

Advance in PID Technology Give Resistance to Humidity Effects and Allow Continuous, Benzene-Specific Monitoring

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Dr. Werner Haag, Senior Applications Chemist at Ion Science, discusses recent advances in Photo-Ionisation Detector (PID) technology, with the focus on the petrochemical industry in particular.

Whilst oil refineries produce gasoline, diesel and jet fuels, petrochemical plants manufacture a wide range of industrial chemicals, including solvents, dyes, lubricants, detergents, plastics, synthetic rubbers, pharmaceuticals, process oils and resins, as well as asphalt, wax and coke.

Employees who work in these hazardous environments are at risk from exposure to toxic compounds such as benzene, toluene, ethylbenzene, & xylenes (BTEX), butadiene and other volatile organic compounds (VOCs), from routine sampling and maintenance operations, releases from large bulk facilities, surface spills and pipeline leaks. VOCs are released into the environment most often by volatilisation (evaporation) where they move freely in the air, and sometimes through spills, resulting in contamination not only of air, but also soil and water.

Workforce exposure can occur through inhalation or absorption through the skin. Common exposure symptoms include skin and sensory irritation, central nervous system depression, and respiratory problems. Severe or prolonged exposure may result in kidney, liver and blood system failures. Benzene is identified as a human carcinogen that can cause myeloid leukemia, and butadiene is listed as a probable human carcinogen. For these reasons, it is vital to monitor employees' exposure to VOCs and other gases in hazardous industrial environments – especially those working in confined spaces.

Photo-Ionisation Detectors (PIDs)

Handheld Photo-Ionisation Detectors or PIDs are the most efficient and inexpensive way to continuously detect and measure VOCs and will give instantaneous readings. PIDs normally measure in concentrations from low parts per billion (ppb) to >5000 parts per million (ppm), can data-log results, and give visual and audio alarms when concentrations exceed predefined set-points including time-weighted average (TWA) and short-term exposure limit (STEL).

PIDs use high-energy photons in the ultraviolet (UV) range to break VOC molecules (A) into positively charged ions (A+) and negatively charged electrons (e-), as shown in the inset in Figure 1. The A+ ions travel to the cathode and the electrons are collected at the anode, resulting in a current proportional to the concentration of VOC. This is amplified and output as a ppb or ppm concentration on the instrument display.

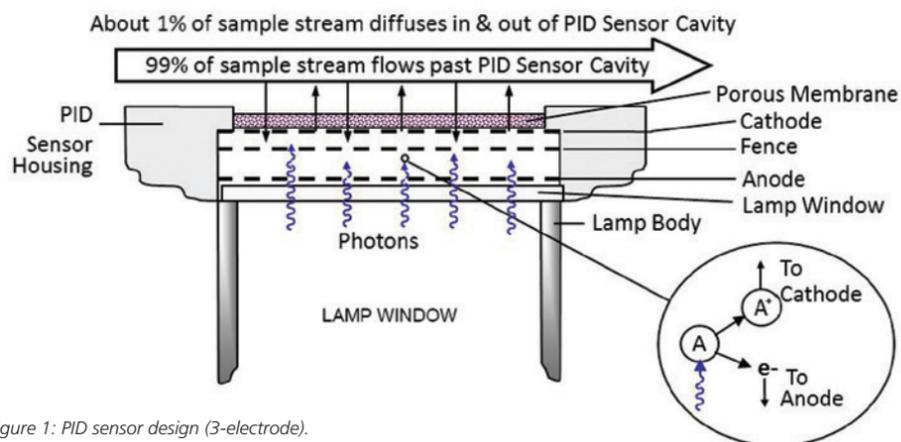


Figure 1: PID sensor design (3-electrode).

Most of the VOCs pass through the instrument without being ionised, and therefore PIDs are considered non-destructive detectors.

By their nature, PIDs are a non-specific, broad band technology and give a total VOC reading for the atmosphere examined. As a result, PIDs do not provide specific readings nor differentiate between each VOC present. However, PIDs can be made to read compound-specific concentrations if 1) there is only one major component present, as in the case of many solvent operations, 2) pre-treatment tubes are used to filter out interfering components, such as benzene tubes in refinery applications and butadiene tubes in polymer manufacturing, or 3) a chromatographic technique is used to measure individual components separately. In addition, some selectivity is afforded by use of lower-energy lamps. Handheld PIDs are commonly available with 11.7 eV, 10.6 eV, and 10.0 eV lamps. The 11.7 eV lamp detects the broadest range of compounds while the 10.0 eV lamp responds to the

fewest and thus is the most selective. This can be of interest when analysing combinations in which only some of the components are of interest.

