PI4012.0205

Continuous Environmental Monitoring of Benzene, Toluene, Ethyl Benzene, and Xylenes (BTEX)

Key Words

- Benzene
- Toluene
- Xylenes
- Fugitive Emissions
- Environmental Protection
- Toxic Gas
- Leukemia

Thermo Industrial Solutions Note

Introduction

Benzene is a known leukemia-causing carcinogen with a mandated maximum shift exposure of 1 ppm or 5 ppm for any 15-minute period. The VG Sentinel δB provides rapid detection of ppb levels of benzene in air drawn from various points on the plant, thereby providing early warning in the event of accidental benzene release.

Benzene is an aromatic hydrocarbon that is produced by the burning of natural products. It is a component of products derived from coal and petroleum and is found in gasoline and other fuels. Benzene is used in the manufacture of plastics, detergents, pesticides, and other chemicals.

People who work with benzene or who are exposed to it over a long period of time are at the highest risk for developing benzene-related illnesses, which range from anemia to cancer. Research has shown that individuals have developed and died from leukemia due to less than five years to more than 30 years of exposure to benzene. Long-term exposure may affect bone marrow and blood production. Short-term exposure to high levels of benzene can cause drowsiness, dizziness, unconsciousness, and death.

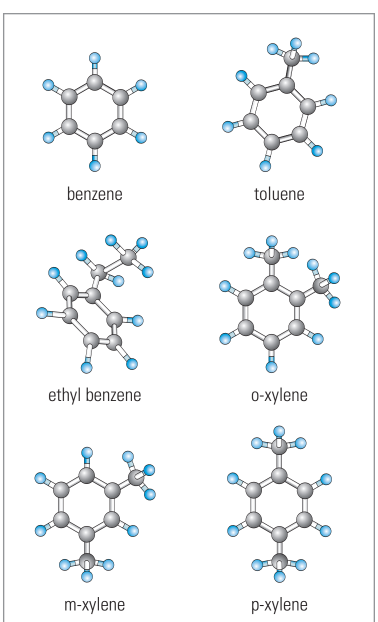


figure 1 – Aromatic Molecules

Worker Protection

Unfortunately, the odor of benzene does not provide adequate warning of its hazard and many blood disorders associated with benzene exposure may occur without symptoms. For these reasons, governments around the world mandate maximum allowable industrial exposure. In 1987, the U.S. Occupational Safety and Health Administration (OSHA) set the eight-hour shift maximum to 1 ppm* but recent studies suggest that this level may be too high. Researchers reported in the December 2, 2004 issue of *Science* that workers in a Chinese shoe factory exposed to less than 1 ppm of benzene experienced a significant decline in disease-fighting white blood cells. Further research will likely force a reduction in the OSHA "Action Level" from 0.5 ppm to 0.1 ppm—a level that can be accurately measured by the VG Sentinel δB.

Industrial Exposure

Workers in various industries that make or use benzene may be at risk of being exposed to high levels of this potentially lethal chemical. Industries that involve the use of benzene include oil refineries, chemical plants, coke oven plants and the rubber industry.

**OSHA Standard Number 1910.1028*

VG Sentinel δB
Environmental Mass Spectrometer

Today, most benzene is produced by the petrochemical industry using one of three processes. The output from a catalytic reformer provides a mixture of hydrocarbons that can be blended with hydrogen and exposed to a catalyst at high pressure to form aromatic compounds. The benzene is separated out using solvents. Alternatively, toluene can be used as the starter material in a process called hydrodealkylation. Finally, pyrolysis gasoline (a benzene rich liquid byproduct of the ethylene cracking unit) can be distilled to extract the benzene.

Traditional Monitoring Methods

Employers have the obligation of selecting a monitoring method which meets the accuracy and precision requirements of the prevailing standard taking into account the local unique field conditions. The OSHA standard, for example, requires that the method of monitoring must have an accuracy, to a 95 percent confidence level, of not less than plus or minus 25 percent for concentrations of benzene greater than or equal to 0.5 ppm. The traditional method of achieving this is to use field-deployed Summa canisters that are collected, once per shift, for laboratory analysis by gas chromatography/mass spectrometry (EPA Method TO-15). These six-liter, stainless-steel vacuum cylinders are so-called because their internal surfaces are passivated using a "Summa" process. Whereas this method complies with the law when the maximum exposure remains below the action level (0.5 ppm), it cannot be relied upon where there is the potential for this level to be exceeded. In such cases, the "breathing zone" of workers must be monitored in order to protect them at the short-term exposure limit (STEL) which is currently set at 5 ppm in the U.S.A. Current methods for measuring personal exposure include adsorbent tubes which are worn for several days. Once these are returned to the laboratory for analysis, the results can take several more days to come back. Clearly, neither of these methods is able to provide immediate warning of an accidental release.

