Technical/Application Article 01

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What is a PID?

Introduction

PID is the abbreviation for “Photoionisation Detector”. PID sensors measure a broad range of volatile organic compounds (VOCs) and some inorganic compounds in the parts-per-million (ppm) to parts-per-billion (ppb) range. They are used in handheld, wearable and wall mounted detectors. PIDs are commonly used to measure very low levels of vapours that are harmful to human health and the environment, common applications include:

- Air quality monitoring
- Fence line monitoring
- Fugitive emissions
- Industrial health and safety
- Decontamination
- Semi-conductor
- Leak detection
- Power storage
- Site investigation
- Fertility & clandestine labs
- Emergency response
- Fracking
- HVAC & building control
- Li-ion battery monitoring
- Solar farm

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How a PID Works

Figure 1, is a schematic of an ION SENSE® (a brand of ION Science®) sensor. A UV lamp generates high-energy photons, which pass through the lamp window and a mesh electrode into the sensor chamber. Sample gas diffuses through a porous membrane filter into the sensor chamber.

The inset on the right of Figure 1 shows what happens on a molecular level when a photon with enough energy strikes a molecule M, an electron (e^-) is ejected. The M^+ ion travels to the cathodic electrode and the electron travels to the anode, resulting in a current proportional to the gas concentration.

The electrical current is amplified and typically displayed as a ppm or ppb concentration on a gas detector. The major components of air, i.e., nitrogen, oxygen, carbon dioxide, argon, etc., do not cause a response, but most VOCs do give a response.

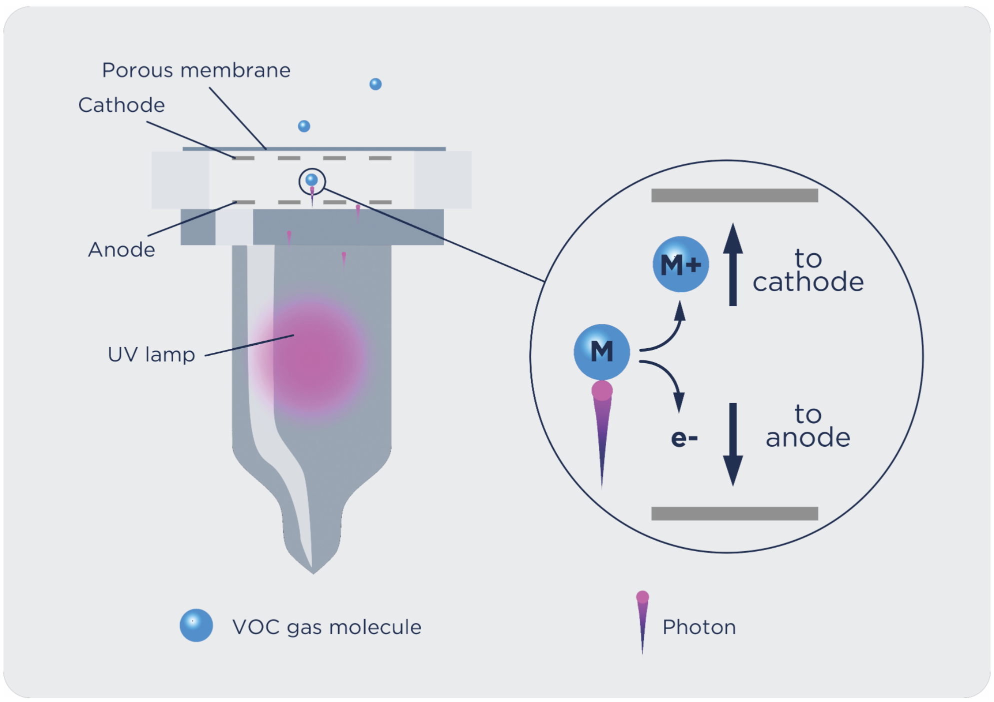

Figure 1: ION SENSE® PID Sensor Design.

Lamp Selection

Three PID lamps are available with maximum photon energies of 10.0 eV, 10.6 eV, and 11.7 eV. Figure 2 illustrates that a sensor can only detect those compounds with ionisation energies (IE) equal to or below that of the lamp photons. Thus, a 10.6 eV sensor can measure ethanol with an IE of 10.43 eV and all compounds with lower IE but cannot detect methanol or compounds with higher IE.

