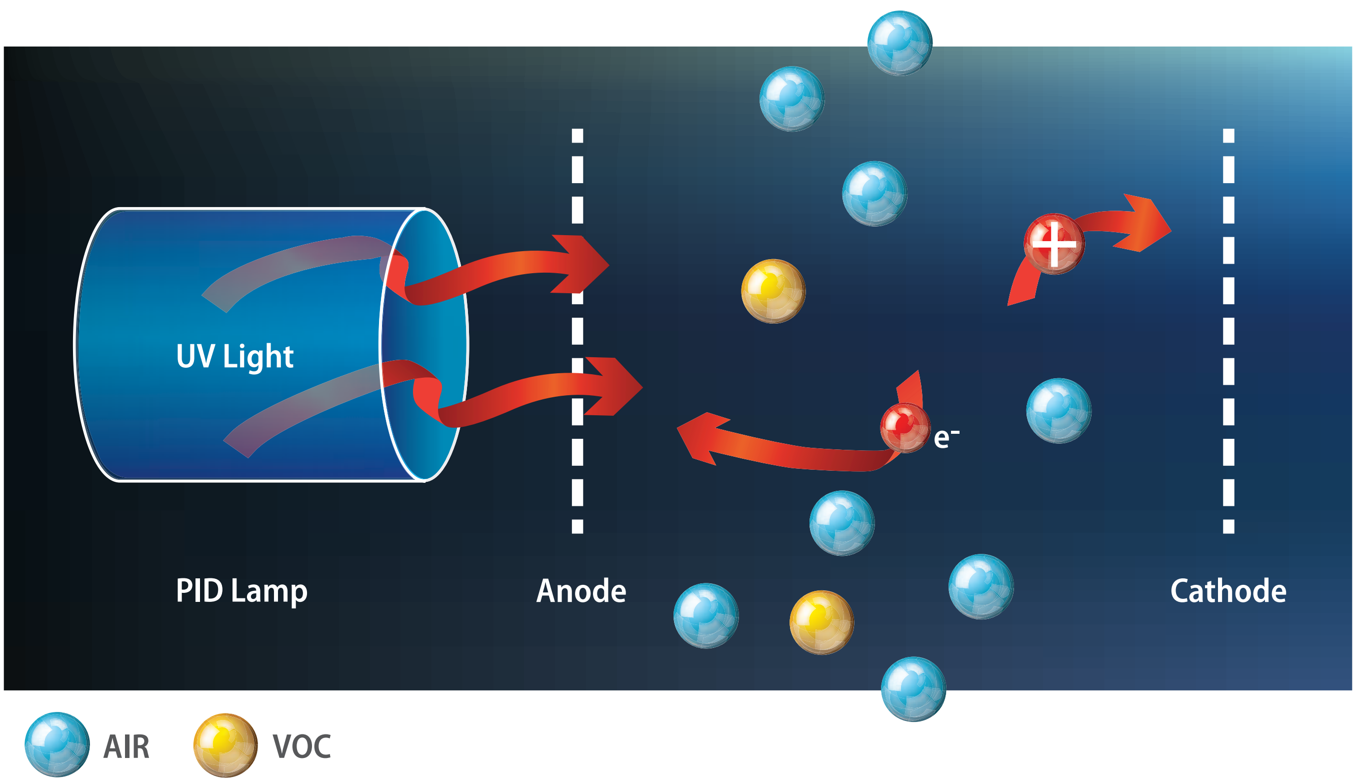
Photoionization Detectors (PIDs)
Theory, Uses and Applications

MSA
The Safety Company

Photoionization Technology and Operation

PIDs effectively detect and monitor for numerous hazardous substances, providing maximum benefit and safety to users. While many hazardous gas detection methods are available, photoionization detectors offer the combination of speed of response, ease of use and maintenance, small size, and ability to detect low levels, including most volatile organic compounds (VOCs).

