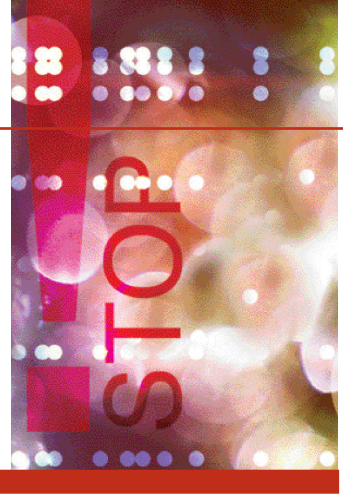
Questions, Myths and Misconceptions

ABOUT USING PHOTOIONIZATION DETECTORS



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Solvent, fuel and other VOC vapours are pervasively common in many workplace environments. Increased awareness of the toxicity of these common contaminants has led to lowered exposure limits, and increased requirements for direct measurement of these substances at their Occupational Exposure Limit concentrations. Photoionization detector (PID) equipped instruments are increasingly viewed as the best choice for measurement of VOCs at exposure limit concentrations.

Understanding the capabilities as well as the limitations of photoionization detectors is critical to interpreting test results and making decisions based on the use of this important atmospheric monitoring technology.

What are VOCs?

Volatile organic compounds (VOCs) are organic compounds characterised by their tendency to evaporate easily at room temperature. Familiar substances containing VOCs include solvents, paint thinner and nail polish remover, as well as the vapours associated with fuels such as gasoline, diesel, heating oil, kerosene and jet fuel. The category also includes many specific toxic substances such as benzene, butadiene, hexane, toluene, xylene, and many others. Most VOC vapours are flammable at surprisingly low concentrations. For most VOCs however, the toxic exposure limit is exceeded long before readings reach a concentration high enough to trigger a combustible range alarm.

How do PIDs detect VOCs?

Photoionization detectors use high-energy ultraviolet light from a lamp housed within the detector as a source of energy used to remove an electron from neutrally charged VOC molecules, producing a flow of electrical current proportional to the concentration of contaminant. The amount of energy needed to remove an electron from the target molecule is called the ionisation energy (IE) for that substance. The larger the molecule, or the more double or triple bonds the molecule contains, the lower the IE. Thus, in general, the larger the molecule, the easier it is to detect. On the other hand, small hydrocarbon molecules such as methane are not detectable by means of PID. A PID is only able to detect substances with ionisation energies lower than the energy of the ultraviolet photons produced by the PID lamp. The energy required to detect methane exceeds the energy of the ultraviolet light produced by the PID lamp.

What are the differences between PID and LEL sensors?

PID and lower explosive limit (LEL) sensors are based on entirely different detection techniques. Most LEL range sensors detect gas by catalytically oxidising the gas on a pellistor-bead located within the sensor. Oxidisation of the gas causes heating of the active pellistor-bead. The heating is proportional to the amount of gas present in the atmosphere being monitored, and is used as the basis for the instrument reading. Pellistor sensors are excellent for the detection of methane, propane, pentane and other small hydrocarbon molecules. However, catalytic-bead sensors, at least when operated in the percent LEL range, are not readily able to detect "heavy" or long-chain hydrocarbons or the vapours from high flashpoint temperature liquids such as turpentine, diesel fuel or jet fuel. Consult the Operator's Manual, or contact the manufacturer directly to verify the capabilities of the instrument design when using a catalytic-bead LEL sensor to monitor for the presence of these types of contaminants.

What are broad-range sensors?

Broad-range sensors provide an overall reading for a general class or group of chemically related contaminants. Both pellistor-bead LEL and PID are broad-range sensors. They cannot distinguish between the different contaminants they are able to detect. The reading provided represents the aggregate signal from all of the detectable molecules present in the monitored environment. Both PIDs and pellistor-bead sensors are broad-range sensors. Unless an additional separation technique is used (such as a filter tube or separation column) broad-range detectors are not able to provide substance-specific readings.

Many manufacturers include a user selectable library of correction factors (or "CFs") in the instrument design. In this case, the user simply selects "methane" or "propane" or any other correction factor in the library, and the instrument automatically recalculates readings according to the selected relative response. Changing the CF ONLY changes the scale used to calculate the displayed readings. Selecting the "propane" CF does not prevent the LEL sensor from responding to methane. It just reinterprets the readings as if they were entirely due to propane.

Misconception Number 1:

Changing the PID correction factor (CF) or choosing a chemical from the on-board library makes the instrument readings specific for that substance.

