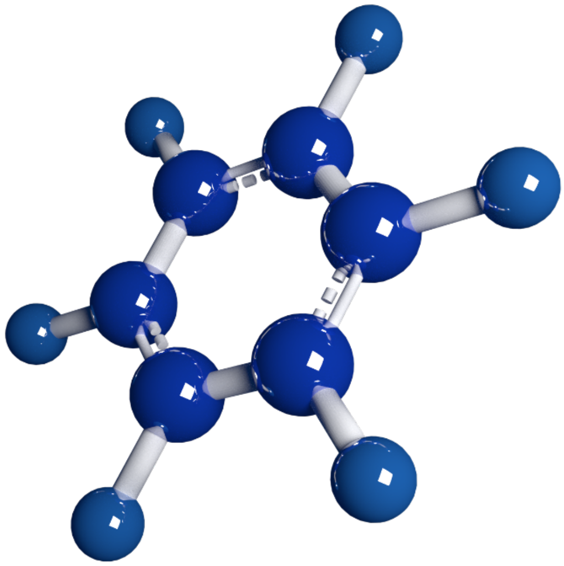
A Complete Guide to Benzene

Benzene *is an important organic chemical compound with the chemical formula* C_6H_6*. The benzene molecule is composed of six carbon atoms joined in a ring with one hydrogen atom attached to each. As it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon.*

Benzene is a natural constituent of crude oil and is one of the elementary petrochemicals. Due to the cyclic continuous pi bond between the carbon atoms, benzene is classed as an aromatic hydrocarbon, the second [n]-annulene ([6]-annulene). It is sometimes abbreviated Ph–H. Benzene is a colourless and highly flammable liquid with a sweet smell.

Source: Wikipedia



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Protecting people and the environment

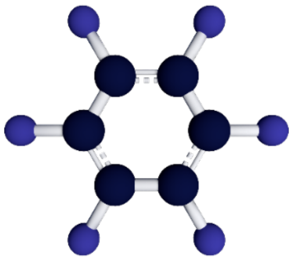
Protecting both people and the environment whilst meeting the operational needs of your business is very important and, if you have operations in the UK you will be well aware of the requirements of the CoSHH Regulations[1] and likewise the Code of Federal Regulations (CFR) in the US[2].

Similar legislation exists worldwide, the common theme being an onus on hazard identification, risk assessment and the provision of appropriate control measures (bearing in mind the hierarchy of controls) as well as health surveillance in most cases.

And whilst toxic gasses such as hydrogen sulphide and carbon monoxide are a major concern because they pose an immediate (acute) danger to life, long term exposure to relatively low level concentrations of other gasses or vapours such as volatile organic compounds (VOC) are of equal importance because of the chronic illnesses that can result from that ongoing exposure.

Benzene, a common VOC

Organic means the chemistry of carbon based compounds, which are substances that results from a combination of two or more different chemical elements. The atoms of the different elements are held together by chemical bonds that are difficult to break. These bonds form as a result of the sharing or exchange of electrons among the atoms. Some VOCs are hydrocarbons but not all hydrocarbons are VOCs.



Benzene, also known as benzol, is one such common VOC, identified by its unique numerical CAS[3] number 71-42-2.

It is also a hydrocarbon as you can see from its chemical formula C_6H_6 represented diagrammatically as a ring (figure 1).

It belongs to the BTEX family (Benzene, Toluene, Ethylbenzene, Xylene) of so called aromatics because of their sweet, pleasant smell.

Figure 1: Benzene Ring

Benzene is the simplest such aromatic hydrocarbon and it was the first one named as such, the nature of its bonding was first recognised in the 19th century. It is:-

- a highly flammable, colourless to light yellow liquid
- occurs naturally in crude oil, natural gas and some ground waters
- found in ambient air as a result of burning fuels, such as coal, petrol and wood and is common in unleaded fuel, where it is added as a substitute for lead, allowing smoother running
- present in cigarette smoke.

Benzene evaporates easily and most people can just detect its distinctive smell at concentrations between 2.5 and 5 parts per million (ppm) in air.

In the following diagram (figure2) the importance of benzene and other aromatics can be seen in the manufacture of many commonly used plastics.