Humidity Effects

A major limitation to the use of PIDs in the past was their susceptibility to ambient humidity, which is often found in hazardous environments. This is a particular issue in refineries which are typically located near water, or when measuring VOCs in steam, wastewater, or contaminated soil (which is usually moist).

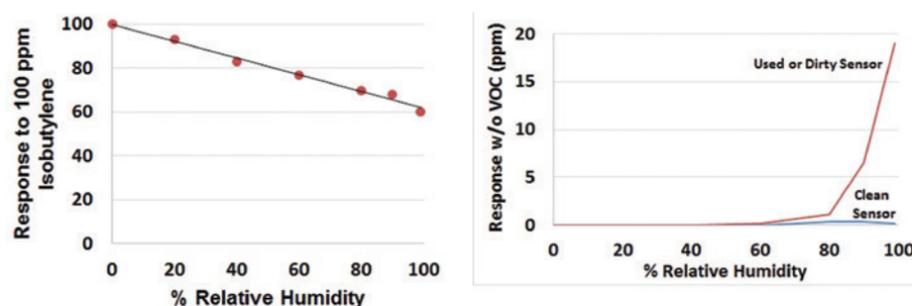


Figure 2: Left: Quenching of VOC response at high RH. Right: Drifting reading in clean air at high RH.

Humidity has two effects:

1. a decrease in response to VOCs due to a quenching effect as humidity increased (false negative);
2. an increased and drifting signal when subjected to high humidity (false positive).

The latter response is avoided when the sensor is new or recently cleaned but can become a problem within a few days' use as microscopic dust accumulated on the sensor, causing a current leakage along the sensor walls in humid environments. This drifting rise in readings is particularly prominent when doing soil headspace measurements, or in such areas as the U.S. Gulf Coast, where instruments calibrated in an air conditioned building are brought outside into humid air often approaching 100% RH.

Various solutions have been proposed to minimise these humidity effects:

1. desiccant tubes are placed in the inlet to dry the gas stream.
2. the calibration gas is humidified by running it through a Nafion tube to equilibrate it with the ambient air humidity.
3. the instrument is fitted with a humidity sensor and the PID reading corrected using a compensating algorithm.

These approaches have various limitations. Desiccant tubes are an added cost, slow the PID response, and can reduce the response by adsorption, especially of heavier compounds. Humidifying the calibration gas works only for the particular humidity used and is no longer accurate when the humidity changes. Humidity sensors generally have slower response than the PID sensor, causing a drifting compensation. Although newer RH sensors are faster, the humidity effect varies from sensor to sensor making compensation difficult.

Compensation algorithms and calibration gas humidification do nothing to solve the drifting high readings at very high humidity.

New Design PIDs are Not Affected by Humidity

Ion Science has developed a new generation of PIDs with almost no humidity effects, without the need for RH sensor compensation, desiccant tubes, or calibration gas humidification. This is accomplished by a combination of:

1. an improved sample inlet system to reduce

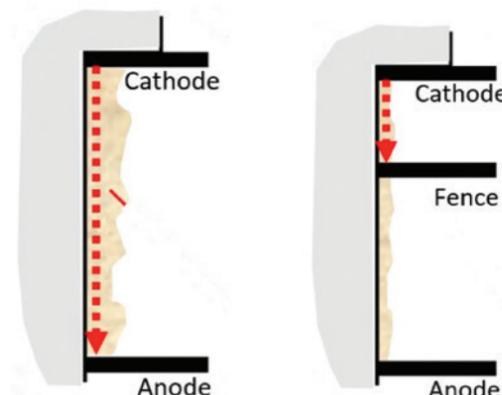


Figure 3: Leakage current at high humidity is trapped in the fence-electrode system.

dust and moisture entering the sensor;

2. thinner sensor cell to suppress the loss of photons by water adsorption;
3. the patented "Fence-Electrode" design that grounds any spurious current and thus eliminates humidity-induced drift

As shown in Figure 1, this inlet system allows only about 1% of the sampled gas to actually enter the ionisation chamber, resulting in far less contamination issues than conventional PIDs where 100% of the sample gas passes through the sensor. Figure 3, is an exaggerated depiction of the microscopic dust build-up on the sensor walls, resulting in leak current at high humidity. The combination of anti-contamination design and fence electrode results in eliminating this humidity problem.

