Benzene – Monitoring Technologies to Mitigate Risk and Create a Safer and More Compliant Plant Environment

a report by

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The Threat of Benzene

The aromatic hydrocarbon benzene is almost everywhere. It is a component of gasoline and is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber and dyes. It is a natural constituent of crude oil, but it is usually synthesised from other compounds present in petroleum. It is found in high concentrations in cigarette smoke.

Similar to asbestos, the use and handling of benzene has changed over the past several decades as its toxic properties have become better comprehend. As the understanding of the threat has developed, various sensing technologies and regulations have been used to provide better protection for people at higher risk of exposure.

History and Uses

Benzene was first discovered and isolated from coal tar in the 19th century. Prior to the 1920s, benzene was frequently used as an industrial solvent, especially for degreasing metal. As its toxicity became obvious, other solvents replaced benzene in applications that directly exposed the user to benzene.

Now, benzene is made mostly from petroleum sources and ranks in the top 20 in production volume for chemicals produced in the US. The largest use of benzene is as an intermediate to make other chemicals. The most widely produced derivatives of benzene are styrene, which is used to make polymers and plastics, phenol for resins and adhesives (via cumene) and cyclohexane, which is used to manufacture nylon. Smaller amounts of benzene are used to make some types of rubbers, lubricants, dyes, detergents, drugs, explosives and pesticides.

As many as 238,000 people may be occupationally exposed to benzene in the US. These industries include benzene production (petrochemicals, petroleum refining, and coke and coal chemical manufacturing), rubber tyre manufacturing and storage or transport of benzene and petroleum products containing benzene. Other workers who may be exposed to benzene due to their occupations include steel workers, printers, rubber workers, shoe makers, laboratory technicians and gas station employees.

Characteristics and Health Effects

Benzene is a colourless liquid with a sweet odour. Benzene evaporates into air quickly, dissolves slightly in water and is highly flammable. Most people can begin to smell benzene in air at 1.5–4.7 parts of benzene per million parts of air (ppm) and can begin to taste benzene in water at 0.5–4.5ppm. Benzene's health hazards are well documented. It is a recognised carcinogen, developmental and reproductive toxicant. It is also suspected as a toxicant in cardiovascular, endocrine, gastro-intestinal, immunological, neurological and respiratory systems. Short-term exposure to high doses (700–3,000ppm) of benzene may cause drowsiness, dizziness, headaches, tremors, confusion and/or unconsciousness. Death may occur after oral ingestion or inhalation of very high concentrations (approximately 10,000–20,000ppm) of benzene.

People who breathe benzene for long periods may experience harmful effects in the tissues that form blood cells, especially the bone marrow. These effects can disrupt normal blood production and cause a decrease in important blood components. A decrease in red blood cells can lead to anaemia. Reduction in other components in the blood can cause excessive bleeding. Blood production may return to normal after the exposure to benzene stops. Excessive exposure to benzene can be harmful to the immune system, increasing the chance for infection and perhaps lowering the body's defence against cancer.

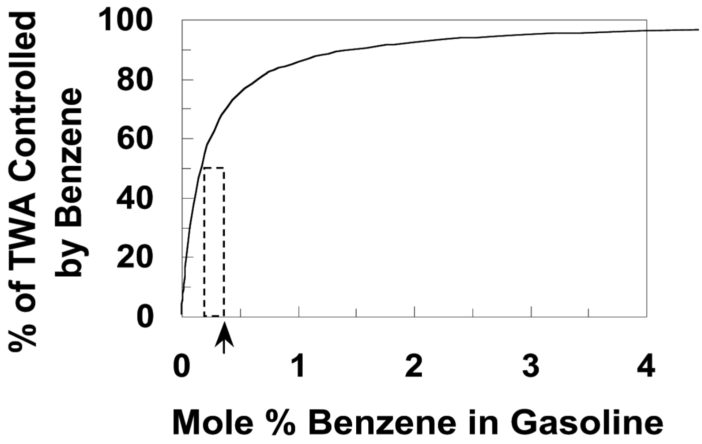
A number of human studies provide evidence that links benzene and cancer. Initially, increased risks of acute myelogenous leukaemia (AML) were reported among workers with high levels of benzene exposure in the chemical, shoemaking and oil refining industries. More recently, the focus of studies has shifted to workers with relatively lower

Table 1: Exposure Limits for Benzene

Agency	TWA Type	TWA Value	STEL
OSHA	8-hour PEL	1.0ppm	5.0ppm
ACGIH	8-hour TLV	0.5ppm	2.5ppm
NIOSH	10-hour REL	0.1ppm	1.0ppm

ACGIH = American Conference of Industrial Hygienists, NIOSH = National Institute for Occupational Safety and Health, OSHA = Occupational Safety & Health Administration, PEL = permissible exposure limit, PPM = per million parts of air, REL = recommended exposure limit, TLV = threshold limit value, TWA = time-weighted average.

