

Chapter 6

Photoionization Detectors

The photoionization detector (PID) utilizes ultraviolet light to ionize gas molecules, and is commonly employed in the detection of volatile organic compounds (VOCs). This technique originally found use in bench top laboratory instruments, but its complexity limited its use elsewhere. The heart of the photoionization detector is an ultraviolet source, which is essentially a lamp. Early versions of this lamp used electrodes inside the lamp similar to those used in the early days of the vacuum tube and were quite costly to manufacture.

The lamps used today do not contain electrodes and are both less costly and have a longer life expectancy. In the 1980s, with the advent of integrated circuit (IC) technology, the electronics that were designed were better able to process the small signal from PID sensors into useful and reliable data.

Additionally, requirements for the monitoring of underground storage tanks to help prevent ground water contamination began to emerge, which required monitoring of VOCs.

These events led to the design of small, portable PIDs (see Figure 1) that have proven to be both practical and reliable, and which offer fast response and the ability to detect low gas concentrations. To this

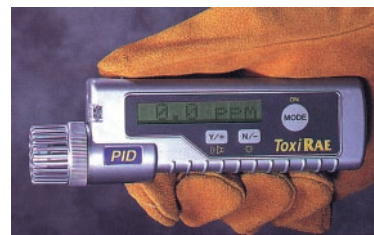


Fig. 1 A Pocket PID Monitor

day, PID sensors are the preferred choice for the detection of VOCs.

Principle of Operation

Ultraviolet (UV) light is the radiation group that has frequencies that are higher and are directly above visible light in the electromagnetic radiation spectrum. UV wavelengths, being in the nanometer ($\eta\text{m} = 10^{-9}$ meters) region, are much shorter than IR wavelengths. The wavelengths of infrared light used for gas analysis are in the micron region, 10^{-6} meters.

Because shorter wavelengths have higher frequencies, and hence more energy, UV radiation has more energy than IR radiation. UV radiation energy levels are commonly described in terms of electron volts, or eV.¹ Wavelength is related to eV through Planck's Constant² which is 4.135×10^{-5} eV. [An electron volt equals $1.2395 \times 10^{-6}/\text{wavelength} (\eta\text{m})$. The term eV is used for convenience, to give a simple numerical expression of the radiant strength.]

The PID Lamp. The heart of the detector is the PID lamp which has an exterior shape resembling a medical ampule and comes in different sizes and dimensions, depending on the manufacturer. The lamp is filled with a low-pressure inert gas. When this gas is energized with energy in resonance with the natural frequency of the gas molecules, an ultraviolet spectral radiation is produced.

The wavelength of the UV light emitted depends on the type of gas in the lamp. For instance, krypton, when excited, will emit 123.9 ηm and 116.9 ηm radiation, or the equivalent of 10 eV and 10.6 eV. This 10.6 eV lamp happens to be the most popular lamp currently used in PID instruments. Various other gases are also used. Figure 2 on the following page shows wavelengths emitted by argon, krypton, and xenon.

Many different techniques are employed to power the PID lamp. A high voltage is required for the lamp

¹ eV = energy gained when a particle of one electronic charge is accelerated through a potential of one volt.

² Planck's Constant is a fundamental constant in quantum physics. The radiant energy only changes in "quanta" or discrete steps.

