MONITORING BENZENE AND CHOOSING AN APPROPRIATE MONITOR FOR PERSONAL PROTECTION AND COMPLIANCE WITH EXPOSURE LIMITS

WHAT IS BENZENE?

Benzene, CAS 71-43-2, is an organic compound having the formula C_6H_6. This is a highly flammable compound. A real world example of a fire involving Benzene is the Hazardous Material (HazMat) incident that occurred in a University of California Irvine (UCI) laboratory in 2001 (UCI lab fire). The incident involved a small quantity of Benzene but a laboratory was damaged and several people were wounded. However, a larger scale incident could have involved the nuclear reactor located on campus in a nearby building. Select data are presented below:

Typical Properties:

- Molecular Weight: 78.11 g/mol
- Vapor Density 2.1 (air=1)
- Flash Point: -11° C (12.2° F)
- Lower Explosive Limit (LEL): 1.2 % vol
- Upper Explosive Limit (UEL): 7.1 % vol

*Fischer Scientific MSDS

WHERE IS BENZENE USED?

Benzene is a major industrial chemical with petroleum being the main source from which the compound is derived. It is widely used as an intermediate in chemical processes used to produce products ranging from plastics to pesticides to pharmaceuticals. Key industries involved in the production or use of benzene include:

- Petroleum refining (Oil refineries)
- Coke and Coal manufacturing
- Rubber tire manufacturing
- Storage sites (tank farms)
- Transportation services (ships, tanker trucks)
- Laboratories
- Chemical manufacturing

In Europe the INRS provides a database of information from which estimates of exposure to Benzene for a number of industrial sectors. Regardless of the type of industry using Benzene the type of exposure, chronic or acute, occur. A typical scenario for either exposure event would be during routine operations involving plant, tank, piping, or shipping vessels/vehicles. These activities can involve large numbers of personnel working in the immediate vicinity of Benzene as opposed to managers or non-field staff which are normally protected due to distances. As a side note it is therefore important to recognize the need for monitoring equipment to be staged near the work site. Manual operations such as the filling of transport vessels may involve spillage or overflow of product containing benzene so it is recommended that a monitor capable of benzene specific monitoring is on site for the protection of personnel and to identify spills for cleanup.

In the United States benzene use is as a feedstock ingredient for the preparation of benzene-derivatives, examples are listed in the Table below.

Product	Percent of Benzene Use
Ethylbenzene	52
Cumene	22
Cyclohexane	14
Nitrobenzene	5
Chlorobenzenes	2
Linear detergent alkylate	2
Other	3

Source: Kirk-Othmer Encyclopedia of Chemical Technology.

BASIC BACKGROUND INFORMATION ABOUT BENZENE

Benzene is formed from both natural and human processes. Burning trees and geologic events such as volcanoes generate the chemical. Environmental exposure to benzene is found in large cities where concentrated release of hydrocarbon emissions is highest. Leakage of fumes from stored reserves of petrochemicals, incomplete combustion and in poorly maintained household sources such as leaky stoves or poorly vented heating systems.

Certain professions have higher risk of exposure due to constant contact with automobile fumes these being truck drivers, police, and conductors of urban buses. Although the base risk is the same as other people these types of professions have repeated daily exposure throughout their careers. The actual risk by measurement of the atmospheric readings of the European Counsel and the National Board of Health and Welfare is on the order of 10mcg/m3 of atmosphere or less, this being overall a low risk (INRS).

However, the industrial concerns regarding benzene include crude oil and gasoline. Benzene is widely used in the United States, ranking in the top 20 chemicals for production volume. As previously indicated benzene is important in the manufacture of other chemicals to make plastics, resins, and nylon and synthetic fibers. Benzene is also used to make:

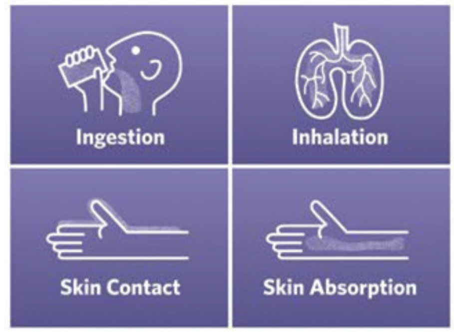
- Lubricants
- Rubbers
- Detergents
- Drugs
- Pesticides
- Dyes

WHY SHOULD WE MONITOR BENZENE?

