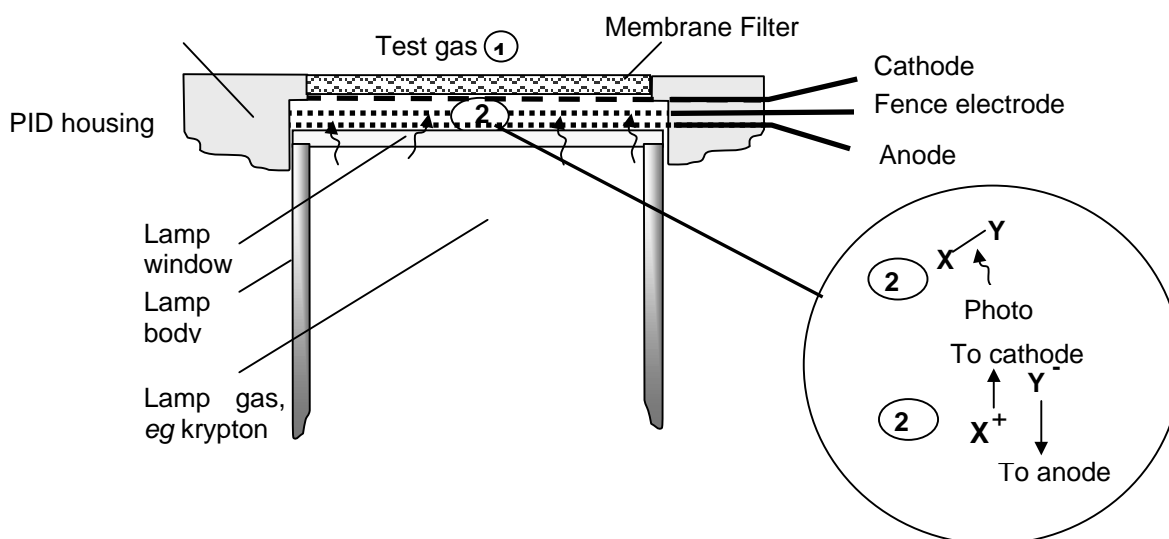


AAN 301-04 Introduction to Photoionisation Detection (PID)

This Application Note gives an introduction to photoionisation detection (PID) and answers some frequently asked questions.

How does a PID work?

The PID-A1 and PID-AH measure volatile organic compounds (VOCs) in air by photoionisation detection (PID), which is shown schematically below. Test gas (1) is presented to the membrane filter at the top of the photoionisation cell and freely diffuses into and out of the underlying chamber formed by the filter, housing walls, and a UV lamp window. The lamp emits photons (shown by arrows) of high energy UV light, transmitted through the window. Photoionisation occurs in the chamber when a photon is adsorbed by the molecule, generating two electrically charged ions, one positively charged, X^+ , and one negatively charged, Y^- (2a). An electric field, generated between the cathode and anode electrodes, attracts ions (2b). The resulting current, which is proportional to the concentration of the VOC, is measured and used to determine the gas concentration. The PID-A includes a third fence electrode (patented) to ensure that the amplified current does not include significant contributions due to other current sources such as water condensation on the chamber walls.



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What is a volatile organic compound (VOC)?

A volatile organic compound, or VOC, is a carbon-containing chemical, which is significantly or completely vaporised at ambient temperatures.

What volatile organic compounds (VOCs) are sensed by PID?

Most VOCs can be detected by PID. Notable exceptions are low molecular weight hydrocarbons. Each VOC has a characteristic threshold energy of light (photon energy) which, when directed at the VOC, causes it to fragment into ions. This is called the *Ionisation Potential*, or IP. VOCs are ionised (and hence detected) if light of *photon energy* greater than the IP interacts with the gas sample. The peak photon energy generated in a detector depends on the PID lamp used: Xenon = 9.6 eV, Deuterium = 10.2 eV, Krypton = 10.6 eV and Argon = 11.7 eV. Hence, the use of an argon lamp leads to detection of the largest range of volatile compounds, while using a Xenon lamp can increase selectivity. The instability of the window means that Alphasense does not recommend nor provide the 11.7eV lamp. Lamps of a particular type do not typically vary in spectral fingerprint, so relative responses to a particular gas, e.g. benzene, to a particular lamp, e.g. krypton, does not vary from lamp to lamp. However, the intensity of lamps does vary to some extent, leading to a difference in absolute response to the calibration gas.

Sufficient volatility of a compound is also essential for measurement by PID as with any other detector. A fairly large molecule such as alpha pinene, (a constituent of turpentine), saturates in air at about 5000ppm at 20°C; this is the maximum concentration at which the compound will usually be detected. Some compounds, for example, machine oils and agrochemicals generate only a few ppm of vapour at ambient temperatures; it is more difficult to detect these compounds in air. Application Note AAN 305 lists VOCs by their common name and their sensitivity to a Krypton lamp, the most common lamp and the lamp supplied as standard with the PID-A1 and PID-AH.

Which lamp is best?

The choice of lamp depends on target gases, selectivity requirements and lamp lifetime considerations. Usually, the krypton lamp is used because of its high sensitivity.

Xenon lamp (9.6 eV)

Many aromatics and unsaturated VOCs compounds containing at least 6 carbon atoms ('C6') or more are detected. Sometimes it is an advantage to use the xenon lamp to ensure more selective detection of compounds such as BTEX. Order the 9.6eV lamp if required.

