDs are extremely sensitive and effective tools, they are not analyzers and cannot determine if the spill is benzene, jet fuel or iodine, for example. A PID can detect that something is present and can alert you to potentially hazardous situations, but additional steps will be necessary to properly identify what the substance is and how much of that substance is present.

Below is a sample procedure to identify the concentration of a substance at a spill site:

1. Set the PID to isobutylene
2. Detect and record a reading
3. Identify, via a placard or MSDS, what the specific substance is

If the placard or MSDS tells you that the substance is vinyl chloride, set the PID response factor to vinyl chloride so that you can get a direct reading of the actual vinyl chloride level.

PID Applications

Homeland Security

Potential terrorist chemical attacks may include industrial chemicals such as chlorine dioxide and ammonia. First Responders can use PIDs to confidently determine whether one of these chemicals is present and, if so, to accurately measure the concentration.

No single technology alone is adequate for First Responders to rely on completely, but PIDs used in conjunction with other tools such as SAW or IMS devices can assure that the most appropriate response is taken in a homeland security incident.

Three ways in which response factors are used with PIDs

Method	Example
Method #1: Preprogrammed Response Factors *Typically, PID detectors are calibrated for 100 ppm isobutylene. Other gases, for which there are hundreds, have corresponding correction values known as response factors. Numerous corresponding response factors are preprogrammed into the PID instrument. After a user selects the desired gas to measure from the instrument menu, the unit will automatically calculate the corrected gas concentration reading for the gas of interest. The direct reading will now measure the selected gas' concentration.*	The instrument is calibrated to read in isobutylene equivalents, for a reading of 100 ppm with 10.6 eV lamp. Ethylbenzene is the target gas, with a response factor of 0.62. Select the pre-programmed response factor and the instrument now reads about 62 ppm when exposed to the same gas, reading directly in ethylbenzene concentration values.
Method #2: Customized Response Factors *Typically, PID detectors are calibrated for 100 ppm isobutylene. If a user does not find a desired gas in the preprogrammed instrument menu list, the user can program a custom gas and response factor into the unit. If the user does not know the corresponding response factor, they can call MSA and request a customized response factor be calculated specific to their application.*	Tetrahydrofuran is the target gas. The response factor for tetrahydrofuran is 2.1 with 10.6 eV lamp. When calibrating the instrument with 100 ppm isobutylene, enter 2.1 times 100, or 210, when prompted for the calibration gas concentration. The instrument now reads directly in tetrahydrofuran concentration values.
Method #3 Manually Calculated Response Factors *Typically, PID detectors are calibrated for 100 ppm isobutylene. If a user chooses to read an isobutylene's direct reading for a different gas and does not want to utilize either the preprogrammed or customized response factors, the user may manually calculate the desired gas' direct reading. If the user knows the response factor of the desired gas, they can manually multiply the isobutylene reading by the known response factor. The result of this equation can be recorded externally to the instrument.*	The instrument is calibrated with isobutylene to isobutylene equivalents, for a reading of 10 ppm with 10.6 eV lamp. Cyclohexanone is the target gas, with a correction factor of 0.82. Multiply 10 by 0.82 to produce an adjusted cyclohexanone concentration of 8.2.