

Crowcon Whitepaper

PID – protection from harmful VOCs



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.

Introduction

Volatile organic compounds (VOCs) tend to be liquids which readily give off vapour at room temperature¹, 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 most frequently hazardous form of VOC exposure is vapour inhalation. The best way of guarding against this is the use of a personal gas monitor, correctly worn – i.e. as close as reasonably possible to the breathing zone, without breathing directly on it (fig 1). In this way, it is exposed to the same levels of toxic gas as its wearer, so it can reliably alert them. This is critical to be able to avoid the long-term, low-level exposure that results in chronic disease.

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.

It is vital that a personal gas monitor is configured correctly for the environment in which it is to be used. Specific sensors are available for the detection of some toxic gases². These should be used where exposure to that specific gas is a realistic possibility. Good examples are carbon dioxide in the carbonated drinks industry; hydrogen sulphide in the steel industry; and in water treatment, ozone and chlorine. There are sensors available for each of these gases, usually based on electrochemical technology. There are no such specific sensors for many of the VOC gases, however. In this case, different technology must be relied upon.

In this whitepaper, we discuss Volatile organic compounds (VOCs), which tend to be liquids that readily give off vapour at room temperature¹, such as solvents and fuels. At high concentrations, these vapours can explode. At extremely low levels, they can be toxic.

Monitoring VOCs

- » Pellistor sensors
- » Photo-ionisation based detection

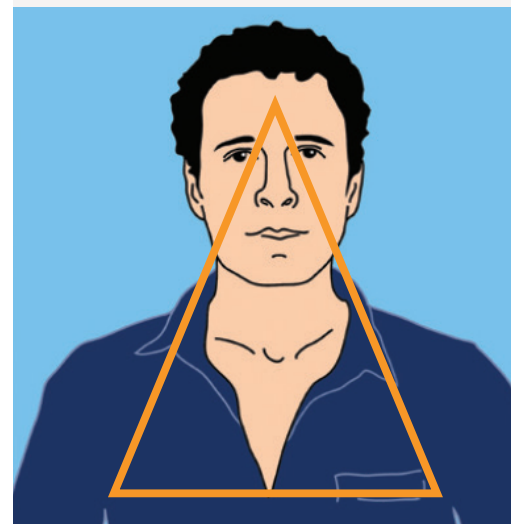


Fig 1. The breathing zone for personal gas detection.

Chronic illness can result from repeated and extended low level exposure.

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 hotbead 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.

Pellistor sensors

Pellistor sensors actually use combustion of a gas to detect it³. 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 industry³. 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 electron⁴.

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 proportionate to the 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! Furthermore, 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.

Fig 2:
Wheatstone
bridge circuit
diagram

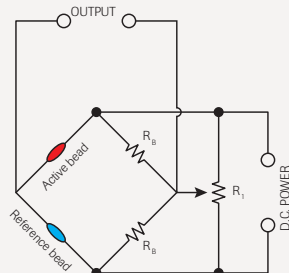


Fig 3:
Pellistor sensor
construction

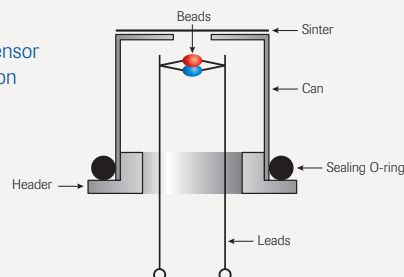
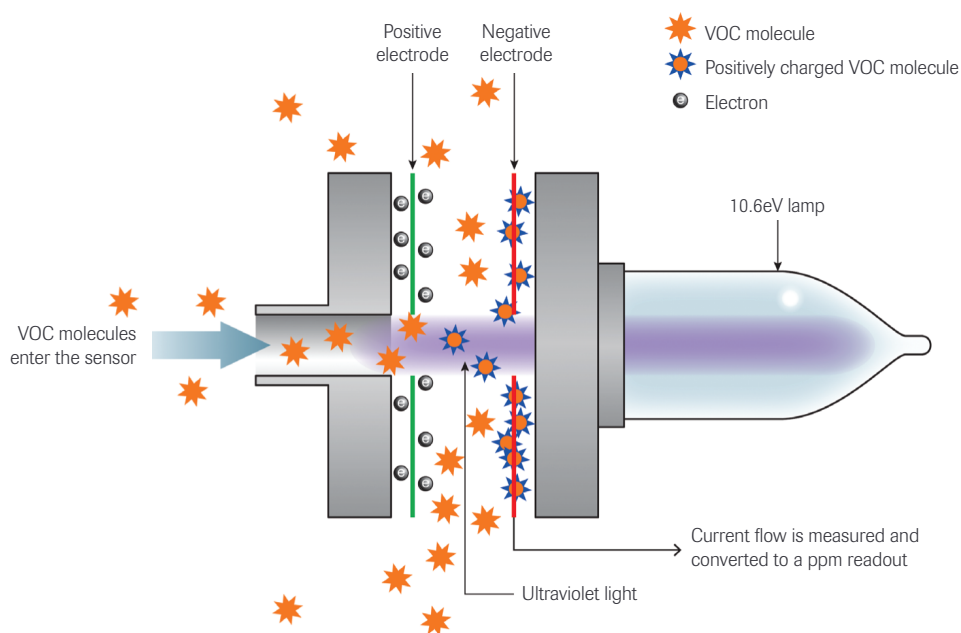