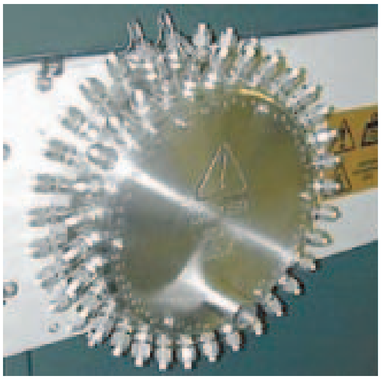
Online analysis using gas chromatography is sometimes used to provide real-time analysis, but the combined sampling and analysis times can be 15 minutes or more, so a large number of analyzers need to be deployed in order to provide an effective area monitoring system.

Area Monitoring by Mass Spectrometer

A very effective alternative is to use online environmental mass spectrometry. The VG Sentinel δB can monitor a single point in about 12 seconds and provides a measurement accuracy that cannot be matched by any other online technology. A typical installation will include the mass spectrometer configured to operate in a potentially hazardous area having at least one 64-port RMS providing 60 sample streams and four calibration ports.

The RMS continually draws on all the sample lines and diverts one sample stream at a time into the heated membrane probe where the pressure is dropped and the toxic organic molecules are preferentially leaked into the mass spectrometer ion source.

The VG Sentinel δB version of the RMS inlet is designed specifically to provide fast switching of high velocity sample gas and to do this without introducing the possibility of cross-port contamination. This highly reliable device is virtually maintenance-free and it can be operated at a high temperature when there is the potential for condensation of the sample vapors.



Rapid Multi-stream Sampler (RMS)

A proportion of the selected sample stream is leaked into the analyzer source where it is ionized by its interaction with an energetic beam of electrons. The charged particles are then accelerated into a scanning magnetic sector that sequentially separates sample ions of interest and measures the intensity of the signal generated at the detector. This arrangement provides a measurement that is linear over several decades and extremely stable over time. Detection limits of the order of 10 parts per billion (ppb) are routinely achieved when the VG Sentinel δB is configured for fugitive emissions monitoring. The short interval between measurements and the highly precise nature of the data ensures that leaks can be identified and corrected long before the mandated action limits are exceeded.

Interactions between the sample molecules and the energetic electrons of the ion source don't always result in the loss of a single electron. A proportion of the many interactions will result in the cleaving of some of the molecular bonds. Additionally, a fixed proportion of the molecules will include isotopes of carbon and hydrogen. The result of all the various fragmentation and isotope possibilities that exist with each molecular species is a unique 'fragmentation pattern' that can be used to identify and quantify the numerous gas components in a typical chemical plant atmosphere. Figure 4 illustrates the composite spectrum when benzene, toluene and xylenes are all present at similar