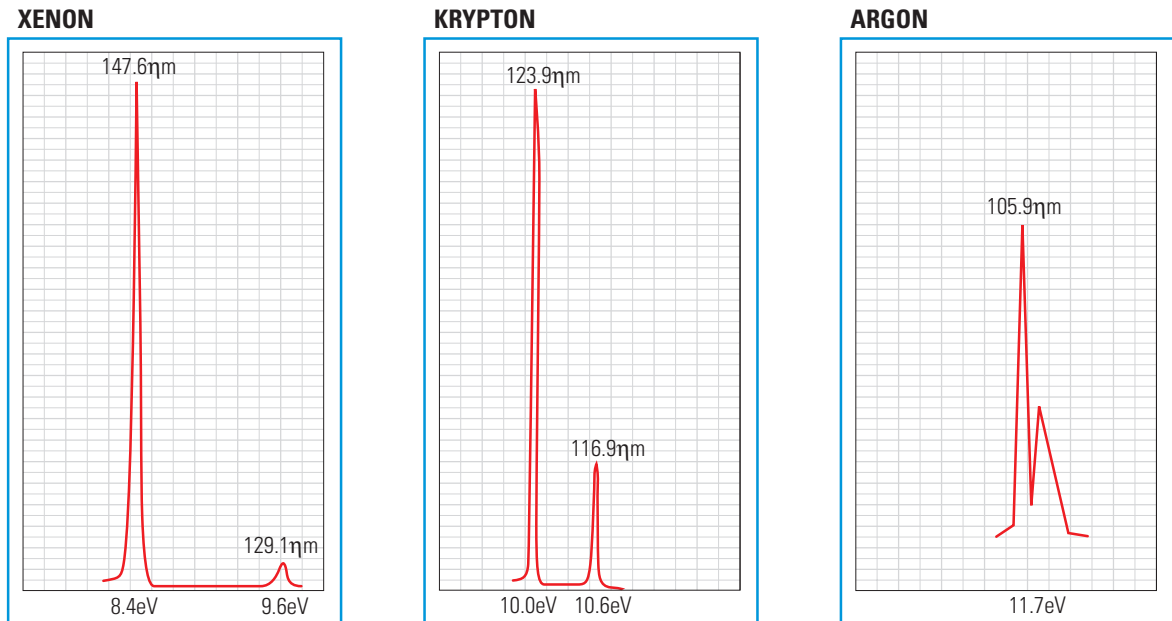


Fig. 2 The wavelengths (ηm) emitted by argon, krypton, and xenon.

to function. The source needs to remain stable over time and also be efficient, so as not to consume too much power. A typical design would place electrodes inside the lamp. These types of lamps look similar to the vacuum tubes used in the early days of radio and TV. There are electrical terminations on the tube, and the gas discharge is confined to a small capillary. While the voltage used is in excess of 1000 volts, the current is very low. Although this type of lamp is used in many laboratories, it is quite expensive. As a result, a more popular lamp in use today is the electrodeless lamp.

The Electrodeless Lamp. This lamp is only filled with a low-pressure inert gas and there are no electrodes inside the lamp. The simplicity of this design allows the lamp to be miniaturized, making the design of the portable instrumentation very compact.

In the electrodeless lamp, the low-pressure inert gas is separated by the lamp wall from the outside world. Because there are no electrodes that provide power directly to the gas, the only way to excite the

gas molecules is to use radiation energy that can penetrate the lamp wall.

There are several different ways this can be accomplished. One method is to use electromagnetic radiation. A more popular technique, however, is to place a pair of electrodes on the exterior wall of the lamp. A high-voltage, low-current charge is applied to the electrodes, and the energy applied is sufficient to excite the low-pressure gas inside the lamp. The design is similar to that of a fluorescent light used in a home or office, except on a much smaller scale.

Special Window Materials. At the *wavelength of radiation*, meaning the wave frequency of UV light, most materials will absorb the radiation and prevent the transmission of such radiation.

Therefore, special window materials are placed at the discharge end of the lamp which allow spectral emissions to pass through. This window material is a crystal that allows good transmission of the targeted UV wavelength. For instance, 10.6 eV lamps commonly use krypton gas and magnesium fluoride windows, while 11.7 eV lamps, which have more energy, use argon gas and lithium fluoride windows. These windows are soft glass and are very fragile. They are quite expensive, and require special care and handling. Figure 3 illustrates typical PID design.

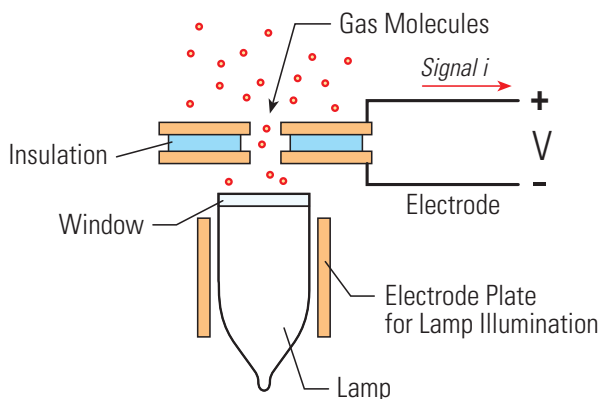


Fig. 3 A Typical Photoionization Detector Configuration

A pair of electrode plates are placed in close proximity to the lamp window where the light is emitted. The electrodes are biased with a stable DC voltage which will generate signals in case any small changes in the electrical field occur. As gas molecules move into the radiated field in the space between the electrodes, they are ionized and the free electrons are collected at the electrodes resulting in a current flow whose magnitude is directly proportional to the gas concentration.

