Effective Benzene Monitoring Saves Lives

By Werner R. Haag, Ph.D.

Learn detection techniques for one of the most toxic fuel components.

Benzene is used in many industries as a solvent or chemical intermediate, and it is by far the most toxic component of gasoline, natural gas condensate, and similar fuels. (See Table 1.) It is also present in many processes as a contaminant or by-product, such as in steel mill coking operations, combustion gas stacks, and groundwater cleanup systems.

Benzene Toxicity and Measurement

Benzene is classified as a known carcinogen by the International Agency for Research on Cancer (IARC), the Environmental Protection Agency, and other agencies. Table 2 shows that OSHA, the American Conference of Governmental Industrial Hygienists (ACGIH), and the National Institute for Occupational Safety and Health (NIOSH) have set time-weighted average (TWA) limits of 1.0, 0.5, and 0.1 parts per million (ppm), respectively. Most industries use a TWA action level of either 0.5 ppm or 1.0 ppm.

Table 1. ACGIH* Exposure Limits for Various Fuel Components

Compound	ACGIH TWA (ppm)*
Benzene	0.5
Trimethylbenzenes	25
n-Hexane	50
Toluene	50
Xylenes	100
Cyclohexane	300
Octane	300
Heptane	400
Butane	800
Pentane	800

*ACGIH 8-hour time-weighted average (TWA).

Table 2. Exposure Limits for Benzene Vapors

Agency/Standards Body	TWA (ppm)	STEL (ppm)	IDLH (ppm)
OSHA Permissible Exposure Limit (PEL)	1.0	5.0	-
ACGIH Threshold Limit Value (TLV)	0.5	2.5	-
NIOSH Recommended Exposure Limit (REL)	0.1	1.0	500

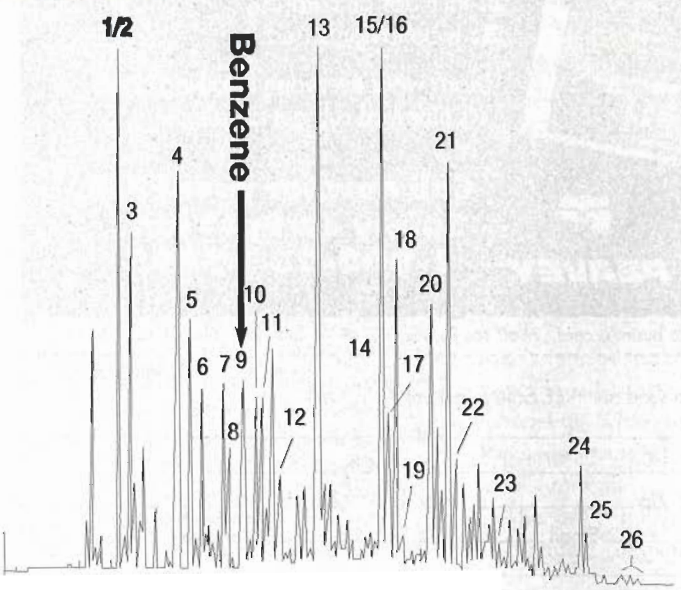
Source: ACGIH

Benzene in Fuels

In addition to the low action levels, benzene measurements are complicated by interferences. One of the most common exposure sources for benzene is from gasoline, where it is present as a mixture with a few hundred other compounds. Figure 1 shows benzene separation from other gasoline components using a laboratory gas chromatograph (GC). It is no small task for a portable instrument to specifically measure the benzene in this complex mixture. As noted in Table 3 on page 21, the TWA for gasoline as a whole is 300 ppm. Because benzene is much more toxic than other fuel components, it controls the overall toxicity of the gasoline. This point is illustrated in Figure 2 on page 21. When the concentration of benzene is more than 0.2 percent, it dominates the TWA calculation for the overall gasoline mixture. Most gasolines contain more than 0.2 percent benzene — typically 0.5 to 2 percent. If a broad-band detector were used to measure gasolines with this range of benzene, the readings would be almost the same, but the toxicities would differ by nearly 400 percent. Therefore, it is important to selectively measure benzene within a gasoline hydrocarbon mixture and not just total hydrocarbons.

Benzene is sometimes present in lower concentrations in other fuels such as diesel and kerosene. However, these two fuels have recently seen their ACGIH TWAs drop dramatically to about 12 ppm for diesel and 30

Figure 1. Laboratory Gas Chromatographic Separation of Benzene in a Gasoline Mixture



1. n-Butane
2. Isobutane
3. n-Pentane
4. 2-Methylpentane
5. 3-Methylpentane
6. n-Hexane
7. Methylcyclopentane
8. 2,4-Dimethylpentane
9. Benzene
10. 2-Methylhexane
11. 3-Methylhexane
12. n-Heptane
13. Toluene
14. Ethylbenzene
15. m-Xylene
16. p-Xylene
17. 2-Methyloctane
18. o-Xylene
19. n-Nonane
20. Propylbenzene
21. 1,2,4-Trimethylbenzene
22. n-Decane
23. n-Undecane
24. 2-Methylnaphthalene
25. 1-Methylnaphthalene
26. Dimethylnaphthalenes

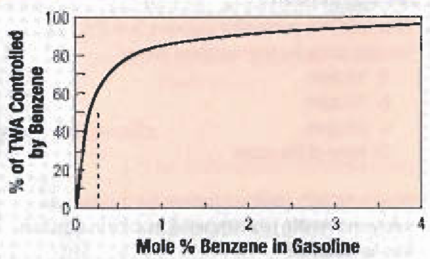
Source: Alltech Assoc. Inc., Deerfield, Ill.

ppm for kerosene (100 and 200 milligrams per cubic meter, respectively). The low benzene content and the higher toxicity of these fuels mean that diesel and jet fuel can and should be measured as total hydrocarbons, unlike gasoline. If diesel or jet fuel readings are below their TWAs, then most likely benzene is also below its TWA.