Exposure to benzene can occur in manufacturing, transport and use of benzene in the oil, chemical and petrochemical industries. Exposure to this chemical may be important or very important for limited periods during routine and non-routine operations (refer to your local regulatory guidelines, agency, and hygienist). Benzene is a carcinogen, meaning it causes cancer.

In addition to triggering cancer, exposure to this compound at high concentrations in the 10,000 to 20,000 ppm range will result in death. Finally, Benzene is a suspected toxicant to numerous systems critical to life.
To include:

- Cardiovascular
- Endocrine
- Gastrointestinal
- Immunological
- Neurological
- Respiratory



MISSOURI HOUSEHOLD HAZARDOUS WASTE PROJECT

Results from a National Occupational Exposure Survey that over 400,000 people who worked around Benzene. Benzene is ranked overall near the top of the list of approximately 12,000 exposure events. Therefore it is important to prevent exposure of employees to this compound through one or more of the pathways shown in the graphic below. As shown, Benzene has numerous entry routes into the body. A combination of regulatory and professional agencies or organizations has established exposure limits to protect workers:

Exposure limits for Benzene

Agency/ Nation	TWA Type	TWA Value	STEL	LTEL
OSHA (US)	8-hour PEL	1.0 ppm	5.0 ppm	n/a
ACGIH	8-hour TLV	0.5 ppm	2.5 ppm	n/a
NIOSH (US)	10-hour REL	0.1 ppm	1.0 ppm	n/a
UK	8-hour	3 ppm[A]	No guideline	1 ppm[B]
France	8-hour	1 ppm[C]	No guideline	n/a
Germany	8-hour	1 ppm[D]	No guideline	n/a
Australia	8-hour	1 ppm[D]	No guideline	n/a

References: A = MSDS B = HPA Compendium C = INRS D = DGU

SYMPTOMS OF EXPOSURE

Include but are not limited to for [acute exposure events] drowsiness, headaches, impaired memory and certain psychological functions. Finally, benzene is responsible for irritation of the skin and mucous membranes (eyes and respiratory tract in particular). Chronic exposure to Benzene is dangerous as this chemical is highly toxic to blood cells and to bone marrow, thus production of blood cells is disrupted and anemia results. As previously mentioned the dose be it large amounts over a short duration or a low quantity over an extended period of time determines the anemia. Cancers such as myeloid leukemia and other forms documented in various studies also result from benzene exposure (note: it is beyond the scope of this work to discuss the cancers in any detail). The injuries associated with cell damage occur more frequently after low exposures and continuous and intermittent pollution episodes. Finally, it was demonstrated in animal studies that benzene can induce genetic damage that is transmitted to the offspring.

For additional information regarding preparing and responding to benzene or facts on this chemical please follow this Centers for Disease Control and Prevention link.

HOW DO WE MEASURE BENZENE?

Numerous technologies are available to detect Benzene; however, each has its strengths and limitations. Our primary consideration is to meet regulatory requirements to monitor and protect the health and safety of workers performing duties in environments where Benzene is or could be present. A short list of potential gas detection monitors and analyzers would initially include:

- Multi-gas monitors
- Gas detection tubes
- Semiconductor or Metal oxide sensors
- Laboratory Gas Chromatograph techniques (GC-MS/FID)
- Portable GC products
- Photoionization detectors with filter tubes

A Comparison of Monitoring Options

The various options are summarized in the table below based on key factors that are critical for making timely decisions based on reliable data regarding Personal Protective Equipment (PPE), work start/stop decisions after opening vessels, and compliance.