Distinct Ionization Potentials. Each gas has its own unique *ionization potential* (IP). Gases with IP values below the eV output of the lamp will be detected. For most portable instruments, the 10.6 eV lamp is most widely used because it detects most volatile organic compounds, and the lamp is easy to clean. However, other lamps are also available, including 10 eV, 9.5 eV, 8.4 eV, and 11.7 eV lamps. Most manufacturers design instruments with a lamp chamber that allows easy interchange of lamps. The ionization potentials for many gases are included in Appendix II at the end of this book.

Following are examples of gases detectable using different lamps:

1. *Gases detected by 9.5 eV lamp* such as benzene, aromatic compounds, amines.
2. *Gases detected between 9.5 eV and 10.6 eV* such as ammonia, ethanol, acetone.
3. *Gases detected between 10.6 eV and 11.7 eV* such as acetylene, formaldehyde, methanol.

A 9.5 eV lamp will ionize gases with ionization potentials below 9.5 eV and will not ionize gases with higher ionization potentials. On the other hand, if one uses an 11.7 eV lamp, gases with ionization potentials up to 11.7 eV will be ionized. Interchanging lamps in an unknown air sample helps to separate it into groups of gases.

Characteristics

PID sensors offer fast response for detection of many volatile organic compounds. They will respond to all gases that have ionization potentials equal to or less than the eV output of their lamps.

Correction Factor. PIDs are typically calibrated with isobutylene, a stable gas with a slightly pungent odor. This gas is easy to handle and can be stored at high pressure, allowing calibration bottles to provide many calibrations. PID instruments typically detect gases at low concentrations, and most of these gases are normally liquid solvents or other gases that are not easy to calibrate. Thus, it is much easier to calibrate these instruments using isobutylene as the calibration gas. Readings for other gases are obtained by multiplying the reading by a *correction factor*. For example, benzene has a correction factor of 0.5, which means that a reading of 100 ppm isobutylene on the sensor indicates a concentration of 50 ppm benzene. For ammonia, which has a response factor of 10, a reading of 100 ppm on the sensor would indicate an ammonia concentration of 1000 ppm. Instrument manufacturers typically supply a list of correction factors with their product.

An important point to remember is that correction factors are *not* absolute, and data can be slightly different from manufacturer to manufacturer. In fact, these factors can even vary somewhat from lamp to lamp, and the results may vary depending on the quality of the UV output of the lamp at the time of measurement. Thus, for the most accurate readings on specific gases, it is necessary to individually calibrate the gas of interest.

PID instruments are very sensitive to the composition of gases in the sample. The results will differ vastly if one uses gas with dry nitrogen as the balance to calibrate, from those results obtained when one uses air as the balance. Therefore, it is important to use

isobutylene in air as the calibration gas when the instrument is used for area air quality and safety applications. Still, there will be some error because the calibration mixture is under high pressure and is dry; therefore, it does not exactly duplicate environmental air.

Zeroing Instruments for Best Results. Generally, high humidity decreases the response by up to 30%, when compared to dry air. In dry nitrogen, readings are typically 10-30% higher than in dry air.

If the sample gas constituents include gas components that are ionizable but the ionization potentials are above the detecting lamp output potential, and although the lamp radiant energy will not ionize these gas molecules, the UV rays can be scattered and absorbed, resulting in a lower output reading. This is known as the “*quenching effect*.” For example, in environmental air, such “quenching” gases are water vapor, carbon dioxide, methane, carbon monoxide, etc. This is another reason why a representative air is needed to zero the sensor and prepare the calibration gas mixture. The common practice of calibrating the instruments with isobutylene in an air mixture, without making corrections, results in an inaccurate reading.

PID sensors will exhibit different zero readings when exposed to nitrogen, dry, clean air, and environmentally clean air. Thus, *it is best to zero the sensor in the same type of conditions that are present in the application in which it will be used*. Clean, ambient air is, therefore, the best choice for zero air as well as for mixing calibration gas.

PID Response Characteristics. The output of the PID sensor is relatively linear below 200 ppm, and the detector output becomes saturated above 2000 ppm. Figures 4, 5, and 6 illustrate

