Photoionization Detectors (PIDs)

[Technology for Detection of Volatile Organic Compounds]

Photoionization Detectors (PIDs)

Introduction

Photoionization detectors (PIDs) are fast responding and easy-to-use for parts per million (ppm) detection of many hazardous volatile organic compounds (VOCs). PIDs are capable of effectively detecting and monitoring many hazardous substances.

While the theory behind PIDs is straightforward, there are many design elements that are important in order to produce a reliable gas monitor for the detection of VOCs under varied environmental conditions. This paper summarizes the theory behind PID sensors and describes some of the factors that affect PID performance.

PID Sensing Technology

Figure 1 shows a typical design for a PID sensor. The first major component of a PID is an ultraviolet (UV) light source (1). This source produces ultraviolet light particles (photons) with discreet energy measured in electron volts (eVs). When these high energy ultraviolet photons are passed through a gas chamber (2), an electron can be ejected from the molecule by a process called ionization. After ionization, the molecule becomes positively charged.

The negatively charged electrode (3) forces the charged molecule to the collector electrode (4). The amount of ionization and the current produced is proportional to the concentration of gas present in the chamber. Thus, the resulting output signal resulting from this current can be related to a gas concentration displayed in ppm.

The energy required to remove an electron (ionization potential or IP) varies from compound to compound, therefore ionization will only occur for compounds which have an ionization potential less than the ionization energy of the ultraviolet source. There are several possible energies that can be used by an ultraviolet light source. The most commonly used is a lamp at 10.6 eV. Many compounds including a majority of the commonly found VOCs have IPs less than 10.6 eV. Water vapor, CO2, nitrogen and oxygen are examples of background gases that have IPs greater than 10.6 eV. These background gases will not be detected by the PID. Hence the PID sensor at 10.6 eV is selective at detecting most VOCs without being drastically affected by environmental changes such as humidity, oxygen, or carbon dioxide levels. Other design considerations influenced by water vapor will also be discussed later in this paper.

Lamps with other energies have been used with PID sensors, although they all have limitations. One example of an ionization energy used in the past is 9.8 eV. This energy is useful at detecting some compounds as many VOCs have IPs between 9.8 and 10.6 eV. Since it will only detect compounds with IPs less than 9.8 eV, this lamp may not effectively detect important VOCs and will not supply an overall picture for the presence of VOCs.

Another lamp that has been used in the past has an ionization energy of 11.7 eV. This very high energy lamp can detect many compounds since it has such a high ionization energy. However, 11.7 eV lamps have relatively short lifetimes (only a few months with continuous operation) and require frequent lamp changes, driving up maintenance time and cost of ownership. For these reasons, the 11.7 eV lamp is considered to be impractical for permanent or transportable gas detection equipment.

Calibration and Response Factors

The optimal way to calibrate a PID for detection of a specific compound is by using a standard of the gas of interest.

