

A Guide to Monitoring Aromatic Gases

Aromatic chemical compounds produced by oil refineries and petrochemical plants form the building blocks for numerous important materials including dyes, detergents, solvents, adhesives, plastics, synthetic rubbers and pharmaceuticals. But the aromatic compounds produced in these process environments such as benzene, toluene and xylene isomers are also highly toxic capable of both short term acute safety issues (headaches, dizziness, and potentially unconsciousness) and longer term chronic illnesses including cancers¹.

The logo for BTEX is rendered in a bold, three-dimensional red font. The letters are thick and have a slight shadow, giving them a 3D appearance. The letters are arranged in a slightly staggered, perspective view.

Aromatic gases

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Fugitive emissions

During normal operations, leaks can occur from pumps, valves, flanges, storage tanks or during loading and unloading. According to the US EPA¹, valves and connectors account for more than 90% of emissions from leaking equipment and there are hundreds of pieces of equipment as shown in Figure 1.

Table 3.2 – Equipment component counts at a typical refinery or chemical plant.

| Component | Range | Average |
|------------------------|------------|---------|
| Pumps | 10-360 | 100 |
| Valves | 150-46,000 | 7,400 |
| Connectors | 600-60,000 | 12,000 |
| Open-ended lines | 1-1,600 | 560 |
| Sampling connections | 20-200 | 80 |
| Pressure relief valves | 5-360 | 90 |

Source: "Cost and Emission Reductions for Meeting Percent Leaker Requirements for HON Sources." Memorandum to Hazardous Organic NESHAP Residual Risk and Review of Technology Standard Rulemaker docket. Docket ID EPS-HQ-OAR-2005-0475-0105

Figure 1: Typical equipment counts (EPA)

This can mean hundreds of tons of VOCs released to atmosphere which can present health risks for workers and operators and pollution of the wider environment. And while a leak detection and repair (LDAR) program using a portable photoionisation detector (PID) is an ideal tool for this application, fixed systems can be sited on the fence line or areas prone to leaks.

Considerations for fixed systems

The choice of UV lamp, central to the PID's measurement depends on the application. Figure 2 illustrates that a lamp can only detect those compounds with ionization energies (IE) equal to or below that of the lamp. Thus, a 10.6 eV lamp can measure Methyl Bromide with an IE of 10.5 eV and all compounds with a lower IE, but cannot detect methanol or compounds with higher IE. When only one compound is present, one can use any lamp with enough energy, often the standard 10.6 eV lamp which has a lower cost point and has a long working life of up to a few years. Conversely the 11.7 eV lamp has a short life of only a few months.

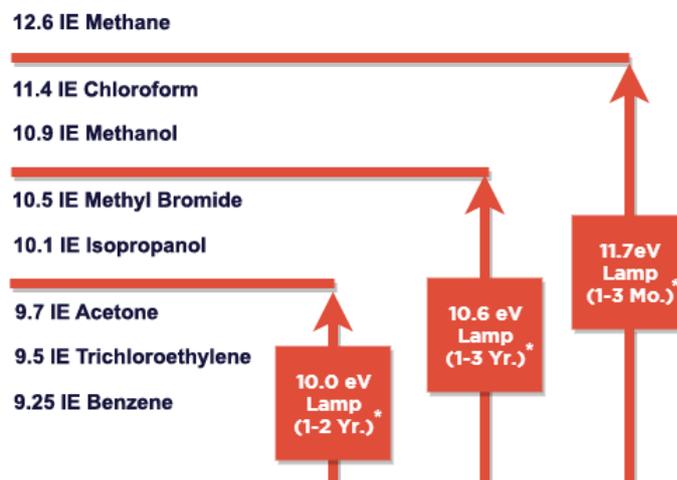


Figure 2: PID lamp energy thresholds

However, it can be seen that benzene has a low IE value as shown in Figure 2 and it is often present in a 'cocktail' of other aromatics and hydrocarbons. In this case using a proprietary 10.0eV lamp means that only the aromatics are detected (amongst other gasses that may be present). Should the total aromatic compounds (TAC) be above the regulatory limit further investigations can be undertaken with a portable device such as an Ion Science Tiger Select.

'Must have' features

- have a high ingress protection (IP) rating against dust and water
- have a high level of intrinsic safety approval
- require no operator intervention during normal use
- have real or near-real time continuous monitoring with industry standard 4-20mA and/or MODBUS outputs
- have hi visibility colour coded visual alerts to warn people entering the area
- be maintainable in situ, without the need for a hot work permit or having to remove power
- be immune to condensing and non-condensing high humidity

Effective of high humidity

Like many sensors and measurement instrumentation, traditional PIDs can be affected by adverse environmental conditions i.e. dirt, water and humidity. Process environments are therefore not ideal and in particular the presence of high humidity can disrupt PID measurements leading to false low or conversely high readings. A heated inlet should suffice in condensing environments but additional safeguards are required for high, non-condensing humidity.