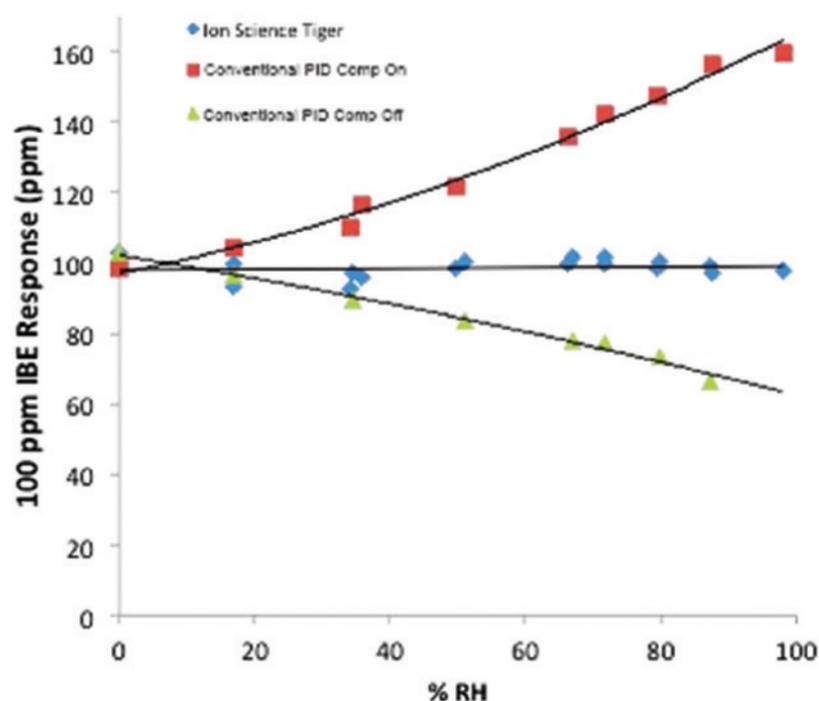


Figure 4: Effect of humidity on the response of a conventional 2-electrode PID and a humidity resistant PID.

Figure 4 compares the humidity effect on a modern fence-electrode type PID with that of a conventional PID using a rapid RH sensor and microprocessor compensation. The thinner fence-electrode type PID is unaffected by humidity, while in these tests the conventional 2-electrode PID gave high readings when the compensation algorithm was turned on, and the expected low readings when the compensation was turned off. The state-of-the-art 3-electrode PIDs with anti-contamination inlet and thinner gas path thus solve both the quenching effects and leak current problems, and therefore are much simpler and more accurate to use than 2-electrode PIDs, without the need for filter tubes and software corrections, etc.

Fixed PID Systems

The humidity-resistance has been extended to fixed PIDs as well. Fixed systems are useful for applications where VOCs are expected on a routine basis, such as in chemical process control, fence line monitoring, wastewater monitoring, chemical storage areas, or locations of frequent chemical use.



Figure 5: Fixed PIDs a) with (left) and b) without (right) condensation control

In some of these instances monitoring is done outdoors, where rain or night-time condensation can result in liquid water being drawn into the PID. Traditional fixed PIDs suffered from the same humidity problems described for portable instruments, as described above, and are even further complicated when inlet condensation occurs. Ion Science has implemented a heated inlet system for condensation control to complement the 3-electrode type, humidity-resistant sensor design. Figure 5 compares two fixed PIDs challenged with condensing humidity levels, and shows that the unit with condensation control reads normally, whereas the unit without goes into error mode.

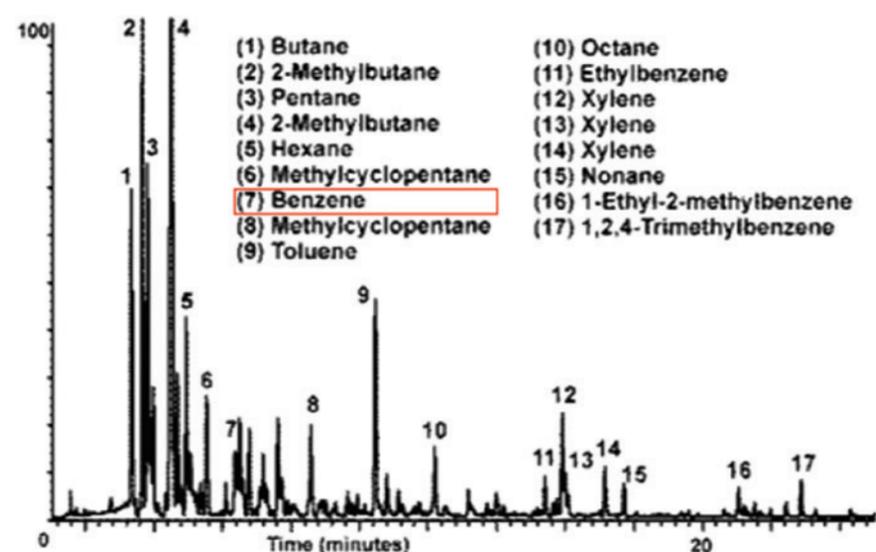


Figure 6: Gas chromatogram of a gasoline mixture indicating the small fraction of benzene.