Krypton lamp (10.6 eV)

Some C2, and most C3, C4+ VOCs are detected. Exceptions usually contain chlorine, fluorine or bromine. For guidance, you can expect the following to be detected with Krypton-PID:

- All hydrocarbons, whose chemical names end in the letters **-ane**, **-ene** or **-yne**, *except* methane, ethane, propane, and acetylene, and also *except* if the name includes '**chloro**', '**fluoro**' or '**bromo**':
- All alcohols, whose chemical names end in **-ol**, *except* methanol, or frequently if the name includes '**chloro**', '**fluoro**' or '**bromo**'
- All aldehydes, whose names end in **aldehyde**, *except* formaldehyde, or sometimes if the name includes '**chloro**', '**fluoro**' or '**bromo**'
- All ketones, whose chemical names end in **-one**, *except* rarely if the name includes '**chloro**', '**fluoro**' or '**bromo**'
- All esters, whose names end in **-ate**, *except* rarely if the name includes '**chloro**', '**fluoro**' or '**bromo**'
- All amines, sulfides

Argon lamp (11.7 eV)

All VOCs detectable with the krypton lamp, *plus* acetylene, methanol, formaldehyde and about 80% of VOCs whose chemical names include '**fluoro**', '**chloro**' and '**bromo**'. However, this lamp has a very short lifetime because the UV window is made from Lithium Fluoride, which is prone to degradation, so is not available from Alphasense.

What is a response factor?

The sensitivity of PID varies according to the type of lamp used (krypton or xenon) and the VOC detected. A response factor is a number, which relates the PID response to a particular VOC, to the PID response to the calibration gas, usually isobutylene. If the response of a PID to a particular VOC is eight times *smaller* than it is for the same concentration of isobutylene, then the *response factor* would be 8. Similarly, if the *response factor* for a particular VOC is 0.5, the PID response is *twice* that for isobutylene at the same concentration.

Example:

- A sensor is calibrated using isobutylene and found to have a sensitivity of 2 mVppm⁻¹.
- If the sensor is exposed to 100ppm isobutylene the output will be 200 mV.
- Toluene is known to generate **twice** the response of isobutylene.
- If the sensor is exposed to 100ppm toluene the output will be 400 mV.
- In order to correct the response it is multiplied by the **response factor for toluene** of 0.5.

If response factors are programmed into an instrument, you are able to specify a volatile compound, and the instrument will internally compensate for the response factor corresponding to that volatile, and display and record the corrected volatile concentration. See '*MiniPID response factors*' and the inverse, *% sensitivity*.

Are there other ways to measure VOCs?

PIDs show excellent sensitivity, a large dynamic range and allow ppb-low ppm measurement of VOCs in a background of higher inorganic gas concentrations. But there are other technologies to measure VOCs:

Flame Ionisation Detectors (FID)

Very similar to PIDs, FIDs are frequently used in laboratories for detecting VOCs eluted from a gas chromatograph. FIDs, like PIDs, are not selective, indeed all organic compounds including methane are measured, and FIDs can be very sensitive and linear. But FIDs require a hydrogen source, are bulky and more expensive. FIDs are good in the lab or for fixed sites, but are not currently a viable alternative in portable VOC monitoring.

Portable GC/MS

This traditional laboratory analytical instrument is seeing its way into the field with mixed results. With micromachined silicon (MEMS), portable MS and portable GC may still become a real alternative, but the cost is prohibitive. It does have the advantage of being selective - it is not a broad band analyser. Size, cost, need for a vacuum pump (MS) and maintenance requirements make this an alternative only when all else fails.

Thermal Desorption or Tedlar sampling bags

For retrospective analysis of all VOCs adsorbed in soil samples, other solids, liquids and gases, ASTM recommends using sorbent tubes or Tedlar sampling bags. Samples are then sent to the lab for thermal desorption of the sorbent tubes and then analysis using GC/MS, traditionally. This is the best technique when surveying a specific problem, but clearly does not provide protection in real time. Also, these are averaged measurements and not point/time-specific.

Electrochemical sensors

You can measure many VOCs with electrochemical cells, with resolution from 10 to 200 ppb. These are low cost, low power, compact sensors. Alphasense offers the ETO-A1 sensor for VOC applications. Both PIDs and electrochemical cells are broad band sensors, but with a different profile - PIDs will measure more VOCs than the ETO-A1, and with much greater sensitivity. If you wish to measure a VOC with electrochemical cells, then you should optimise the electrochemical sensor for the target VOC: each VOC will require a different ideal bias voltage for best sensitivity. Not an easy task. Electrochemical cells respond in about 25 seconds, vs. 1-2 seconds for PIDs.

Metal Oxide Semiconductor sensors (MOS)

Metal oxide sensors will also measure VOCs; they are compact, low cost and higher power than PIDs. MOS sensors suffer from humidity sensitivity, non-linear response and long term drift. They also respond to inorganic gases, so you should not use them if you are trying to measure low concentrations of VOCs where gases such as NO, NO₂ or CO are present in higher concentrations. Unfortunately, it is all too easy to get false positive and false negatives when using MOS technology. If you want to use MOS, then request confirmation of long term stability and humidity sensitivity. If you want high sensitivity, particularly to VOCs that are not measured by PID (*ie* many CFCs), but don't care about accuracy and cross sensitivity, MOS sensors may provide a possible solution.

Colorimetric ("stain") tubes

Well established technology for sampling for specific VOCs, colorimetric tubes have been around for decades, supplied chiefly by Draeger or Kittegawa. They have the advantage of low one-off cost and some specificity, but the disadvantages include disposal of chemical waste (the disposable tubes often contain toxic chemicals), poor accuracy, human interpretation of the colour change, sampling problems and non-continuous measurements: they should not be used to protect, only to qualitatively sample.