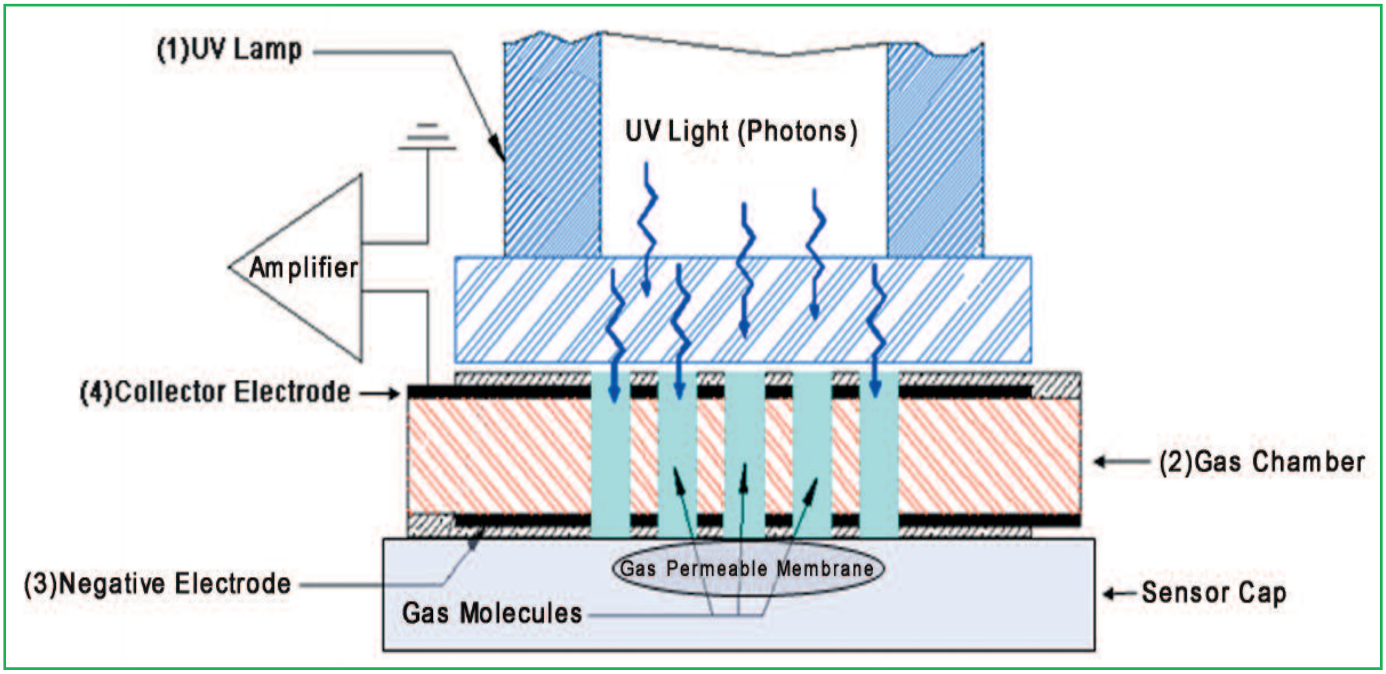

Figure 1.

However, this is not always practical as it requires that a number of different and sometimes hazardous gases be kept on hand for calibration. To address this issue, a synthetic span gas such as isobutylene is typically used for calibration. Response factors, which are a measure of the sensitivity of a PID to a particular gas, can then be used to relate the isobutylene response to the gas of interest. The user simply multiplies the instrument reading (calibrated for isobutylene) by the response factor to get the corrected value for the compound of interest. With response factors, a user can measure a variety of compounds using a single calibration gas. If the compound of interest is known, the instrument can typically be set to indicate a direct reading for that target compound.

One caution; while PIDs are extremely sensitive and effective tools, they are not analyzers and cannot determine if the spill is from a specific compound. A PID can detect that something is present and can alert the user to potentially hazardous situations, but additional steps will be necessary to properly identify the substance and how much of that substance is present.

Factors That Affect PID Performance

While the PID sensor construction appears to be fairly simple, there are many design considerations that can make the difference between a useful PID that can effectively and reliably detect VOCs and a unit that is plagued with limitations and difficulties.

Most PID sensors can detect up to a few thousand ppm. The lowest detection achievable is approximately 0.1 ppm under best conditions (controlled environment). Practically speaking, PID sensors can detect VOCs under real world conditions down to one or two ppm. External influences such as temperature and humidity variation limit detection below ppm levels.

Temperature Effects

The use of a PID may require start-up and operation in varying weather conditions. One well-known effect that can occur with PID sensors is difficulty with lighting the bulb at low temperatures. This cold-start effect has often been seen with portable units, especially after long periods of non-operation. A software routine can be used to automatically supply a repetitive start-up voltage to condition the bulb. Problems with lamp start-up can be virtually eliminated by using this software routine.

As with most gas sensing devices, temperature can affect the performance of various components, influencing the performance of the overall sensor. Temperature compensation that is achieved through internal software is a must for proper operation over typical operating temperature ranges (0 to 40 C).

Humidity and Condensation Effects

While water vapor is not readily ionized by 10.6 eV light, it can produce a small background signal at higher non-condensing relative humidity conditions. Depending upon the manufacturer, this humidity effect can be on the order of several ppm. Through proper design of the photoionization cell, this effect can be reduced to one ppm or less.

Another challenging humidity effect for PID sensors is “quenching”, which can be described as the water molecules blocking UV light from the gas of interest. This quenching effect is directly proportional to the relative humidity (RH), and reduces the span reading when the gas of interest is introduced into the PID chamber. Manufacturers report that quenching can reduce output by up to 50%. However, with optimal detector cell geometry, the ability of water molecules to block the light can be minimized. High relative humidity levels can be reduced to less than 10%.

Under condensing conditions, water droplets may deposit between the two electrodes in the detector. The voltage supplied between the two electrodes will then cause the output of the unit to quickly produce a full-scale deflection. During continuous use of the PID sensor, this effect is most noticeable on a cool morning, especially during a rainfall (Figure 2). Any micro fibers or dirt in the cell can accentuate this effect by forming a surface for condensation.

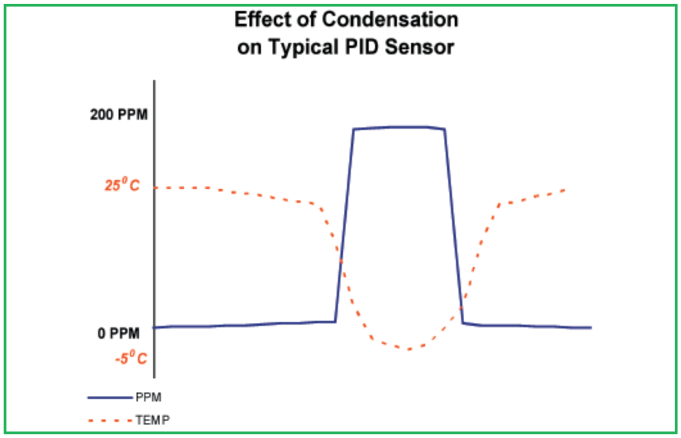

Figure 2.