Benzene-Specific Measurements

Benzene is one of the most toxic VOCs encountered at refineries and petrochemical plants. Typical 8-hour exposure limits in various countries are on the order of 1 ppm or less, and these low levels must often be measured in the presence of hundreds of other fuel components at much higher concentrations.

For hand-held, portable operations, this difficulty has been solved by using a combination of 10.0 eV lamp and a consumable pre-filter tube. The lower-energy UV lamp eliminates response from smaller hydrocarbons, and the filter absorbs heavy compounds and oxidizes all other aromatics, allowing only the benzene to pass through to the PID. A single reading is obtained in 1-2 minutes, and therefore response is not continuous. Nevertheless results are obtained much faster than an on-line GC or sending a sample back to a laboratory, and work can continue in close to real time if benzene is shown to be below the required limit (or appropriate protective equipment donned). After the instantaneous reading, the tube can be left in place to continue for a 15-minute STEL measurement. Detection limits are about 0.1 ppm, adequate for assessment of TWA limits near 1 ppm with a low-cost instrument. The tube also removes moisture from the air, thus eliminating all possible humidity effects.



Figure 7: Pre-filter tube attached to PID for specific benzene measurements in a portable instrument.

To save costs, the hand-held operation can be used in continuous screening mode before a tube is inserted to measure benzene. The 10.0 eV lamp is selective enough that it gives a rough measurement of total aromatic hydrocarbons (TAC) without a tube. Several low-cost, smaller, pocket-sized PIDs with 10.0 eV lamps (called CUBs) can be distributed to a working group to screen for TAC, and the larger PID with pre-tube only used when a reading above the TWA is detected.

For fixed-point measurements, the first semi-continuous and benzene-specific monitor suitable for hazardous environments is now available (Figure 8). This product is based on the same PID technology discussed above, but uses separating technology to rapidly isolate benzene. Samples are taken every minute, giving virtually continuous readings without the need for any carrier gas or detector make-up reagents, as are required for most gas chromatographs (GCs). The system is intermediate between an on-line GC and a portable benzene monitor in cost and performance. The value of continuous and specific benzene detection is demonstrated in Figure 9, where the much longer sampling interval of the on-line GC caused it to miss several benzene exposure events that were detected by the PID system. As with the portable PID, the separation system removes any potential interference by water vapour.



Figure 8: Fixed, semi-continuous benzene-specific sensor for use in hazardous environments.

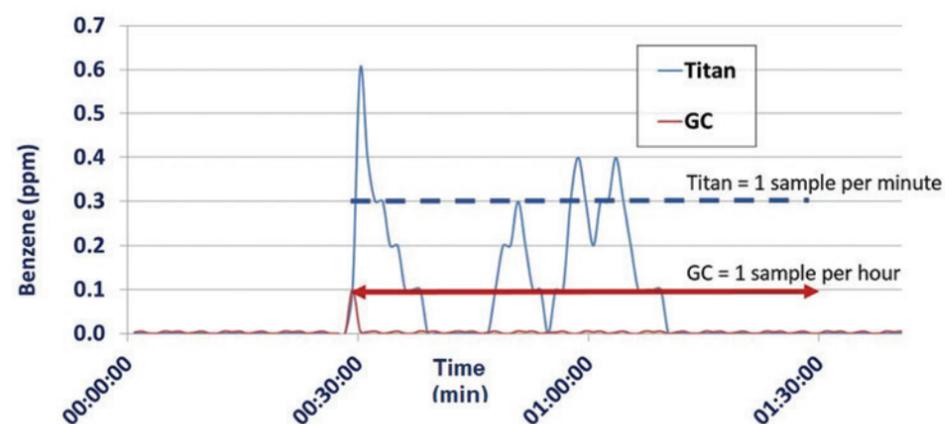


Figure 9: Comparison of on-line GC to a fixed, semi-continuous, benzene-specific PID sensor.

Conclusion

In conclusion, recent advances in PID technology have largely resolved previous issues of humidity effects and condensation problems, and have allowed virtually-continuous benzene-specific measurements in both portable and fixed instrumentation.