Most PID equipped instruments include a built-in library of correction factors. The same principles apply. Choosing the "hexane" correction factor does not make the PID a substance-specific detector for hexane. The PID will continue to respond to other detectable VOCs (such as benzene or toluene) which may be simultaneously present.

PIDs are usually calibrated using isobutylene. Thus, the most commonly used measurement scale for most PIDs is isobutylene. It is very important to understand that no matter how comprehensive the list of correction factors, choosing the CF for any particular chemical never makes the readings exclusive or substance-specific for that contaminant.

Also, if the specific nature of the VOC or mixture of VOCs is not known, PID readings are not truly quantified. Unless you are able to determine the precise nature of the VOCs being measured, readings should be thought of as "Isobutylene Units", or "PID Units", or units of whatever measurement scale has been selected from the instrument's library of correction factors.

Misconception Number 2:

I can't use a PID because I need substance-specific readings

PIDs provide a single reading for the total concentration of detectable volatile organic contaminants (TVOC) present. In point of fact, many of the most common VOCs do not consist of a single type of molecule. They are comprised of a mixture of, in some cases, a very large number of individual molecular species. For instance, the size distribution of molecules in diesel fuel ranges from molecules with nine carbons (or smaller), to molecules with twenty-three carbons (or larger). However, the ratios of the various molecules present are fairly similar from one batch of diesel to the next. That allows PID manufacturers to experimentally determine a CF for use with this fuel. You don't have to go after the individual molecular types that may be present as a minor fraction of the diesel (such as benzene, toluene, xylenes, etc.) to provide a quantified reading. If you have a CF for the mixture you can use this to quantify the readings for the entire range of molecules present.

Misconception Number 3:

I can't use PID because I never know which VOC is producing the reading

Dealing with single-component VOC contaminants or mixtures is easy. Once you know which contaminant you are dealing with, simply assign the correct CF, and set the alarms to the appropriate take action thresholds for that VOC. Dealing with varying mixtures can be a little more challenging. In this case the secret is to identify which chemical is the "controlling" compound.

Every mixture of VOCs has a compound that is the most toxic and / or hardest to detect, and thus "controls" the alarm setpoint that should be used for the entire mixture. Once the controlling compound has been identified, it is possible to determine a hazardous condition threshold alarm that will ensure that the Occupational Exposure Limit (OEL) for any contaminant potentially present is never exceeded.

The first step is to calculate (or look up) the exposure limits in isobutylene units for the VOCs of interest. Remember to leave the PID scale (correction factor) set to isobutylene units when using this measurement technique.

The exposure limit in isobutylene units (ELiso) is calculated by dividing the exposure limit (OEL) for the VOC by the correction factor (CFiso) for the substance. The UK OEL for turpentine is 100 ppm. Thus, if the CF for turpentine

Figure 1: Compact multi-sensor instruments that include O2, LEL electrochemical toxic and miniaturized PID sensors are available in diffusion as well as motorized pump-equipped versions

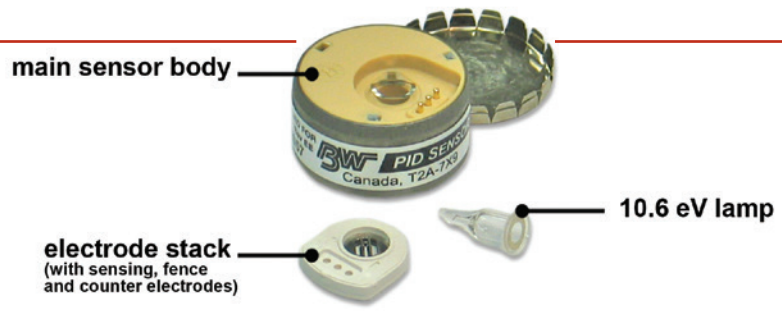

Figure 2: Some miniaturized PID designs include a fence electrode that provides a short circuit path that prevents surface currents from flowing directly between the sensing and counter electrodes

is 0.45, the ELiso = 100 ppm divided by 0.45 = 222 ppm. Many PID manufacturers include a table of ELiso values either in the owner's manual or in a separate applications note.

Consider a situation where you have three VOCs of interest: ethanol, turpentine and acetone. Let's say the owner's manual of the PID you intend to use includes a table with the following set of values:

Chemical Name	10.6eV CFiso	EL Chemical (UK OEL)	ELiso
Ethanol	13.3	1000	75.2
Turpentine	0.45	100	222
Acetone	1.2	500	416.7

Correction factors higher than 1.0 indicate that the PID is less sensitive to the substance than to the isobutylene used to calibrate the PID. Correction factors of less than 1.0 indicate that the PID is more sensitive to the chemical than to the isobutylene used to calibrate the detector.

Although turpentine has the lowest OEL, it is also the most easily detected substance of the three. Acetone is close to isobutylene in terms of detectability, with an OEL that is intermediate between those of the other two chemicals. Although ethanol has the highest exposure limit, it is also the least detectable of the three chemicals, thus, ethanol is the controlling compound when the Exposure Limits are expressed in equivalent "Isobutylene Units". Setting the PID to go into alarm at 75 ppm isobutylene units ensures that no matter which of the three chemicals, or combination of chemicals, is actually present, the OEL will never be exceeded.

Misconception Number 4:

You can use any manufacturer's correction factors for your PID instrument

Photoionization detectors may be equipped with a number of different types of lamps that produce photons of various energy ranges. The energy range of the photons produced by the lamp is expressed in "electron volts" or "eV" units of measurement. The most common types of PID lamps produce photons in the 9.8 eV, 10.6 eV or 11.7 eV energy range. By far, the most commonly used PID lamp is one that produces photons in the 10.6 eV energy range.

Generally speaking, if a VOC is detectable by one manufacturer's PID when equipped with a 10.6 eV lamp, the same substance will be detectable by any other manufacturer's PID when equipped with a similar lamp. The correction factors may be quite different, however between the two instrument designs. The reason is primarily due to the specific energy ranges of the photons produced by the lamp. Not all of the photons produced by a 10.6 eV lamp are actually 10.6 eV photons. The majority of the photons produced are actually in the 10.03 eV energy range. Only about 20 % to 25% of the photons produced (depending on the design of the lamp) are in the10.6 eV energy range. All of the photons produced by the lamp are capable of ionising and detecting VOCs with ionisation energies less than 10.0 eV. But only the higher energy photons are able to ionise and detect VOCs with ionisation energies between 10.1 and 10.6 eV. Thus, correction factors may differ widely between manufacturer designs. PID users should never use the correction factors from one instrument for another manufacturer's design.

Misconception Number 5:

If a 10.6 eV lamp is good, an 11.7 eV lamp must be better

The energy of the photons produced by the UV lamp determines whether a specific chemical is detectable. The energy must be higher than the ionisation potential of the contaminant in order for detection to occur. Lamps are available in a number of output energies including 9.5, 9.8, 10.0, 10.2, 10.6, 11.7 and 11.8 eV (depending on manufacturer). Many manufacturers allow for the use of several lamps in the same detector. The lower the energy of the UV light produced by the lamp, the lower the number of chemicals the PID will be able to detect. The higher the energy of the light produced by the lamp, the wider the range of detectable contaminants.

While it is true that an 11.7 eV lamp is capable of detecting more substances than a 10.6 eV lamp, the actual number of photons produced by the lamp, that is, the intensity of the lamp, is usually lower than that of the 10.6 eV lamp. So, generally speaking, an equivalent concentration of a substance that is detectable by either a 10.6 eV or an 11.7 eV lamp will produce a weaker raw electrical signal with the 11.7 eV lamp. Although the instrument electronics automatically takes this into account when an 11.7 eV lamp is installed, the fact remains that higher energy lamps tend to produce both a weaker ionisation current and have an increased tendency towards drift. Thus, the 10.6 eV lamp usually produces better resolution and accuracy for readings of substances that can be detected with the lower energy lamp.

Higher energy lamps are also subject to more physical limitations. In general, the higher the lamp energy, the shorter will be the service life. In some cases high energy 11.7 eV lamps may only last one or two months in normal operation.

10.6 eV lamps generally have much longer service lives, and frequently last one to two years, or even lomger, in normal operation. At the same time, 10.6eV lamps have an energy output sufficient to detect a wide range of VOCs. As a consequence, 10.6 eV lamps tend to be the most widely used.

Misconception Number 6:

PIDs can be used to replace traditional LEL sensors

Catalytic hot-bead combustible sensors and photoionization detectors represent complementary, not competing detection techniques. PIDs are not able to detect methane and hydrogen, two of the most common combustible gases encountered in industry. On the other hand, catalytic pellistor-bead sensors are excellent for the measurement of methane, propane, and other common combustible gases. And of course, PIDs can detect large VOC and hydrocarbon molecules that are effectively undetectable by hot-bead sensors, even when they are operable in PPM measurement ranges. The optimal strategy for measurement of combustible range concentrations of combustible gases and VOCs is to include both types of sensors in the same instrument.