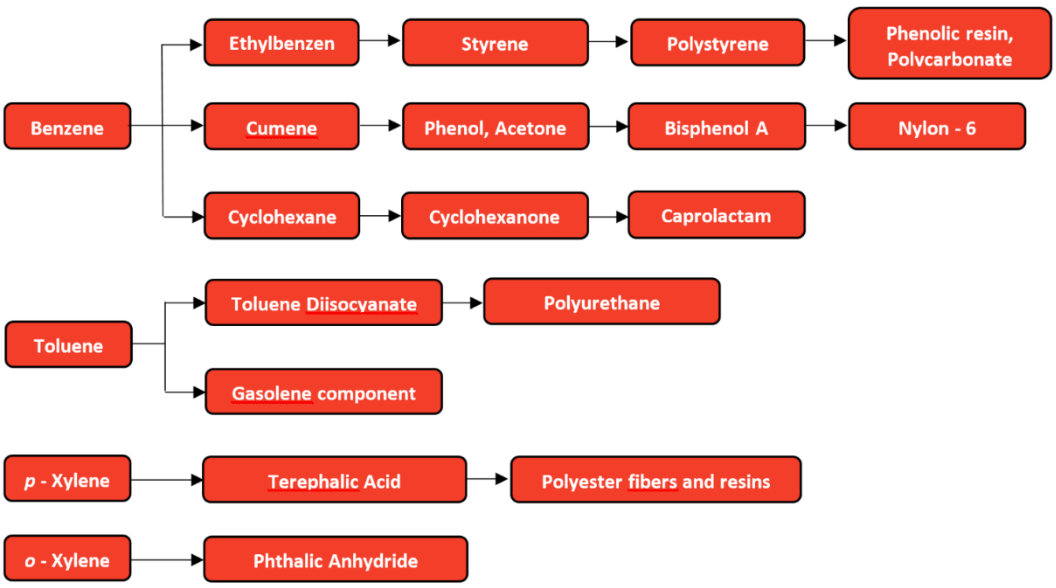


Figure 2: The chain of petrochemicals derived from the BTEX aromatics (source Wikipaedia[4])

Workers might be exposed to benzene during certain jobs, for example, in:-

- Oil refineries
- Chemical and petrochemical plants
- Coke works
- Foundries
- The storage, distribution and use of petrol or benzene itself

Why is Benzene so hazardous?

VOCs have a significant vapour pressure at normal ambient temperature which means they evaporate (volatilise) at low temperatures so they can easily enter the body through normal breathing but can also be absorbed through the skin or by swallowing material containing it.

The effects on worker's health depends upon how much benzene they are exposed to *and* for how long and as with other organic solvents, the immediate effects of a single exposure to a high concentration (hundreds of ppm) e.g. from a fugitive process leak, include headache, tiredness, nausea, dizziness and even unconsciousness if the exposure is very high (thousands of ppm) meaning an acute safety incident.

From a long term (chronic) health perspective, the World Health Organisation (WHO) and International Agency for Research on Cancer (IARC) classify benzene as a group one carcinogen. Prolonged exposure to high concentrations of benzene causes leukaemia and impacts red and white blood cells. Regular exposure can lead to chronic effects including:-

- myeloid leukaemia
- lymphocytic leukaemia
- non-Hodgkins lymphoma
- multiple myeloma
- aplastic anaemia

Health surveillance by conducting a urinary test or blood count can of course show evidence of exposure but these are lagging indicators i.e. after exposure has already taken place by which time damage may have been done.

Individuals who have experienced benzene poisoning requiring treatment show a substantially increased risk of mortality from leukaemia.

Benzene legislation

According to the European Agency for Health and Safety at Work (EU-OSHA) [5], 15 % of workers across the European Union (EU) have to handle dangerous substances as part of their job, and another 15 % report breathing in smoke, fumes, powder or dust at work which could be hazardous to their health. The EU has brought forward essential legislation relating to so-called physical and chemical agents in the workplace over the last two decades and the Chemical Agents Directive [6] is 'celebrating' its 20th anniversary during 2018. In the UK, it is implemented as the Control of Substances Hazardous to Health (COSHH) Regulations 2002 and transposition across the EU has been summarised by in an informative document EU-OSHA [7].