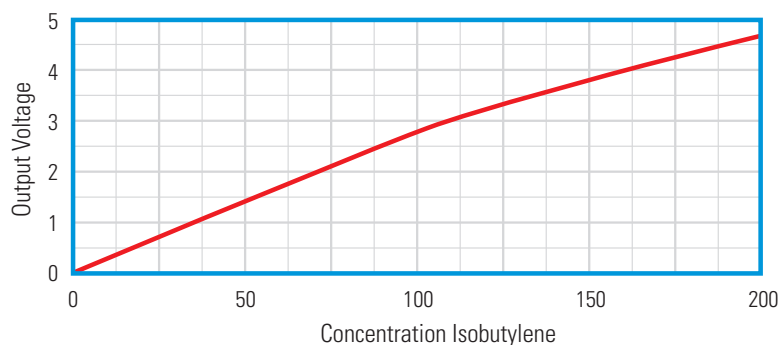


Fig. 4 Zero-to-200 ppm Curve

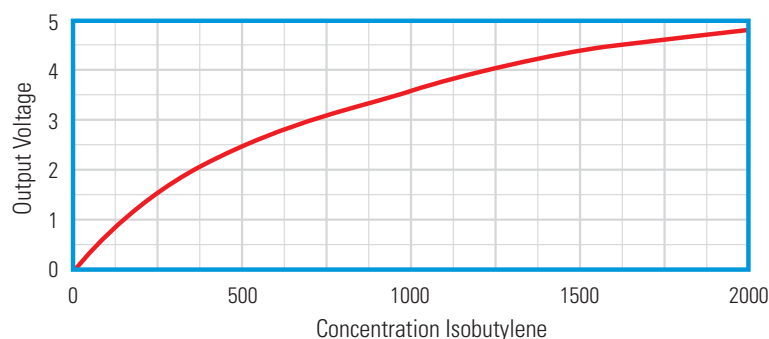


Fig. 5 Zero-to-2000 ppm Curve

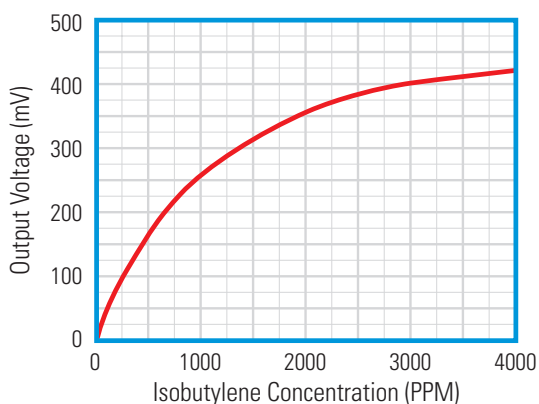


Fig. 6 Zero-to-4000 ppm Curve

the response curves for 200 ppm, 2000 ppm, and 4000 ppm isobutylene in room air.

You will notice that the 200 ppm curve is relatively linear, while on the 2000 ppm curve, 1000 ppm produces an output of 3.6 volts and 2000 ppm produces an

output of 4.8 volts. The additional 1000 ppm produces only 1.2 volts, or one third of the initial 1000 ppm. From the 4000 ppm curve, you can see that the detector becomes saturated.

Thus, this output region does not provide a reading with a good resolution.

Applications

PID instruments offer very fast response, high accuracy, and good sensitivity for detection of low ppm volatile organic compounds (VOCs). The major shortcom-

ing of these instruments is that the PID lamp requires frequent cleaning. Because the lamp window is directly exposed to the sample stream, the condition of the window is very critical to accurate readings, and a dirty window will produce much different results than a clean window. The frequency of cleaning needed for the window depends on the sample stream conditions.

Because PID sensors require periodic cleaning and have limited life expectancies, they are not practical choices for use in stationary monitors, which sample continuously. Their use is limited to portable models in which only periodic readings are required.

Lamp Life Expectancy. The life expectancy of the lamp depends on the type of lamp. Generally, 10.6 eV lamps have the longest life expectancy, approximately

6000 hours.

The 11.7 eV lamps have lithium fluoride windows that transmit the shorter UV wavelength light at 11.7 eV, which allows for the detection of many more gases when compared to lower eV lamps. However, the intensity of the light they emit is weaker than the light emitted from lower eV lamps. The weaker energy emitted means less signal, which results in less stable and more temperature-sensitive instruments. Thus, 11.7 eV lamps are not typically used for general applications. Furthermore, lithium fluoride is hygroscopic, which means that lithium fluoride crystals attract and absorb moisture from the air, causing the window to degrade. They also cannot be exposed to cleaning solvents because most solvents contain small amounts of water. Therefore, a special, fine solid aluminum oxide powder is needed to clean the lamp.

Typical Specifications for PID Instruments

Detector: 10.6 eV electrodeless discharge lamp. 11.7 eV lamp optional.

Response Time: 3 secs. to 90% reading.

Ranges: 100 ppm, 1000 ppm, and 2000 ppm isobutylene equivalent, auto-ranging.

Sensitivity: 0.1 ppm isobutylene.

Accuracy: 1-10%, depending on range.

Temperature Range: -20°C to +50°C.

Humidity: 0-95% relative humidity, noncondensing.