The potential for low readings is because water vapour absorbs the photons normally released by photoionisation as can be seen in the simplified cross section of a PID sensor (figure 3). The effect worsens with increasing humidity as shown by figure 4.

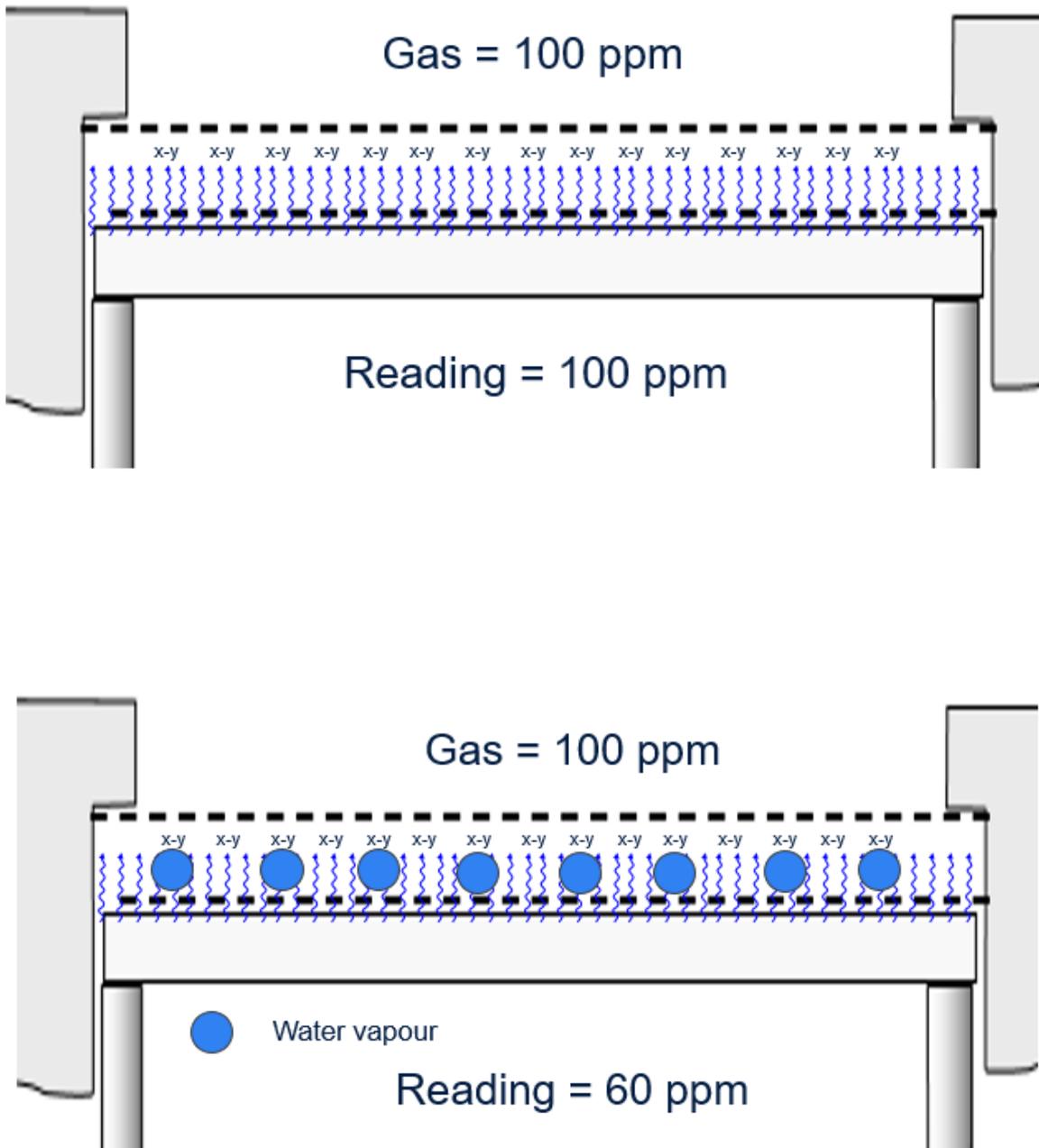


Figure 3: Cross section of a PID sensor with and without water vapour present

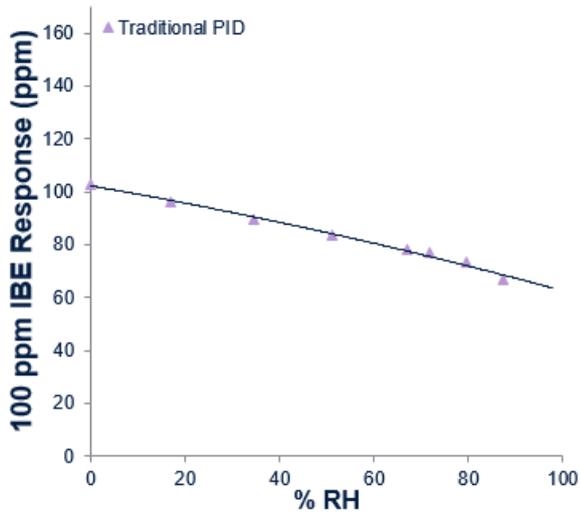


Figure 4: Effect of water vapour absorption

Contamination can also build up between the electrodes effectively short circuiting them, leading to a high, 'false positive' reading at high humidity with no VOC present i.e. > 90% RH (see figure 5).