In addition, Directive 2004/37/EC [8] was specifically introduced for carcinogens or mutagens at work and essentially requires that the employer assess and manage the risk of exposure to carcinogens or mutagens and to:-

- limit the quantities of a carcinogen or mutagen at the place of work;
- keep as low as possible the number of workers exposed;
- design the work processes so as to minimise the substance release;
- evacuate carcinogens or mutagens at source, but respect the environment;
- use appropriate measurement procedures (especially for early detection of abnormal exposures from unforeseeable event or accident);
- apply suitable working procedures and methods;
- use individual protection measures if collective protection measures are not enough;
- provide for hygiene measures (regular cleaning);
- inform workers;
- demarcate risk areas and use adequate warning and safety signs (including "no smoking");
- draw up emergency plans;
- use sealed and clearly visibly labelled containers for storage, handling, transportation and waste disposal.

Recognising the specific concerns over benzene, the EU turned to the European Chemicals Agency (ECHA) to "review and evaluate the information already available and assess the most recent scientific information". The review, entitled *Proposal in support of occupational exposure limit values for benzene in the workplace* [9] was published for public consultation in October 2017. The aim of the review was to make recommendations to the next (4th) amendment to the directive on carcinogens and on the 17th March 2018, the ECHA through its Committee for Risk Assessment (RAC) recommended a reduction to 0.05 ppm (50 ppb) [10].

Occupational exposure limits

Whilst there is nothing new in the concept of workplace exposure limit values, a more recent EU Directive 2017/164/EU [11] has introduced indicative occupational exposure limit values (IOELV). These are health-based, non-binding values, derived from the most recent scientific data available and availability of measurement techniques. For any chemical agent for which an IOELV has been set at EU level, member States are required to establish a national occupational exposure limit (OEL) value. They are required to take into account the EU limit value, determining the nature of the national limit value in accordance with national legislation and current practice.

Member States are required to bring into force the laws, regulations and administrative provisions necessary to comply with this Directive by 21 August 2018 at the latest. IOELVs are established in relation to an 8 hour, time-weighted average (TWA) and, for certain chemical agents, to shorter reference periods, in general 15 minutes TWA also known as short-term exposure limit values (STEL) to take account of the effects arising from short-term exposure.

In the UK, the Health and Safety Executive (HSE) already publish OELs for a plethora of chemicals, including benzene, in a document known as EH40[12] *Workplace Exposure Limits* (WEL). They refer to a WEL value which means the same thing as an OEL.

The EU-wide 8 hour TWA for benzene is currently set at 1 part per million (ppm), equivalent to a concentration of 3.25 mg/m^3 and it is also important to note the EU does not recommend an EU-wide benzene STEL value. However, the ECHA review showed that some member states already have a significantly lower OEL value and, given that WHO state there is no safe level of exposure [13], has probably influenced their recommendation for a radical reduction to 0.05 ppm.

By contrast, legislation in the USA exists in the form of Federal Regulation 29 CFR part 1910 [2] and while the legislative framework is less complex than the EU, the limit values vary according to different ‘agencies’ plus they all state a value for the STEL.

The table shows the existing OELs indicated as an 8-hour time TWA and 15-minute STEL (where stated) for selected EU member states and USA.

Selection of existing OEL's for EU member states and USA

	TWA (8 hours)		**STEL** (15 minutes)	
	ppm	mg/m³	ppm	mg/m³
EU	1	3.25	-	-
France	-	3.25	-	-
UK	1	3.25	-	-
Germany*	0.6	1.9	-	-
Denmark	0.5	1.6	-	-
Sweden	0.5	1.5	3	9
Netherlands	0.2	0.7	-	-
OSHA (USA)	1	3.2	5	15
ACGIH (USA)	0.5	1.6	2.5	8
NIOSH (USA)	0.1	0.3	1	3.2

* Tolerable risk 1:1000

Correct as at 17th October 2017

What are my workplace exposures?

Knowing the obligations of legislation and OELs, the question remains, how do I know if workplace benzene exposures are below the limits for my country? Unlike other health and safety issues that are managed by risk assessment, this can only be determined by monitoring. There are several monitoring solutions on the market including chemical specific detector tubes, air sampling pumps with charcoal tubes or sample bags (later analysed in the laboratory using a GC) but photoionization detection (PID) has proven to be the ideal tool. PID based solution are used in the following ways:-

- fixed instrumentation
- portable instrumentation
- personal instrumentation

Indeed, a combination of all three solutions provides complete worker and environmental protection and these are discussed later in more detail.