	PID	MOS	LEL	CMS	Tubes	UltraRAE 3000	GC
15 min continuous STEL monitoring						X	
Resolution	X			X		X	X
Sensitivity	X					X	X
Ease of use	X	X	X	X	X	X	
Lowest total cost of ownership	X	X	X		X	X	
Specificity				X	X	X	X

Multi-gas Monitors

These monitors typically measure oxygen (O_2), the lower explosive limit (LEL) of combustible gases, carbon monoxide (CO) and hydrogen sulfide (H_2S). Many products such as the MultiRAE also contain a photoionization detector (PID). To learn more about PID technology please read this RAE Systems PID Training Outline Application Note AP-000. The objective of monitoring for Benzene, particularly in environments such as refineries and fuel storage areas, demands a compound specific monitoring technique. While a PID provides the sensitivity to detect and monitor Benzene, by itself a PID lacks the specificity required to monitor this chemical.

The LEL sensor, be it a stand-alone sensor or part of a multi-gas monitor is designed to provide a response to VOCs present at concentrations that pose an explosive hazard. The amount of organic molecules in the vapor state meeting an explosive condition are several orders of magnitude above established exposure limits thus the threat we are attempting to mitigate, is long surpassed an a greater threat exists. Since our goal is to protect workers from exposure to a few ppm of Benzene an LEL sensor will not meet our needs.

MEASUREMENT TECHNIQUES FOR BENZENE: PID VS. GC/FID/MS VS. COLORIMETRIC TUBES VS. ULTRARAE 3000.

Single-use gas detection tubes

Colorimetric gas detection tubes have been used for gas detection for many years. These function by exposing a gas sample to a reagent. If the chemical of interest is present then a chemical reaction will occur and a color change in the tube is observed. The concentration of Benzene is determined based on the length of color change observed in the tube. Tubes are an inexpensive and have a legacy or history of being used to monitor toxic gases in the ppm range This type of monitoring technique has several limitations:

- Tubes only provide one-time snapshots.
- They do not provide continuous monitoring with alarms.
- The "spot check" nature of tubes also makes them more prone to sample error.
- Tubes are slow to respond.
- They give readings in minutes rather than seconds.
- Tube readings are subject to interpretation.
- Tubes expire
- The accuracy of detector tubes is usually agreed to as +25%

Semiconductor or Metal Oxide Sensors (MOS)

MOS sensors are one of the oldest and least expensive measurement technologies used in portable instruments. These have several shortcomings that limit their effectiveness:

- Lack Benzene specificity unless used in sophisticated sensor arrays
- Sensitivity is well above the detection range required to monitor Benzene
- MOS sensors are at best gross indicators of chemical concentration
- Relatively slow response times
- Respond positively to moisture and temperature

Gas Chromatograph/Mass Spectroscopy lab 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 lab, the tubes are desorbed and analyzed with gas chromatography/mass spectrometry. This is the most sensitive and selective method available and is used as the standard for comparison. During a plant turnaround, every minute of shut-down time is critical and much more rapid PID feedback is needed to make personal protective equipment decisions for workers.

- Laboratory based techniques require hours or days to complete
- This technique does not provide continuous monitoring

Portable GC Systems

Portable gas chromatographs, usually with PID or FID detectors, provide selective benzene measurements down to 0.1 ppm, but have several drawbacks.

- These are large and heavy thus difficult to use in confined spaces, on ladders, and catwalks.
- Relatively complex therefore it requires training and typically limits usage to an industrial hygienist.
- Sampling and analysis times require 5-10 minutes.

PHOTOIONIZATION DETECTORS

Photoionization detectors (PIDs) measure VOCs and other toxic gases in low concentrations, from ppb (parts per billion) up to 15,000 ppm or greater (parts per million, or 1.5% by volume) Isobutylene. A PID is a very sensitive broad-spectrum monitor which can be configured to scale readings for a particular compound so, when using on-board correction factors, the ranges will vary quite considerably.