Fig 4: Typical configuration of a 10.6eV photo-ionisation sensor



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 LEL⁵, 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 IEC60079-20-1:2012⁶. We used the UK exposure limits listed in EH40/2005 Workplace Exposure Limits⁷.

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

VOC	UK OEL ³	100% LEL* (vol. %)	5% LEL (as ppm)
Acetone	TWA 500ppm	2.5	1250ppm
Benzene	TWA 1ppm	1.2	600ppm
Hexane	TWA 20ppm	1.0	500ppm
Hydrogen sulphide	TWA 5ppm	4.0	2000ppm
Isopropyl alcohol (also propan-2-ol)	TWA 400ppm	2.0	1000ppm
Styrene	TWA 100ppm	1.0	500ppm
Toluene	TWA 50ppm	1.0	500ppm

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



Conclusion

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.

» For information about Crowcon gas detection solutions for the oil & gas and petrochemical industries, visit www.crowcon.com/industries-and-applications/oil-and-gas-exploration-and-production.html

References

1. VOCs (Volatile Organic Compounds), Vermont Department of Health Agency of Human Services, http://healthvermont.gov/enviro/indoor_air/voc.aspx - accessed 06/02/14
2. Henderson, R. Gas Detection for VOC Measurement, Occupational Health and Safety 01/10/04 <http://ohsonline.com/Articles/2004/10/Gas-Detection-for-VOCMeasurement.aspx> - accessed 06/02/14
3. The CoGDEM Guide to Gas Detection, chapter 5.5, edited by Leigh Greenham, 2012, ILP Publications, St Albans
4. Introduction to Photo-ionisation Detection (PID), Alphasense Application Note AAN 301-04, http://www.alphasense.com/WEB1213/wp-content/uploads/2013/07/AAN_301-04.pdf - accessed 06/02/14
5. The Selection And Use Of Flammable Gas Detectors, Health and Safety Executive, UK <http://www.hse.gov.uk/pubns/gasdetector.pdf> - accessed 06/02/14
6. IEC60079-20-1:2012, Explosive atmospheres. Material characteristics for gas and vapour classification. Test methods and data.
7. EH40/2005 Workplace Exposure Limits, Health and Safety Executive, UK <http://www.hse.gov.uk/pubns/books/eh40.htm> - accessed 06/02/14

www.crowcon.com

UK:
Tel: +44 (0) 1235 557700
Fax: +44 (0) 1235 557749
Email: sales@crowcon.com

US:
Tel: +1 859 957 1039
Toll Free: 800-527-6926
Fax: +1 513 957-1044
Email: salesusa@crowcon.us

NL:
Tel: +31 10 421 1232
Fax: +31 10 421 0542
Email: eu@crowcon.com

SG:
Tel: +65 6745 2936
Fax: +65 6745 0467
Email: sales@crowcon.com.sg

CN:
Tel: +86 (0) 10 6787 0335
Fax: +86 (0) 10 6787 4879
Email: saleschina@crowcon.com

IN:
Tel: +91 22 6708 0400
Fax: +91 22 6708 0405
Email: salesindia@crowcon.com