Figure 1:



exposure. Since the amount of benzene in the workplace has decreased over the years and protective equipment is more readily available, fewer workers have symptoms of benzene poisoning. However, the National Cancer Institute (NCI) in collaboration with the Chinese Academy of Preventive Medicine observed almost 30,000 workers exposed to benzene in 233 factories in China and a similar group of unexposed control workers. The large sample size permitted elevated risks to be detected at low levels of exposure, and the study suggested an increased risk of leukaemia in workers exposed to less than 10ppm.

Regulation and Monitoring

Many regulatory agencies, including the Department of Health and Human Services (DHHS), the National Toxicology Program (NTP), and the International Agency for Research on Cancer (IARC), have determined that benzene is a known human carcinogen and that long-term exposure to relatively high levels of benzene in the air can cause leukaemia or cancer of the blood-forming organs. The Environmental Protection Agency (EPA), through its Integrated Risk Information System (IRIS), uses a classification scheme very similar to that of IARC. It classifies exposures into one of five categories:

- known human carcinogen;
- probable human carcinogen;
- possible human carcinogen;
- not classifiable as to human carcinogenicity; and
- evidence of no carcinogenicity for humans.

The EPA classifies benzene as "a known carcinogen" (Group A) (EPA, 1996). As a result of these health effects, the US Department of Labor's Occupational Safety & Health Administration (OSHA) Permissible Exposure Limit (PEL) for benzene has been set at 1ppm as an eight-hour time-weighted average (TWA). The American Conference of Industrial Hygienists (ACGIH) threshold limit value (TLV) and National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) have even lower TWAs of 0.5 and 0.1ppm, respectively (see Table 1). The short-term exposure limits (STEL) are the maximum concentrations a worker can be exposed to for any 15-minute period. STEL values range from 1–5ppm (see Table 1).

By contrast, gasoline as a whole has an ACGIH TWA of 300ppm. Therefore, the toxicity of gasoline is controlled by the benzene content. *Figure 1* shows that above 0.2% benzene, the TWA of gasoline is dominated by the benzene content rather than the hundreds of other compounds present. Various commercial gasolines contain benzene typically in the range 0.1%–2%. Therefore it is critical to measure the benzene concentration directly rather than total hydrocarbons. Many broadband monitoring techniques such as flame ionisation detectors (FIDs) or photoionisation detectors (PIDs) would give the same response on a gasoline that contains 0.5% versus 1% benzene, even though the overall toxicity is nearly double with the higher benzene content. Therefore, specific analytical tools are needed to measure benzene in the presence of complex mixtures of gasoline hydrocarbons.

The OSHA has set forth regulations on the sampling and analytical methods for benzene monitoring and measurement procedures in Standards–29 Code of Federal Regulations (CFR). There are a number of methods available for monitoring employee exposure to benzene, including portable direct reading instruments, realtime continuous monitoring systems, passive dosimeters or other suitable methods.

According to OSHA, the employer has the obligation of selecting a monitoring method that meets the accuracy and precision requirements of the standard under their unique field conditions. The standard requires that the method of monitoring must have an accuracy, to a 95% confidence level, of not less than plus or minus 25% for concentrations of benzene greater than or equal to 0.5ppm.

Conventional Four-gas Health and Safety Monitors

Four-gas monitors make up the bulk of realtime monitoring in industry today. However, because four-gas monitors typically only measure oxygen (O^2), the lower explosive limit (LEL) of combustible gases, carbon monoxide (CO) and hydrogen sulphide (H^2S), they miss many common toxic gases and vapours that are major constituents or by-products of industrial processes. As a result, workers are often either underprotected, with negative health consequences, or overprotected, with a loss of worker productivity. Although LEL sensors can measure benzene at very high concentrations (above a few hundred ppm), these monitors cannot detect benzene at the necessary low ppm levels. Moreover, LEL sensors are broadband monitors and cannot measure benzene specifically in gasoline mixtures.

Types of Technologies Available for Benzene and Other Harmful Volatile Organic Compounds Monitoring

There are multiple technologies available for benzene detection; as a result there are many suggestions for the most appropriate methods for protecting the long-term health and safety of workers. Each type of sensing technology has its particular uses, strengths and weaknesses, but photoionisation detection is frequently the optimal choice for realtime monitoring where benzene is present. There are a number of other technologies available for benzene monitoring.

