

Keeping you safe!



This column is intended to provide operational guidance to the hazmat/ CBRNE community regarding the selection and performance of equipment and tactics. In this issue, we focus on the use of photoionisation detectors (PIDs) in hazmat/ CBRNE response. PIDs have been used in field operations since the mid 1970s, but it was the products fielded in the mid 1990s that transitioned PIDs into the lightweight devices that are used today. The major focus since then has been in software improvements, development of correction factors for a broad range of chemicals, and sensor/detector improvements, especially to decrease the lower limit of detection into the parts per billion (ppb) range.

PIDs operate by pulling a gas sample into a small cell where the gas is ionised using a short wavelength ultraviolet lamp. When the gas is ionised, a change in electrical current is measured inside the cell, where the magnitude of the current is proportional to the gas or vapour concentration. To quantify the concentration, systems are calibrated against a standard gas such as isobutylene - the most common calibration gas - and correction factors are developed for other gases of interest. It is important to note that correction factors are not transferrable between different instrument types or manufacturers.

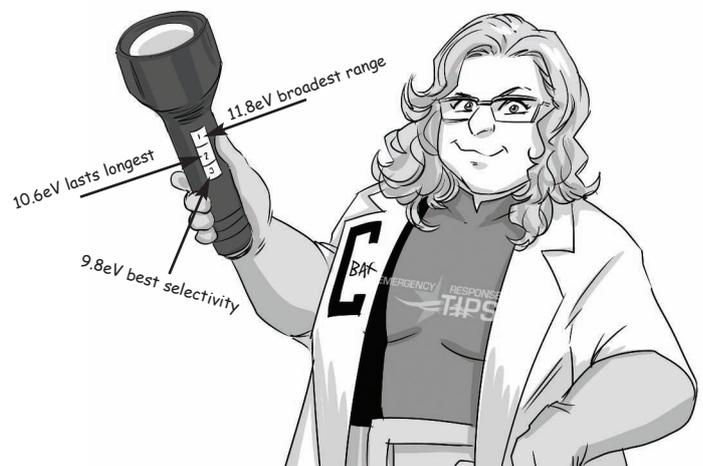
PIDs provide a linear response at low ppb and intermediate concentrations, but begin to lose that linearity at approximately 500 to 1,000ppm isobutylene, and begin to drop signal at high concentrations (10,000 ppm). Some of the loss in linearity can be corrected mathematically, however signals greater than 1,500ppm isobutylene units should be used with caution and only as a qualitative indicator of concentration.



Lamp selection

In general, any chemical with an ionisation energy less than the photon energy of the selected lamp, measured in electron volts (eV), can be ionised, and detected. There are many lamps available for use in a PID with the highest photon energy being 11.7/11.8eV. The maximum photon energy is dictated by the ionisation energies of the major components of air which range from 12.07eV for oxygen to 24.59eV for helium.

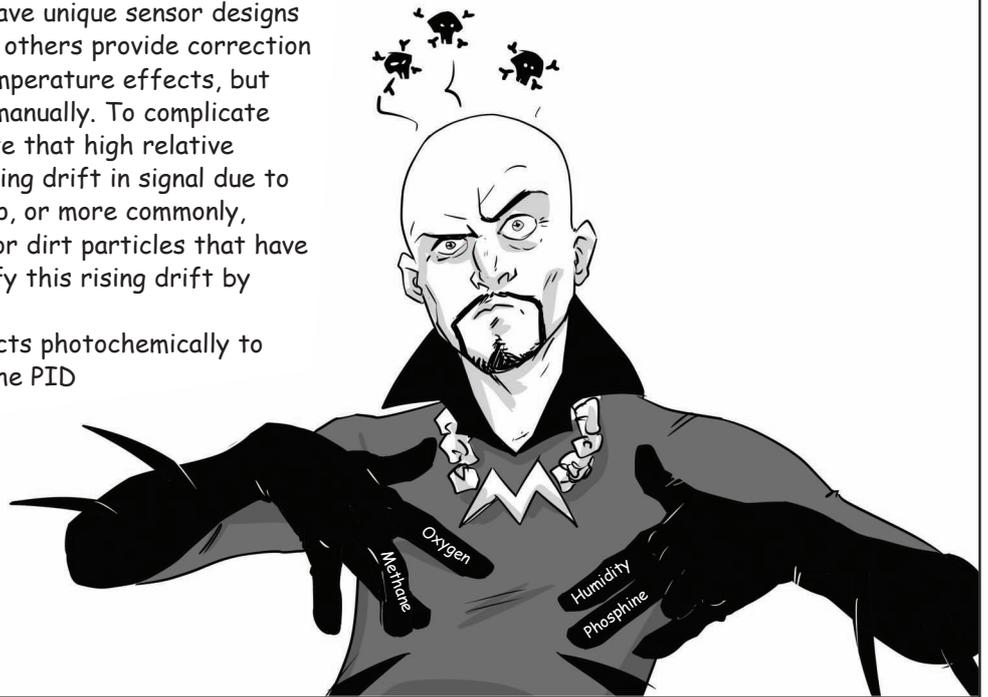
The 11.7/11.8eV lamps detect the broadest range of chemicals of interest but suffer from weak outputs and short working lives due to issues with the lamps' lithium fluoride windows (thermal expansion, water etching, etc). Lamps operating at different energies use other, more robust materials, therefore most hazmat/ CBRNE response elements utilise a 10.6eV lamp in PIDs as it lasts longest (years) and can measure a broad selection of chemicals of interest. Low energy lamps, such as the 9.8eV, are also available and provide the best selectivity as they detect the least number of chemicals, however they are generally relegated to industrial applications with known materials of interest.