PIDs rely upon *ionization* as the basis of detection. When sampled gas absorbs energy from a PID lamp, the gas becomes excited and its molecular content is altered. The compound loses an electron (e-) and becomes a positively charged ion. Once this process occurs, the substance is considered to be *ionized*. Here we see an illustration of photoionization.



Most substances can be ionized, some more easily than others. The ability of a substance to be ionized is measured as ionization potential (IP) using an electron volt (eV) energy scale. This 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 of between 12 and 16 are extremely difficult to ionize. IP ratings of some common substances include:

SUBSTANCE	IP
BENZENE	9.25
HEXANE	10.13
TOLUENE	8.82
STYRENE	8.47
METHYL ETHYL KETONE (MEK)	9.51
XYLENE	8.56
PHOSPHINE	9.87

When monitored chemicals are ionized using a PID instrument, current is produced and compound concentration displays as parts-per-million (ppm). PIDs use 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. A 10.6 eV lamp puts out enough energy to ionize any compound with an eV rating of less than 10.6 including everything that can be ionized with a 9.8 eV lamp. While there are a limited number of compounds that require an 11.7 eV lamp, there is an inherent instability of available lamps that results in a very short operating life and many customers seek alternative detection methods for these compounds.

• Propyl alcohol	10.22 eV
• Phosphine	9.87 eV
• Vinyl chloride	9.99 eV
• Toluene	8.82 eV
• Benzene	9.25 eV
• Styrene	8.47 eV
• Vinyl acetate	9.19 eV

SUBSTANCE TYPES 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 compounds measured or detected contain a carbon (C) atom, a PID can be used. However, such is not always the case, as methane (CH4) and carbon monoxide (CO) cannot be detect with a PID. Listed here are some common substances that a PID can detect and monitor:

- Benzene
- Toluene
- Vinyl chloride
- Hexane
- Isobutylene
- Jet 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 method of calibrating a PID to different compounds is through use of a standard of the gas of interest. However, such is not always practical, as doing so requires that an assortment of 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 PID sensitivity to a particular gas. Using response factors, users can measure a large number of compounds via a single calibration gas – typically *isobutylene*. Isobutylene is used because it is near the midpoint ionization point of most VOCs and is not flammable or toxic at low concentrations used in calibration. Users simply multiply the instrument reading (calibrated for isobutylene) by the response factor to obtain the corrected value for the compound of interest.

Instruction manuals for most PIDs list response factors; some PIDs have response factors for common gases programmed into the instrument's software, enabling all response factor calculations to be 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 (TLV) AND PERMISSIBLE EXPOSURE LIMITS (PEL)

Default low and high alarm values are typically set for isobutylene. If users must monitor a different gas, they must determine TLVs for the gas of interest and change the instrument's alarm level accordingly. Instrument manuals should be referenced to ensure that correct instructions are followed. Chemical limit values can be found by referencing ACGIH, NIOSH, OSHA, or local regulations.

INDICATOR VERSUS ANALYZER

A common misconception about PIDs is that they are *analyzers*. Many expect that a PID will provide exactly the vapor present at a spill site; such is not the case. While PIDs are extremely sensitive and effective tools, they are not analyzers and cannot determine if a spill is benzene or jet fuel, for example. A PID can detect that a substance is present and can alert you as to potentially hazardous situations, but additional steps are necessary to properly identify the substance's exact composition and quantities present. Listed here is a sample procedure to identify a substance's concentration at a spill site:

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

If the placard or MSDS reads that the substance is vinyl chloride, set the PID response factor to vinyl chloride to enable direct reading of actual vinyl chloride level.

INDUSTRIAL HYGIENE PID APPLICATIONS

PIDs are great for use as screening tools in hazard assessments due to their ability to detect multiple risks at very low concentrations. While PIDs do not identify specific compounds, they are widely used to identify sources and compound types. Potential chemical attacks may employ industrial chemicals; first responders can use PIDs to confidently determine if a chemical is present and, if so, to accurately measure its concentration using a reference factor.