Condensation can be dramatically reduced by maintaining a sensor temperature that is a few degrees above ambient conditions. By maintaining this elevated temperature in the cell, condensation will not occur in the sensor. Dramatic results show a stable zero, even when the ambient temperature is below freezing (Figure 3).

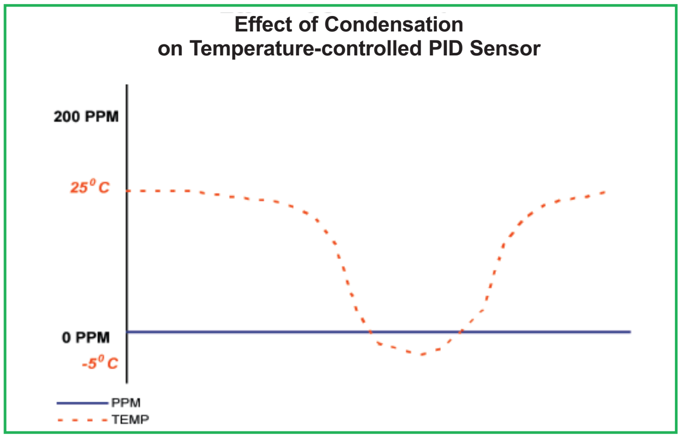

Figure 3.

Non-Linearity

The possibility of non-linearity at higher concentration levels is also an important design consideration. Typically, this non-linearity can be corrected through internal linearization algorithms in the software. However, non-linearity can be seen with some PID sensors due to self-quenching (also known as rollover effect). Self-quenching can occur when the concentration is high enough for some of the gas molecules to block the light before the UV light reaches other molecules in the gas chamber. The net result of self-quenching can actually be a decrease in the output of the sensor at higher concentrations. By minimizing the internal volume of the ionization cell, self-quenching can be greatly reduced. With small internal volume, there will be insufficient gas cross-section to block the light before it passes through the gas chamber.

Conclusion

PIDs are extremely valuable tools for detection of VOCs. Their sensitivity, low levels of detection, and ability to detect many different compounds enable PIDs to be used in many different applications. However, one must choose the PID manufacturer carefully as not all PID sensors are created equal. Failure to account for design considerations in the PID sensor may well lead to a sensor that will not be effective or reliable at detecting VOCs.

Common Compounds Detected with a PID

1,4-Dioxane
1-Butanol
1-Propanol
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,2-Dibromoethane
1,2-Dichlorobenzene
1,3,5-Trimethylbenzene
1-Methoxy-2-propanol
Methylacetate
Methylacrylate
Methylacetoacetate
Methylbenzoate
Methylmethacrylate
2-Butanone
2-Pentianone
2-Propanol
2-Methoxyethanol
n,n-Dimethylforamide
n,n-Dimethylacetoamide
4-Hydroxy-4-methyl-2-pentanone
Acetone
Acetophenone
Amylacetate
Benzene
Bromomethane
Butadiene
Butylacetate
Tetrachloroethylene
Trichloroethylene
Dichloroethane
Ethylbenzene
Ethylacetoacetate
Chlorobenzene
Cumene
Cyclohexane
Cyclohexanone
Decane
Diethylamine
Dimethoxymethane
Ethyleneglycol
Ethylacetate
Ethylene
Heptane
Hexane
Iso-amylacetate
Iso-propylamine
Iso-propylether
Iso-butanol
Iso-butylene
Iso-octane
Iso-phorone
Meta-xylene
Mesityloxide
Methyl Isobutyl Ketone
Methyltertiarybutylether
Ortho-xylene
Octane
Para-xylene
Phosphine
Propylene
Propylene Oxide
Pyridine
Quinoline
Tertiarybutylamine
Trisdichloroethene
Tetrahydrofuran
Thiophene
Toluene

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Corporate Headquarters:
P.O. Box 426, Pittsburgh
PA 15230 USA
e-mail info@MSAnet.com
www.MSAnet.com

U.S. Customer Service Center:
Phone 1-800-MSA-2222
Fax 1-800-967-0398

MSA Canada:
Phone 1-800-MSA-2222
Fax 905-238-4151

MSA Mexico:
Phone 52-55 2122-5770
Fax 52-55 359 4330

MSA International:
Phone (412) 967-3354
Fax (412) 967-3451

Offices and representatives worldwide
For more information: