PID – protection from harmful VOCs

Richard Dunn
Portables Product Manager
Crowcon Detection Instruments
richard.dunn@crowcon.com

Introduction

Volatile organic compounds (VOCs) tend to be liquids which readily give off vapour at room temperature\(^1\), such as solvents and fuels. At high concentrations, these vapours can explode. At extremely low levels, they can be toxic. While the impact of exposure can sometimes be felt immediately, frequently symptoms may not become apparent for months if not years afterwards. This type of chronic illness can result from repeated and extended low-level exposure. Increased awareness of the chronic toxicity of VOCs has led to reduced occupational exposure limits (OEL) and increased requirements for direct measurement.

The nature of gas hazards posed by some working environments can be complex, and complete protection is not available from a single solution. Volatile organic compounds (VOCs) pose a particular hazard, because they are both combustible and, even at very low levels, toxic. Pellistor based sensors can detect many VOCs at combustible levels, but are not sensitive enough to protect against chronic toxic effects. In general, photo-ionisation detection sensors are the favoured solution to monitor individual, low-level VOC exposure, usually incorporated into a personal multigas detector.

Abstract

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Different detectors for VOCs

There are several technologies that can measure VOC vapours.

These include: colorimetric detector tubes; passive (diffusion) badge dosimeters; sorbent tube sampling systems; pellistor sensors (also known as catalytic hot-bead or wheatstone bridge); photo-ionisation detection (PID); flame ionisation detection (FID) and infrared spectrophotometry. All of these techniques are useful and even mandatory in certain monitoring applications.

However, due to cost and size constraints, when it comes to personal detector devices, only pellistor or PID based sensors are commonly used. Neither technology is specific to one gas, so they can’t be used to distinguish one VOC/flammable risk from another.

Fig 1. The breathing zone for personal gas detection.

A number of different toxic and explosive gases could be present in some working environments. A common approach when using personal instruments is to use a multi-sensor instrument capable of simultaneous monitoring for different atmospheric hazards which may pose a threat. The information from the different sensors helps interpret what could be a complex mixture of gases.
Pellistor sensors

Pellistor sensors actually use combustion of a gas to detect it. While the use of combustion to detect combustible gases may sound unwise, the design of pellistor sensors ensures the safety of the method. A pellistor is based on a wheatstone bridge circuit (fig 2), and includes two “beads”, one of which (the active bead) is treated with a catalyst. The catalyst lowers the temperature at which the gas will burn, and the active bead becomes hot from the combustion around it. The resulting temperature difference between the active and reference bead causes a difference in resistance, which is measured. The amount of gas present is directly proportionate to the difference in resistance, so gas concentration can be accurately measured.

The hot bead and electrical circuitry are housed inside the pellistor sensor (fig 3), but the gas must have access in order for it to be detected. The sensor housing, therefore, includes a sintered metal flame arrestor (or sinter) which the gas passes through. Confined within the sensor housing, a controlled combustion can occur, isolated from the outside environment by the sinter.

While this works well for many combustible gases, pellistor sensors have some significant disadvantages when it comes to monitoring VOCs.

• Pellistors detect at the percent (parts-per-hundred) range. This is suitable to detect the risk of combustion, but many VOCs also pose a toxic threat. This usually requires sensitivity at a parts-per-million (ppm) level.

• Many VOCs are large hydrocarbon molecules that can’t readily diffuse through a pellistor sinter. This means that sensitivity is further reduced.

• Pellistors can be poisoned by many chemicals used in industry. Compounds containing silicone, lead, sulphur and phosphates at just a few ppm can degrade these sensors.

Photo-ionisation based detection

Photo-ionisation detection technology is generally considered the technology of choice for monitoring exposure to toxic levels of VOCs. The sensors include a lamp housed within as a source of high-energy ultraviolet (UV) light (fig 4). The lamp (consisting of a sealed borosilicate glass body) encases a noble gas, most commonly krypton, and electrodes. The UV light’s energy excites the neutrally charged VOC molecules, so removing an electron.

Having lost an electron, which is negatively charged, the VOC molecule now has a corresponding positive charge. The positively charged molecule and the negatively charged electron collect at oppositely charged electrodes, resulting in a current flow. The magnitude of current flow is directly proportional to concentration of gas, and is converted to a ppm readout on a detector display.

The amount of energy needed to remove an electron from a VOC molecule is called the ionisation potential (IP). The larger the molecule, or the more double or triple bonds the molecule contains, the lower the IP. Thus, in general, the larger the molecule, the easier it is to detect! Further more, this technology does not require use of a sinter which might prevent the gas reaching the sensor. It is also not susceptible to poisoning by commonly available compounds.
PID is very sensitive and will respond to many different VOCs. The magnitude of the response is directly proportionate to the concentration of the gas. However, 50ppm of one gas will give a different reading to 50ppm of a different gas. To cope with this, detectors are usually calibrated to isobutylene and then a correction factor is employed to get accurate readings for other gases. Each gas has a different correction factor. Therefore, the gas must be known for the right correction factor to be applied. Additionally, correction factors are sensor manufacturer specific.

For a gas to explode, it must reach a certain environmental concentration, the lower explosive limit (LEL). A first alarm level on a detector should preferably be set no higher than 10% of its LEL, possibly lower, if indicated by circumstances. Even 5% LEL tends to be a significantly higher concentration than statutory occupational exposure levels set to protect against toxicity.

To illustrate this point, see table 1, which compares 8-hour time weighted average (TWA) limits with 5% LEL as stated in IEC60079-20-1:2012. We used the UK exposure limits listed in EH40/2005 Workplace Exposure Limits.

Consequently, pellistor sensors and photo-ionisation detectors can be considered complementary not competing detection technologies for many applications. Pellistors are excellent at monitoring for methane, propane and other common combustible gases that are not detectable by PID. On the other hand, PID detects large VOC and hydrocarbon molecules that may be virtually undetectable by pellistor sensors, certainly in the parts-per-million range required to alert to toxic levels. Thus, the best approach in many environments is a multi-sensor instrument equipped with both.

### Table 1: Comparison of explosive and toxic limits

<table>
<thead>
<tr>
<th>VOC</th>
<th>UK OEL²</th>
<th>100% LEL* (vol %)</th>
<th>5% LEL (as ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>TWA</td>
<td>500ppm</td>
<td>2.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>TWA</td>
<td>1ppm</td>
<td>1.2</td>
</tr>
<tr>
<td>Hexane</td>
<td>TWA</td>
<td>20ppm</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>TWA</td>
<td>5ppm</td>
<td>4.0</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>TWA</td>
<td>400ppm</td>
<td>2.0</td>
</tr>
<tr>
<td>(also propan-2-ol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>TWA</td>
<td>100ppm</td>
<td>1.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>TWA</td>
<td>50ppm</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* LEL taken from IEC60079-20-1:2012
Summary

It has long been understood that volatile organic compounds are a significant risk to health, but the full extent of their toxic nature has only been recognised more recently. To protect workers from low-level toxicity, use of pellistor sensors alone is not sufficient. This technology can’t detect VOCs at concentrations low enough to protect against toxic exposure. For this, the most widely adopted technology is photo-ionisation detection. For many applications, this is incorporated into a compact multi-sensor instrument equipped with oxygen, electrochemical toxic, LEL combustible (pellistor) and VOC toxic (PID) sensors, designed to protect against a wide range of gas hazards.


References

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