CONFINED SPACE

Industrial activity produces many toxic gases and vapors as components or byproducts. Using a PID for assessment and continuous monitoring within confined space allows for a more comprehensive evaluation and greater protection than when used to supplement standard 4-gas instrument configuration.

Three Methods in which Response Factors are used with PIDs

METHOD	EXAMPLE
Method #1: Preprogrammed Response Factors Typically, PID detectors are calibrated with 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 PID instruments. After users select the desired gas to measure from the instrument menu, units will automatically calculate the corrected gas concentration reading for the gas of interest. The direct reading now measures 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 response factor of 0.51. Select the pre-programmed response factor; the instrument now reads approximately 51 ppm when exposed to the same gas, reading directly in ethylbenzene concentration values.
Method #2: Customized Response Factors Typically, PID detectors are calibrated with 100 ppm isobutylene. If users do not find a desired gas in the preprogrammed instrument menu list, users can program a custom gas and response factor. If users do not know the corresponding response factor, they may call MSA and request that a customized response factor be calculated that is specific to their application.	Tetrahydrofuran is the target gas. The response factor for tetrahydrofuran is 1.6 using a 10.6 eV lamp. Program a custom gas for tetrahydrofuran with RF 1.6 and select this RF for use. The instrument now reads directly in tetrahydrofuran concentration values.
Method #3 Manually Calculated Response Factors Typically, PID detectors are calibrated with 100 ppm isobutylene. If users choose to read isobutylene's direct reading for a different gas and do not want to use the preprogrammed or customized response factors, users may manually calculate the desired gas' direct reading. If users know 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.

LEAK DETECTION

Often, leak concentration is too low to be smelled by humans. PIDs are often used to detect low-level leaks in order to detect compounds at levels of less than 1 ppm.

PIDs can be used for leak detection to detect leak sources. Higher concentrations of gases are found at or near the source of a leak. When a substance is detected, users wearing adequate personal protective equipment should move in the direction of higher concentrations when trying to identify the leak source.

PERIMETER MONITORING

At HazMat sites, perimeters are set to contain hazardous areas. PIDs can be used to set and, if necessary due to changing environmental conditions, change perimeter lines. For example, toluene concentration reads 5 ppm at Perimeter Line A at 10:50 a.m. At 11:05 a.m., the Line A reading rises to 10 ppm due to wind direction, telling HazMat workers that the perimeter line may need to be extended.

SPILL DELINEATION

As water and foam are often used at HazMat sites, a variety of liquids may be present on the ground in addition to any material inadvertently spilled. A PID is effective in locating hazardous substances while ignoring foam and water, as PIDs will not respond to foam or water.

REMEDIATION

HazMat spills can contaminate bodies of water or soil, potentially posing long-term environmental concerns. PIDs are extremely useful in taking samples from soil to determine if remediation is necessary in conjunction with applicable environmental regulations.

ARSON INVESTIGATION

PIDs are often used to detect accelerants at post-fire scenes. When a PID reading is detected, a sample from that specific area can be taken to a laboratory for analysis. For this application, it is recommended that PIDs be set to the isobutylene response factor for general purpose indications.

DIESEL FUEL TLV MONITORING

Marine chemists follow diesel fuel TLV limits that are determined by the American Conference of Governmental Industrial Hygienists (ACGIH). The presence of diesel fuel in the workplace and associated exhaust has long been connected with carcinogens, and particulate pollution associated with lung disease. Diesel vapor TLV is 15 ppm; sampling for diesel fuel vapors and recording results are significant aspects of inspections. Surveys are conducted in fuel tanks, cargo spaces and engine rooms.

CONCLUSION

PIDs are extremely valuable tools for industrial, homeland security, law enforcement, fire service, and HazMat applications. PID sensitivity, low level detection and ability to detect many different compounds enable PIDs to make accomplishing these difficult jobs easier and more efficient.

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