PID theory of operation

Figure 3 is a schematic of a proprietary PID sensor system. A UV lamp generates high-energy photons, which pass through the lamp window and into the sensor chamber. Ambient air is pumped over the sensor and about 1% of it diffuses through a porous membrane into the other side of the sensor chamber. The inset on the lower right of figure 3 shows what happens on a molecular level. When a photon with enough energy strikes a molecule M, an electron (e-) is ejected. M+ ion travels to the cathode and the electron travels to the anode, resulting in a current proportional to the VOC concentration. The electrical current is amplified and displayed as a part per million (ppm) or part per billion (ppb) concentration. Not all molecules can be ionized. Conveniently, the major components of clean air i.e. nitrogen, oxygen, carbon dioxide, argon, etc., do not cause a response, but most accelerants do give a 'broadband' response.

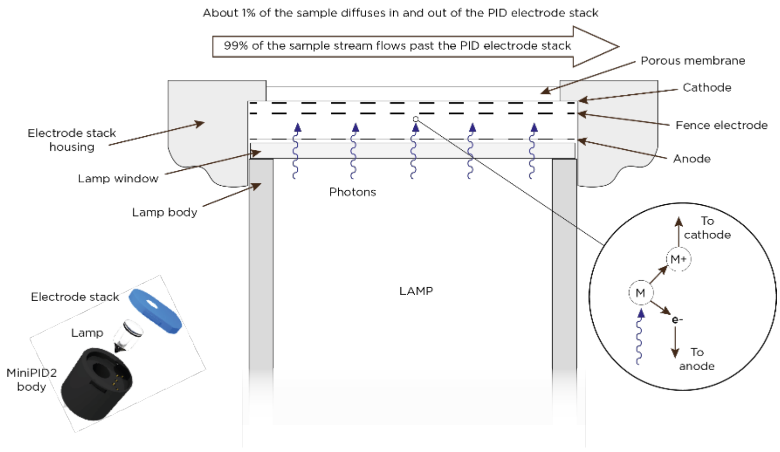


Figure 3: Ion Science Ltd PID sensor design

Which PID lamp do I need?

Three PID lamps are available with maximum photon energies, measured in electron-volts (eV), of 10.0 eV, 10.6 eV, and 11.7 eV.

Figure 4 illustrates that a lamp can only detect those compounds with ionization energies (IE) equal to or below that of the lamp photons. Thus, a 10.6 eV lamp can measure hydrogen sulphide with an IE of 10.5 eV and all compounds with lower ionization energy, but cannot detect methanol or compounds with higher IE.

The choice of lamp therefore depends on the application. When only one compound is present, one can use any lamp with enough photon energy, often the standard 10.6 eV lamp which is the lowest cost 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 so in the case of compound mixtures, use the lowest energy lamp possible.

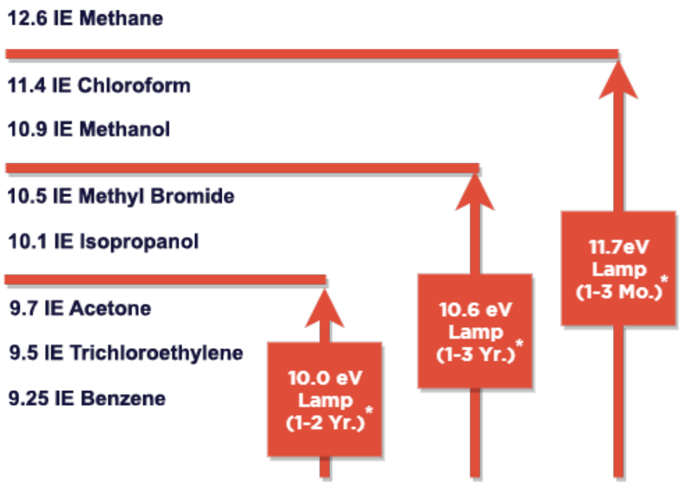


Figure 4: PID lamp energy thresholds

Benzene has a low IE value as shown in Figure 4 and it is often present in a cocktail of other chemicals including aromatics. Using a proprietary 10.0eV lamp means that only the aromatics are detected and should the total aromatic compounds (TAC) be above the regulatory limit a benzene pre-filter tube can be used to provide an accurate reading.