Single-use Gas Detection Tubes.

Colorimetric gas detection tubes have been the foundation of gas detection for many years. They work by drawing a gas sample through a tube filled with a reagent that changes colour upon reaction with the chemical of interest. The length of stain is used to estimate the concentration of the chemical. It is an inexpensive and proven means of measuring many toxic gases and vapours at ppm levels. Most benzene-specific tubes use a combination of a pre-tube to filter out interferences connected to a measurement tube. The primary drawbacks to colorimetric tubes are that:

- tubes are slow to respond, requiring multiple pump strokes and five to 20 minutes of manual sampling;
- readings are subject to interpretation and errors are ≥35% at 0.5ppm;
- the ‘spot check’ nature of tubes makes them more prone to sampling errors due to small sample volume, air currents or poor technique; and
- tubes generate glass splinters and chemical waste.

The Dräger chip measurement system (CMS) uses a miniaturised double-tube system for benzene and improves the precision by incorporating an electronic pump and an optical tube reader. Nevertheless, it still requires about ten minutes to measure at 0.5ppm and cannot resolve readings below 0.5ppm.

Semi-conductor or Metal Oxide Sensors

Metal Oxide Sensors (MOS) are one of the oldest and least expensive measurement technologies used in portable instruments. These sensors are made of a metal oxide semi-conductor such as tin dioxide (SnO^2) on a sintered alumina ceramic bead contained within a flame arrestor. In clean air the electrical conductivity is low, while contact with reducing gases such as carbon monoxide or combustible gases increases conductivity. MOS sensors can detect a wide range of contaminants; however, they have several shortcomings that limit their effectiveness.

- They generally are not benzene-specific unless used in sophisticated sensor arrays with pattern recognition.
- They have limited sensitivity, with detection limits usually in the tens of ppm.
- They produce a non-linear output, making them not particularly accurate. MOS sensors are, at best, gross indicators for toxic gases and vapours.
- They have relatively slow response.
- They respond positively to moisture and temperature.
- They can be poisoned and dirtied, and are not easily cleaned.

Gas Chromatography/Mass Spectrometry Laboratory Analysis

In this method of monitoring, a gas sample is collected either by pumping through an adsorbent tube such as activated carbon, or by filling into an evacuated gas cylinder or Tedlar bag. Sent to the laboratory, the tubes are desorbed and analysed with gas chromatography/mass spectrometry (GC/MS). This is the most sensitive and selective method available and is used as the standard for comparison. However, it is also the most expensive and time-consuming approach, typically requiring hours to several days before results are available. During a plant turnaround, every minute of shut-down time is critical and rapid feedback is needed to make personal protective equipment decisions for workers.

Portable GC Systems

Portable GC systems, usually with PIDs or FIDs, provide selective benzene measurements down to 0.1ppm, but have several drawbacks. They are usually heavy and bulky, making them difficult to use in tight spaces and on ladders and catwalks. In addition they tend to be relatively expensive and complex; therefore only the company industrial hygienist operates one. Sampling and analysis time is relatively long, similar to gas detection tubes, i.e. on the order of five to ten minutes.

FIDs

FIDs work by burning a gas in a hydrogen flame. In this environment, organic compounds produce ions, which are measured on an electrometer. The resulting current is proportional to the concentration of organic vapour. The FID is very sensitive and linear over many orders of magnitude, but because it requires hydrogen and a mechanically stable environment for the flame, the resulting instruments are complex. FIDs do respond to a broad range of organic compounds but are non-selective and therefore cannot measure benzene specifically unless connected to some type of separation system such as a gas chromatograph. FIDs are also relatively expensive, maintenance-intensive and complex, which limits their use in most industries.

PIDs with Filter Tubes as an Optimal Monitoring Method

PIDs are broadband detectors, but they can give benzene-specific response by using a combination of a low-energy (9.8eV) ultraviolet (UV) lamp and pre-filter tubes that remove organic interferences. This system provides rapid response down to 0.1ppm in one minute with an accuracy of 10% in the 0.5–5ppm range. Measurements of TWA levels of benzene can be made in the presence of up to about 300ppm of gasoline. The tubes also absorb moisture and, thus, benzene-specific measurements can even be made in steam vents. Compared to portable gas chromatographs, the PID filter systems are much smaller and lighter, considerably less expensive, easier to operate, much faster and provide about the same accuracy and detection limits. The instantaneous feedback enables rapid personal protective equipment decisions to be made and allows tasks to be performed with the confidence that there is no exposure to hazardous levels of benzene. ■