The choice of lamp depends on the application. When only one compound is present, one can use any lamp with enough photon energy, often the standard 10.6 eV lamp which is the lowest cost and has a long working life of up to a few years.

For high IE compounds like chloroform, it is necessary to use the 11.7 eV lamp, which has a short life of only a few months. In the case of compound mixtures, use the lowest energy lamp possible. For example, to measure benzene in the presence of isopropanol one could use the 10.0 eV lamp, which does not have any interference from isopropanol.

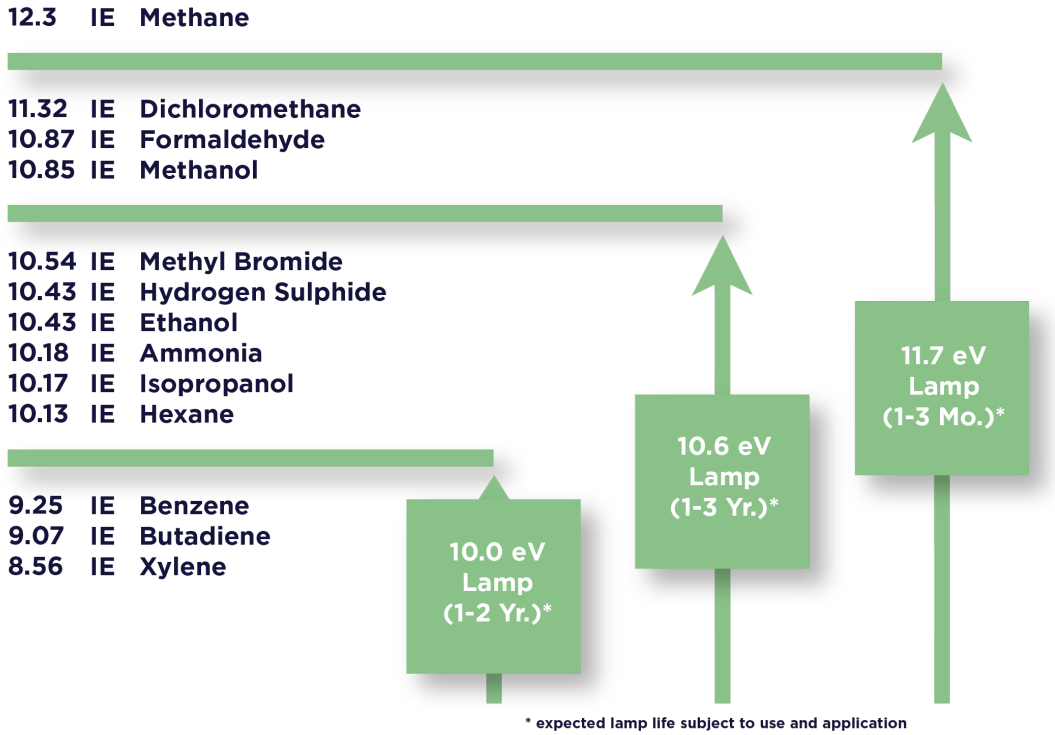

Figure 2: PID lamp energy thresholds.

What Compounds a PID Can Measure

PIDs can detect many thousands of VOCs. The sensitivity is roughly in the following decreasing order:

- **Aromatics**, like benzene, toluene, xylene, pyridine, phenol, aniline and naphthalene…
- **Olefins**, like butadiene, cyclohexene, trichloroethylene, vinyl chloride, turpentine, limonene cleaner…
- **Bromides & Iodides**, like methyl bromide fumigant, n-bromopropane degreaser, iodine disinfectant…
- **Sulfides & Mercaptans**, like methyl mercaptan natural gas odorant…
- **Organic Amines**, like methylamine, trimethylamine… (prone to unstable response)
- **Ketones**, like acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK)…
- **Ethers**, like ethyl ether solvent, methyl-t-butyl ether gasoline additive, ethyl cellosolve…
- **Esters & Acrylates**, like ethyl acetate solvent, methyl methacrylate glues, PGMEA…
- **Aldehydes**, like glutaraldehyde sterilant, acetaldehyde, formaldehyde…
- **Alcohols**, like butanol, isopropanol, ethanol, propylene glycol…
- **Alkanes**, like hexane & Isopar solvents, octane & diesel fuels…
- **Some Inorganics**, like ammonia (NH_3), hydrogen sulfide (H_2S), and phosphine fumigant (PH_3)

In addition, there is varying response to chlorinated compounds, organic acids, silicate-, borate- and phosphate- esters, isocyanates, and many others. Fuels like automotive gasoline (petrol), diesel, kerosene and jet fuels are mixtures of aromatics, olefins and alkanes, and thus give a strong response.