Operational efficiency

Generally speaking, health and safety has historically been seen as a barrier to productivity, even the butt of the occasional joke. The worst scenario is people continuing to act in an unsafe manner when no one is looking thinking that in cutting corners they are getting the job done more quickly. However, there is now widespread consensus to the contrary that a strong health and safety (H&S) culture is good for business when viewed as an investment, not a cost and as a vital component of overall business strategy. Creating a sustainable business through continuous improvement leading to operational excellence (OpEx) is a major strategic objective.

LNS Research in their February 2018 webcast[14] reference Alcoa, who achieved an order of magnitude reduction in the rate of lost working days (LWD) with a near equal and opposite increase in shareholder value (see figure 5). They put this down to strong leadership from the very top, cross functional teamwork and working hard to close the gap between good intentions and implementation.

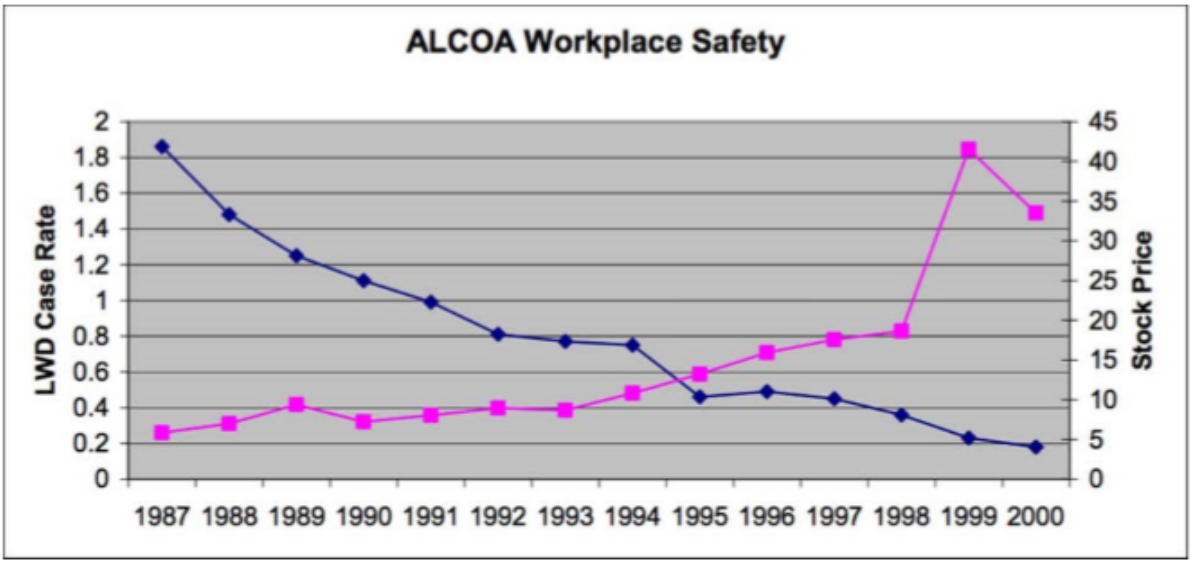


Figure 5: Correlation between a focus on safety and stock price (LNS Research)

Their research also throws up further compelling evidence between the investment in safety and a financial return but in addition to financial gains and a reduction in incidents & accidents other outcomes include minimising the operations' impact on the environment and the promotion of employee health & wellbeing.

Figure 6: Return on investment in safety (LNS Research)

LNS say that continuous improvement initiatives depend on a cross-functional OpEx 'platform' comprising:

- Energy - reduced usage
- Environment, Health and Safety (EHS)
- Quality – zero defects
- Asset performance management (APM)
- Operations - efficiency

LNS go on to say “fall short on any one pillar and the OpEx platform is fragile, fall short on two and it is totally unstable”.

Clearly in safety critical sectors such as oil and gas there can be no compromise in EHS because of the immediate danger to life but for a long time, according to the British Occupational Hygiene Society (BOHS), “we have been shouting safety and whispering health”. This was actually said in the context of toxic dust exposure but is equally applicable VOCs like benzene.

Plant turnaround

Hazardous chemicals that pose a risk to humans are normally safely transported within the process but obviously during plant turnaround this is no longer the case. As lines and reaction vessels are opened they pose a significant risk of over-exposure, without appropriate control measures. Concentrations can be several hundred (or even thousand) times higher than the occupational exposure limit (OEL)!