Table 3. ACGIH Exposure Limits for Various Fuels

Chemical	TWA (ppm)
Benzene	0.5
Diesel Fuel	12
Jet Fuel (Kerosene)	30
Gasoline	300

Figure 2. Gasoline TWA Controlled by Benzene



Percentage of gasoline TWA controlled by benzene, based on a benzene TWA of 0.5 ppm and a gasoline TWA of 300 ppm.

Table 4. Benzene Measurement Methods for Industrial Hygiene

Benzene Method	Advantages	Disadvantages
Colorimetric Tubes	Low cost. Marginal accuracy at 0.5 ppm.	Single point. Slow (5 to 10 minutes).
Automated Tubes	Moderate cost. Marginal accuracy at 0.5 ppm.	Single point. Slow (5 to 10 minutes).
Prefiltered PID	Small and lightweight. Fast (1-2 minutes). Good accuracy and specificity to 0.1 ppm.	Single point.
Portable GC	Good accuracy and specificity to 0.1 ppm. Measures other aromatics.	Single point. Slow (5 to 10 minutes). Heavy.
Portable Infrared	Good accuracy and specificity. Fast (<1 minute). Measures other aromatics.	Single point. Heavy. High cost. Detection limit of 2 ppm.
Transportable GC	Very accurate and specific. Measures other aromatics.	Single point, slow (10 to 50 minutes). Limited portability.
Badge or Activated Carbon Sampling and Lab Analysis	Most accurate and specific.	Single point, cumulative sample. High cost, very slow (days to weeks).

Combustible Gas Sensors

Benzene is a flammable vapor. However because of the low hygiene exposure limits, measurements are needed at much lower concentrations than a combustible gas sensor can detect. Catalytic bead lower explosive limit (LEL) sensors typically have detection limits for benzene of a few hundred ppm or, at best, 30 to 50 ppm. In addition, LEL sensors are broadband detectors that measure all the components of gasoline. LEL sensors have neither the sensitivity nor specificity to make accurate benzene measurements at TWA levels. In addition, LEL sensors are notoriously poor at measuring diesel and jet fuels; therefore, other sensors such as photoionization detectors (PIDs) or flame ionization detectors (FIDs) are needed to measure TWA levels of these fuels. With the new lowered TWA values, LEL sensor measurements no longer provide adequate protection.

Benzene Analysis Methods

Common benzene-specific methods with sensitivity approaching 0.5 ppm are shown in Table 4 and include colorimetric tubes, photoionization detectors (PIDs) using prefilter tubes, infrared detectors, portable GCs, transportable GCs, and sampling followed by laboratory GC analysis. Sampling methods rely on a gas bag or adsorbent such as activated carbon tubes or diffusive badge samplers, followed by laboratory analysis. This method is one of the most accurate, but it is relatively expensive and takes hours to weeks to get results back from the laboratory and thus cannot be used for real-time decisions. Colorimetric tubes provide closer-to-real-time results but still require several minutes and have limited accuracy near the action level of 0.5 ppm. Automated tube pump/readers are available that improve the accuracy somewhat but still require up to 10 minutes at 0.5 ppm benzene. Portable infrared detectors are fast and have good selectivity, they have detection limits over 1 ppm and are relatively expensive and heavy.

The most practical and accurate field-portable instruments are PIDs using pre-filter tubes and portable GCs. PIDs use a combination of a 9.8 eV lamp and filter tubes to specifically measure benzene. The instruments are lightweight at about one pound, and measurements are fast, taking about one to two minutes, and accurate to 0.1 ppm. The chief disadvantage is the need to dispose of the filter tubes after one use. However, the monitors can be used in total VOC (volatile organic compound) mode to monitor continuously, and a benzene tube is used only when something is detected. Portable GCs offer similar accuracy for benzene and can often also measure other aromatics such as toluene and xylene. They tend to be heavier, more complicated to operate, and more expensive and they take longer per sample.

Continuous Monitoring

None of the techniques in Table 4 give continuous monitoring at sub-ppm levels. There is currently no moderately priced sensor capable of detecting benzene accurately at 0.5 ppm that is both continuous and specific. One solution suitable for refinery analyzer shelters has been to use a PID with 9.8 eV lamp instead of the standard 10.6 eV lamp. Filters used to make the PID selective for benzene do not last long enough to run continuously. The 9.8 eV lamp has less interference to other fuel hydrocarbons than the 10.6 eV lamp and can detect down to 0.01 ppm. By setting the alarm limits to 0.5 ppm for all hydrocarbons detected, the safety professional can be assured that benzene is below that level. Other continuous benzene systems including infrared and pyrolysis sensors do not have the proper sensitivity and may be more expensive than a PID. **CM**

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Benzene References, Standards

- OSHA – Standard 29 CFR Part 1910.1028, osha.gov.
- NIOSH – Safety and Health Topic Web Page, cdc.gov/niosh/topics/benzene.
- ACGIH - 2005 ACGIH Guide to Occupational Exposure Values, (513-742-6163); Internet: acgih.org.