Vapours that meet the following criteria are well detected:

- Less than 10 carbon atoms
- Have boiling point of less than 250°C
- Have a vapour pressure greater than 4.0×10^{-5} mbar

What a PID Does Not Measure

There is no response to:

- **Components of Clean Air**, like nitrogen, oxygen, carbon dioxide, water vapor, argon…
- **Noble Gases**, like helium, xenon, krypton, argon…
- **Most Small Molecules**, like hydrogen, carbon monoxide, HCN, ozone, hydrogen peroxide, SO_2…
- **Natural Gas**, including methane and ethane…
- **Mineral Acids**, like hydrochloric acid, nitric acid, sulfuric acid…
- **Fluorinated Compounds**, like Freon® refrigerants, anesthetic gases, sulfur hexafluoride…
- **Non-Volatiles**, like PCBs, PAHs, MDI, greases, waxes…
- **Radioactives**, like uranium, plutonium, radon…

Response Factors

TA-02 (ION SENSE® PID Response Factors) quantitates the sensitivity of over 900 compounds in the form of response factors (RFs) relative to the response of isobutylene. Although it is most accurate to calibrate with the compound to be measured, such calibration gas is often not readily available, making calibration with standard isobutylene gas very convenient. When a PID is calibrated with isobutylene, the readings of other compounds need to be converted, as follows:

True concentration = PID Reading x RF

Table 1 gives some RF values for a few chemicals. For example, if a PID calibrated with isobutylene is used to measure benzene with a 10.6 eV lamp and the reading is 10 ppm, the true concentration is:

Benzene concentration = 10 ppm x 0.50 = 5.0 ppm benzene

If the same result is obtained with ethanol, the true concentration is:

Ethanol concentration = 10 ppm x 11 = 110 ppm Ethanol

Compound	Ionisation Energy	RF 10.0 eV Lamp	RF 10.6 eV Lamp	RF 11.7 eV Lamp
Benzene	9.24 eV	0.54	0.50	0.53
Ethanol	10.47 eV	ZR*	11	3
Chloroform	11.42 eV	ZR*	ZR*	0.8

* ZR = No Response

Table 1: Response Factors of Example Compounds with PID Lamps

Note that RFs are inverse to sensitivity, i.e., the lower the RF, the more sensitive the compound. It takes 110 ppm of ethanol to give the same 10 ppm response as 5.0 ppm benzene.

PIDs for LEL Testing

PIDs are useful for measuring the flammability of an atmosphere. Measurement of vapor flammability, or LEL (lower explosive limit) is usually done with a pellistor, or catalitic bead sensor. Commonly the alarm is set at 10% of LEL in order to have a good margin of safety. The LEL for many VOCs is a few Vol %. Since 1% Vol equals 10,000 ppm, 10% of LEL is typically in the range of several 100 to a few 1000 ppm, which is an easy range for a PID. For example, styrene and vinyl chloride have LELs of 1.1 Vol % and 4.0 Vol %, for which 10% LEL equal 1100 ppm and 4000 ppm respectively. LEL sensors are lower cost than PIDs, but have drawbacks:

- Weak response to heavy hydrocarbons like diesel & jet fuels, turpentine, etc.
- Are posioned by
    - a) polymerisable compounds like styrene & vinyl chloride
    - b) silicones, and compounds containing sulfur, chlorine, bromine, phosphorus, lead, etc.

PIDs do not suffer from these problems and thus are useful for measuring LEL in these situations. Examples include; airlines relying on PIDs for LEL safety during wingtank entry (jet fuel), manufacturing plants using silicone lubricants and a deodorant filling plant, and polystyrene manufacturing and curing.

PIDs Do Not Require Oxygen

PIDs can function in cases where it is necessary to measure toxic compounds in the absence of oxygen. By contrast, most electrochemical sensors and pellistor-type LEL sensors require oxygen to function. Even though workers use supplied air in such situations, it may be necessary to measure VOCs because of skin exposure hazard, or the potential for explosion should air suddenly intrude. Some chemical processes control situations also are run in inerted atmospheres and thus can use a PID to monitor VOCs.

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