The workforce increases many folds too and the clock is ticking to get the plant back up and running on time (time literally is money[15]). This also increases the potential risk due to the sheer numbers of contractors that presents an H&S management challenge. Remember the old adage *you can’t manage what you don’t measure*? Well, it is not surprising that monitoring instrument sales peak at this time according to Gary Smith, Export manager for Ion Science.

Fugitive emissions

During normal operations, leaks can occur from pumps, valves, flanges, storage tanks or during loading and unloading. According to the US EPA[16], 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 7.

Table 3.2 – Equipment component counts ata 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 7: Typical equipment counts (Source US EPA)

This can mean hundreds of tons of VOCs released to atmosphere (see Figure 8) which can present health risks for workers and operators and pollution of the wider environment. A leak detection and repair (LDAR) program can significantly reduce product loss running to many hundreds of thousands of dollars, increase worker safety, decrease exposure to the surrounding environment, reduce emission fees and help avoid enforcement actions. There are also hidden costs associated with the reputational damage should an EHS incident occur. A portable PID is the ideal tool for this application.

Table 3.3 – Uncontrolled VOC emissions at a typical facility.

Component	Average uncontrolled VOC emissions (ton/yr)	Percentage of total emissions
Pumps	19	3
Valves	408	62
Connectors	201	31
Open-ended lines	9	1
Sampling connections	11	2
Pressure relief valves	653	1

Source: Emission factors are from Protocol for Equipment Leak Emissions Estimates, EPA-453/R-95-017, Nov 1995, and equipment counts in Table 3.2.

More recent data indicates that open-ended lines And sampling connections each account for Approximately 5-10% of total VOC emissions

Figure 8: VOC emissions at a typical plant (Source US EPA)

Buyer's guide

Unlike other health and safety hazards, the only way to carry out a risk assessment for benzene exposure is to monitor quantitatively. Like other volatile organic compounds (VOC), benzene evaporates easily and most people can just detect its distinctive 'aromatic' smell at concentration between 2.5 and 5 parts per million (ppm) in air but regulatory occupational exposure limits (OEL) are typically 1 ppm.

However, if the EHCA recommendation of 0.05ppm (50ppb) is adopted in the EU, it imperative that the measurement solution is sensitive and accurate. It must also be capable of operating in harsh process plant environments in the likely presence of dirt, dust, high humidity and interference from other VOC/aromatic compounds. The photoionization detector (PID) has proven to be an ideal solution but there are several considerations that must be borne in mind when choosing an instrument.

Effects of humidity

The presence of humidity in the sample gas can unfortunately disrupt the measurement leading to inaccurate results. Heated inlets to achieve a stable temperature (typically 50°C) are effective but power hungry and are clearly only applicable to fixed systems. They are still a challenge to achieve in, say a refinery, where stringent intrinsic safety (IS) requirements have to be met.

However, looking at Figure 3, the presence of an additional fence electrode can overcome the problem and practically eliminate the effect of humidity. It does this by behaving as a conductive break when there is excess current flow due to an effective short circuit caused by the presence of contamination between the electrodes which occurs at high humidity (>90% RH) shown in figure 9.

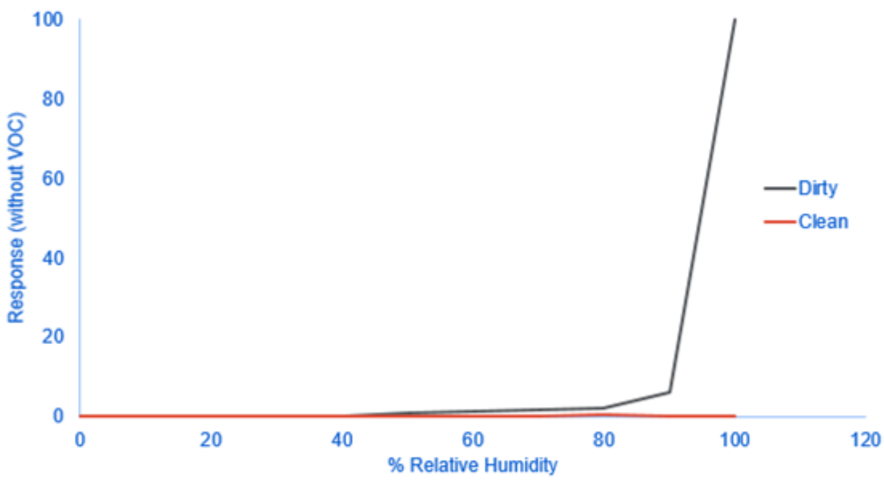


Figure 9: Effect of contamination at high humidity

Conversely, low readings are possible due to the photons being absorbed by the water vapour and the effect with increasing humidity can be seen in figure 10. This is mitigated by the presence of a porous membrane made from a hydrophobic material and can be seen in figure 3.