Many industrial processes include VOCs such as Benzene. The sensitivity of PIDs to VOCs and their fast response time make them an invaluable tool for employee exposure monitoring and for quickly executing HazMat response tasks, including:

- Initial personal protective equipment (PPE) assessment
- Leak detection
- Perimeter establishment and maintenance
- Spill delineation
- Decontamination
- Remediation
- Confined
- space entry

Note: For a detailed description of how PIDs work, refer to RAE Systems Application Note AP-000: RAE Systems PID Training Outline and Technical Note TN-106.

- PID Pros
  - Immediate result, "point and shoot" – responds in seconds
  - Accurate and Precise to within ±10%
  - Low cost to operate and maintain
  - Does not require a chemist to operate
  - Little to no sample handling, storage, or preparation
  - Continuous real-time monitoring with alarm capabilities
  - Data logging
- PID Cons
  - Broad-spectrum monitor; is not specific to what it "sees" unless additional components are incorporated, such as separation tubes

A PID would be ideal for continuous monitoring of personnel working with Benzene except for one reason it cannot make Benzene specific measurements. To do so a PID requires an intermediate step in which the sample is passed through a pre-treatment tube prior to analysis.

PHOTOIONIZATION DETECTORS (PIDS) WITH FILTER TUBES [ULTRARAE 3000] AS AN OPTIMAL MONITORING METHOD

While PIDs are broadband detectors, they can give benzene-specific response by using a combination of a low-energy (9.8 eV) Ultraviolet lamp and pre-filter tubes that remove organic interferences. This system provides raPID response down to 0.05 ppm in one minute with an accuracy of +/-10%. Measurements of TWA-levels of benzene can be made in the presence of up to about 300 ppm 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 workers to make rapid PID personal protective equipment decisions and allows them to perform their job tasks with confidence that they are not being exposed to hazardous levels of benzene.

As previously reported in Technical Note TN-127 the GC-FID and the UltraRAE were shown to generate similar results and, therefore, correlate. Therefore the real-time monitoring capability of the UltraRAE for providing immediate information regarding protection of personnel becomes an important factor to consider. The UltraRAE 3000 can also be used to screen for VOCs; in other words, as a broadband detector. The PID does not require an annual calibration.

The UltraRAE 3000 has all of the benefits of a PID and since the filter tube makes the device compound specific the PID drawback is eliminated.

Alternatives

A market-available CMS uses a miniaturized double-tube system for benzene. This CMS requires approximately 10 minutes to measure at 0.5 ppm and cannot resolve readings below 0.5 ppm. Further the device requires annual calibration that must be performed by the manufacturer. Shipping the Benzene monitoring device to the manufacturer for calibration requires additional planning and logistics to support monitoring requirements as this need is continual.

UltraRAE 3000 vs. CMS

The UltraRAE 3000 has a built in temperature-pressure-humidity (TPH) sensor. This sensor monitors variations encountered in the field and corrects for these by factoring the reported values into the measurements. The final result displayed on the readout and recorded in the data log is the answer decision makers need in the field. The CMS lacks a TPH sensor therefore the End User must carry one or more additional instruments to record these data and then manually apply these corrections based on interpreting a chart. Ultimately the more independent working pieces introduced into a monitoring program require more logistical support in the form of metrology, parts, consumables, training, and the more chances for something to break or go wrong thus the integrity of the measurement is dubious. For example, if the End User neglects to synch measuring Benzene with the CMS and temperature, pressure, and humidity readings the calculated Benzene data are suspect and the tenants of keeping workers safe are violated.

In order for a CMS to perform measurements a cartridge must be used. In the case of the UltraRAE 3000 the handheld monitor can be used without a RAE-SEP tube, just like a PID, to monitor total volatile organic compounds (TVOC). As long as the TVOC value remains below the value related to Benzene there is no need to use a RAE-SEP tube. This is not true in the case of the CMS system; therefore the cost per use and total cost of ownership for a CMS are greater than that of an UltraRAE 3000.