Interferences

Users are encouraged to consult their instrument technical information to understand the impact of interferences on instrument performance in their own operational settings. A few of the more common interferences are listed below:

- **Oxygen:** Oxygen enriched environments can quench PID signals (60-80% of true signal in pure oxygen).
- **Methane/hydrocarbons:** As methane concentration increases to exceed 1% (10,000ppm methane), the PID signal is quenched. Other hydrocarbons at high concentration may also depress readings.
- **Humidity:** High relative humidity can quench the PID signal, especially at high temperatures. Some instrument manufacturers have unique sensor designs to improve performance and others provide correction factors for humidity and temperature effects, but these are generally applied manually. To complicate things, it is important to note that high relative humidity can also cause a rising drift in signal due to water absorption on the lamp, or more commonly, water absorption onto dust or dirt particles that have collected on the lamp. Rectify this rising drift by cleaning the lamp.
- **Phosphine:** Phosphine reacts photochemically to deposit a thin film coating the PID lamp, resulting in a loss of signal. This becomes more severe as concentrations and exposure time increase. Cleaning the lamp with anhydrous methanol resolves the issue.



Operational applications

Most PIDs have an instrument response time of under three seconds. This is determined by the instrument sample collection pathway and pump capacity as the process being measured is in the order of milliseconds. The fast response time and broad detection capability make PIDs critical tools in the emergency response toolbox.

While PIDs cannot identify a specific material, they can detect that something is there and have an additive response for mixtures when the components have ionisation potentials less than those of the instrument lamp. If the identity of the material is then determined, it can be used quantitatively. It is focused on the concentration range that spans odour thresholds, occupational exposure limits (OELs), acute emergency guideline levels (AEGLs) and immediately dangerous to life or health (IDLH) levels. These values can be also considered action levels for operators.



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This enables the operator to apply the instrument for:

- Problem identification: Characterise the extent of leaks and their direction and origins, or other issues like sick building syndrome.
- Identification of control zones: Hot zone identification often uses the IDLH as a threshold guide while warm zone uses the OEL as a threshold guide.
- PPE selection: The selection of respiratory protection uses the odour threshold, OEL and IDLH as key action levels while chemical protective clothing focuses on dermal notations.
- Decontamination efficacy: PIDs are used to demonstrate whether people or materials need decontamination. Next, they are used to evaluate whether decontamination has succeeded. Measure immediately downwind from the object of interest and compare the results against action levels.
- Reoccupancy: For evacuated buildings or those used for sheltering in place, community protective action levels (eg protective action criteria, AEGLs, etc) can be applied to provide the affected community with reassurance that the building or their local environment is safe to reoccupy.

The Emergency Response Decision Support System (ERDSS, aka Chemical Companion) includes PID correction factors for most common instruments within its detector tool and includes worker and civilian protective action levels for ease of implementation.

Stay safe out there!



CBax away!

*Images are courtesy of Phil Buckenham
<https://philbuckenhamart.wixsite.com/philbuckenham>*