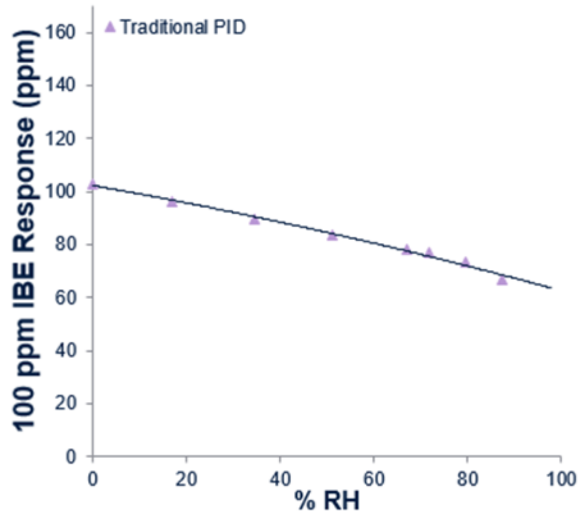


Figure 10: Effect of water vapour absorption

Fixed, portable or personal monitoring

Applications for PIDs include:-

- fixed systems for area or fenceline monitoring of fugitive emissions
- portable instruments for confined space entry checks or leak detection & repair
- personal instruments, to alert a worker to a concentration above the regulatory OEL

Each solution is optimised for the application, offering specific features and benefits but design compromises often have to be made. Let's look at the definitive features to look out for:-

Fixed systems

- be benzene specific i.e. require no calibration correction factor
- have real or near-real time continuous monitoring with industry standard 4-20mA and/or MODBUS outputs
- require no operator intervention during normal use

Portable

- have a specific benzene mode and pre-filter tube capability
- have a high resolution of 1 ppb to cope with the legislative OEL trends
- have a long battery life capable of two 12-hour shifts to maximise data capture and to minimise system down time.

Personal

- be small and lightweight so as not to burden the wearer (the personal PID is having to 'compete' for space alongside gas and radiation detectors, portable radios and other monitoring instrumentation such as noise dosimeters and dust sampling heads/pumps).
- have a high resolution of say 10 ppb for compliance purposes.
- have a high range of 5000 ppm to accommodate the high levels experienced during plant turnaround.
- be capable of 1 second logging of actual exposure for later download and analysis which would highlight areas of concern and help identify where fixed systems could be situated.

Environmental protection

In order to meet mandatory IS requirements and achieve high IECEx ratings of Ex ia IIC T4, instruments have to be environmentally sealed against dust and water ingress that may otherwise lead to an explosion should a fault(s) in the instrument occur when in a flammable atmosphere. An ingress protection (IP) rating of IP54 is a bare minimum and ideally should be IP65 for use in an outdoor, process environment.

Calibration and maintenance

It is important that a PID is maintained due to the potential for contamination of the lamp because of dirty, humid environments plus, the PID requires regular calibration using a reference gas. Isobutylene is an excellent surrogate calibration gas because the response of most VOCs is reasonably close to, and consistent with, this gas.

During factory calibration and maintenance, the manufacturer should also clean the PID sensor lamp and the membrane should be changed prior to factory recalibration which will bring the instrument back to the manufacturer's original specification.

Summary

With a seemingly inexorable rise in the production and release of benzene into the environment it is vitally important that the health dangers and legislative provision are understood. The direction of travel for the exposure limit is decreasing and real-time monitoring using a range of PID solutions in combination will ensure that you go beyond compliance in the safety, health and wellbeing of your most valuable asset, your workforce.

There are also significant savings associated with taking a proactive approach to monitoring exposures that not only mitigate risks but similarly LDAR programs to reduce losses. The resulting gains in operational efficiency are vital in creating a sustainable business and achieving operational excellence which lead to increased shareholder value.

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Ion Science provide a portfolio of handheld, fixed and portable photoionization (PID) detection instruments for the rapid, accurate detection of volatile organic compounds (VOCs). Find out more about our industry leading range of VOC detection solutions by clicking on the links below.

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