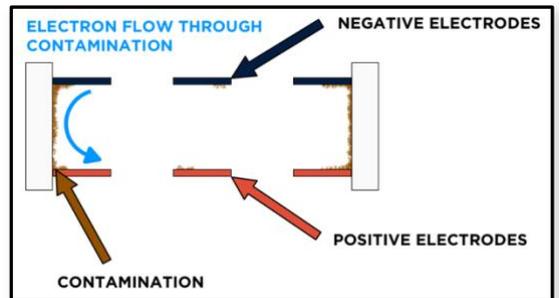
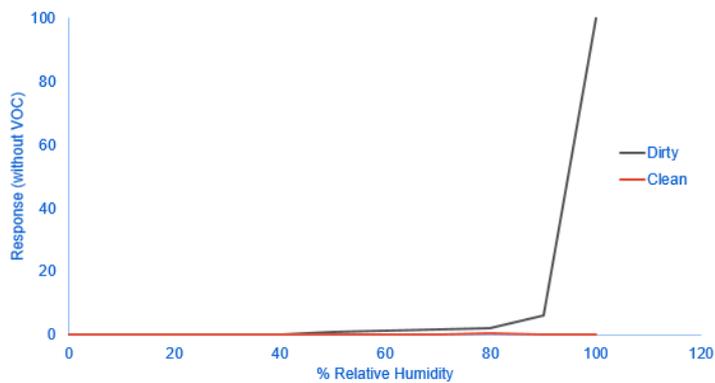


Figure 5: Effect of contamination

Solving the problem of humidity

Conventional PIDs may use humidity suppression/compensation techniques but each of them has disadvantages:

- Humidity sensor – these typically have a slower response than the PID sensor itself which causes a drifting compensation
- Desiccant tube – these both slow the PID response and also reduce it by adsorption plus they need replacing from time to time which adds cost
- Humidify the calibration gas – this only works at one level of humidity and is no longer accurate when the humidity changes

Importantly none of these solutions solves a false positive at high humidity

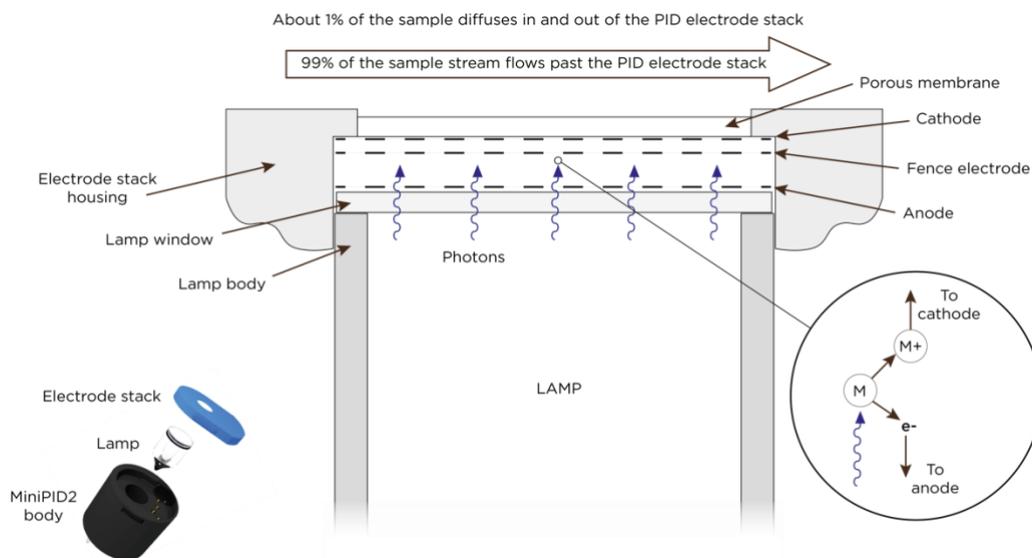


Figure 6: Ion Science Ltd PID sensor design

Looking at figure 6, the presence of the porous membrane should be noted. It is made from a hydrophobic material which means that it rejects the ingress of water and mitigates the chance of low readings. To further deal with high humidity, the addition of a third, fence electrode (also shown in figure 6) overcomes the possibility of high readings since it behaves as a conductive break and stops the excess current flow caused by the presence of high humidity which would otherwise lead to a false positive.

The health effects, limit values and legislation will be covered in more detail in a subsequent guide.

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Reference:

1. <https://www.epa.gov/sites/production/files/2014-02/documents/ldarguide.pdf>



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