Misconception Number 7:

PIDs can't be used in the presence of methane

Methane molecules are capable of absorbing UV light. Because the UV photons are absorbed without the methane being ionised, the presence of high concentrations of methane can "quench" or reduce the ability of the PID to detect other vapours that are present at the same time. The tendency of methane to reduce the PID signal is very design dependent. One of the most important determinants is the distance of the sensing electrode in the PID from the surface of the window of the PID lamp. The further that the photons have to travel before ionising the VOC target molecules, the greater effect that quenching gases such as methane will have on readings. The following table lists the effects of various concentrations of methane on the readings from a set of several BW Technologies GasAlertMicro 5 PIDs when the instruments were exposed to 100 ppm hexane.

% Volume Methane	% LEL Methane	Reading when exposed to 50 ppm hexane in the presence of methane
2.5%	50% LEL	26 ppm
1.0%	20% LEL	45 ppm
0.5%	10% LEL	48 ppm
0.25%	5% LEL	49 ppm

At 50% LEL (= 2.5% volume methane) readings were reduced by 50%. At 5% LEL (= 0.25% volume methane), readings were reduced by less than 2.0%. In this case a true concentration of 50 ppm hexane would be expected to show a reading of about 49 ppm.

As discussed above, instruments used for the detection of combustible gases such as methane should include an LEL sensor directly able to measure these gases. As long as the concentration of methane does not exceed 5% LEL (the combustible hazardous condition threshold alarm setpoint for many industrial applications) the effects of methane quenching on the PID are trivial.

Misconception Number 8:

PIDs don't work in high humidity

Humidity and moisture can have a serious effect on PID performance. Once again however, the effects of humidity are very design dependent. Water molecules, like methane molecules, can absorb UV light without becoming ionised, and thus quench the PID signal similarly to methane. Once again, the tendency of water vapour to reduce the PID signal is very design dependent. Again, one of the most important determinants is the distance of the sensing electrode in the PID from the surface of the window of the PID lamp. Most PID designs deliberately position the sensing electrode as close as possible to the surface of the lamp window to reduce the effects of humidity. PID manufacturers also provide tables of correction factors that can be used to correct readings for humidity at various temperature and RH conditions. Alternatively, it easy to correct for these ambient conditions simply by calibrating the PID in the temperature and humidity conditions in which the instrument is actually used.

A second related issue is the condensation of water on the inside of the PID detector. When dirt or dust particles accumulate on the surface of the lamp, electrodes or PID sensing chamber, they provide points of nucleation around which water vapour can coalesce to produce misting similar to the fog that develops on a bathroom mirror. In two electrode PID designs this can lead to surface electrical current flows directly between the sensing and counter electrodes. This "moisture leakage" can result in a rising signal or positive drift in the PID readings. The potential for moisture leakage can be reduced by cleaning the lamp and / or detector.

Some PID designs include a third "fence" electrode that serves as a short circuit path that mechanically interrupts current flow between the sensing and counter electrodes. In the case of designs that include a fence electrode, condensation of water vapour does not tend to produce a positive drift, or interfere with the ability of the PID to obtain proper readings.

Misconception Number 9:

PIDs must include a built-in pump or fan to obtain readings

Whether or not the PID requires a pump or fan to move the sample through the sensing chamber is a function of the manufacturer's design. Many PID designs include a built-in pump or fan. Other designs allow the addition of a motorised pump to obtain samples from areas that are remote from the detector. The easiest way to determine whether or not a pump is required is to evaluate the instrument before purchase. Most manufacturers and distributors are more than willing to make instruments available to potential customers for field trialing.

Misconception Number 10:

PIDs can be used to replace many common substance-specific electrochemical sensors

PIDs are able to detect a wide variety of VOC and other toxic chemicals including hydrogen sulphide, ammonia, phosphine, chlorine and others. However, PIDs are broad-range sensors that cannot discriminate between a specific toxic contaminant and other detectable chemicals that may be simultaneously present. When a highly toxic specific contaminant like H2S is potentially present, it is better to use a substance-specific sensor that responds only to that particular hazard.

Fortunately, PID equipped multi-sensor instruments are available that include up to five channels of detection, allowing users the latitude of choosing exactly the combination of sensors they need to keep their workers safe.