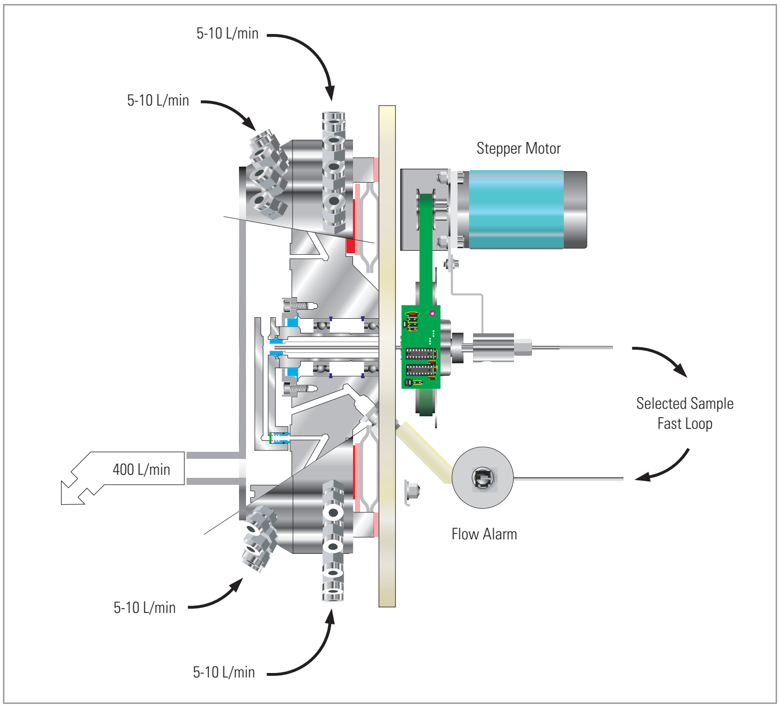


figure 2 - Sample Selection

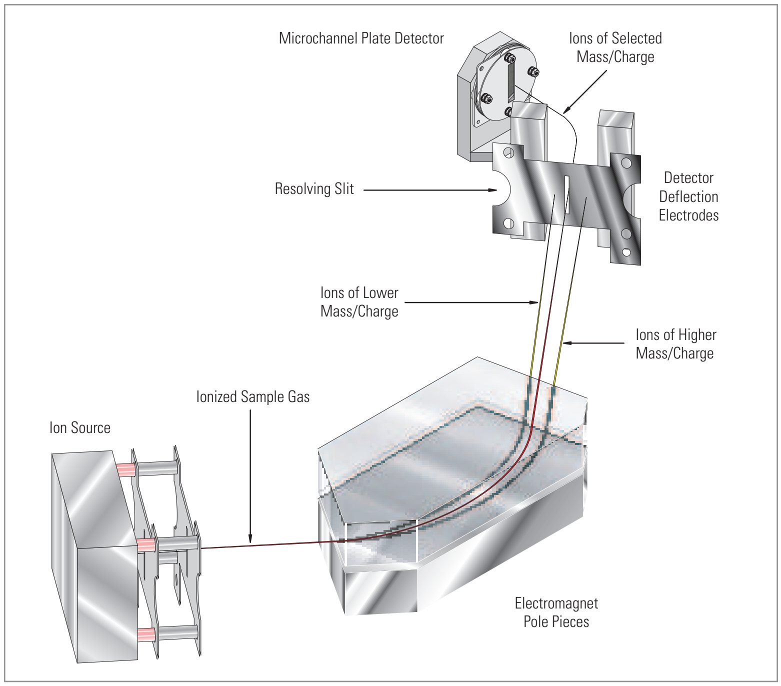


figure 3 - Scanning Magnetic Sector Mass Spectrometer

concentrations. Thermo's *VG GasWorks* software uses matrix inversion to correct for the interference illustrated in the histogram. The analysis of several overlapping or 'interfering' gas mixtures involves measurement by de-convolution of the overlapping peaks. The overlapping peaks, when combined, obey the principle of linear peak superposition. This states that the composite peak height at a particular mass is simply equal to the sum of the peak heights which correspond linearly to the individual concentrations of the contributing components in the mixture.

This may be represented as follows:

$$i_1 = s_1f_{11}c_1 + s_2f_{21}c_2 + s_3f_{31}c_3 + ...\ snf_1ncn$$

where i is a composite peak height, for 1 to n components contributing to this peak, s is the base peak sensitivity, f is its fragmentation pattern and c is its concentration. Values of s and f are determined for each component during calibration. During analysis the peak heights *(i)* are measured for 1 to n (or $>n$) masses so that there are at least n simultaneous equations to determine the unknown values of c. Matrix inversion is used to solve these sets of simultaneous equations. These calculations are executed easily and rapidly by the on-board computer within a fraction of a second, the complete analysis going from sample introduction to giving a reading of gas concentrations takes only seconds. The purpose of calibration is to accurately determine the values of f and s above; therefore overlaps are accurately dealt with and concentration values can be accurately determined.

Long-Term Stability

The high-energy scanning magnetic sector mass spectrometer provides a virtually drift-free analysis. The combination of extended (automated) calibration intervals and the highly reliable nature of the technology provides unattended active service times that often exceed 99.7%.

Analysis Time

A typical BTEX application will require a total of 12 seconds (inlet flushing time + magnetic sector scanning time + calculation time); therefore, 75 sample points can be measured within 15 minutes using a single mass spectrometer.

Benzene in Water

One or more of the VG Sentinel δB's sample ports can be hooked up to a Supported Capillary Membrane Sampler (SCMS) for measuring benzene and other volatile organic compounds in water. This allows a single mass spectrometer to monitor fugitive air emissions, point sources and wastewater discharges. A schematic diagram of the SCMS is shown in figure 6. In operation, a carrier gas of either air or nitrogen enters the probe via a 1/8-inch Swagelok® fitting.

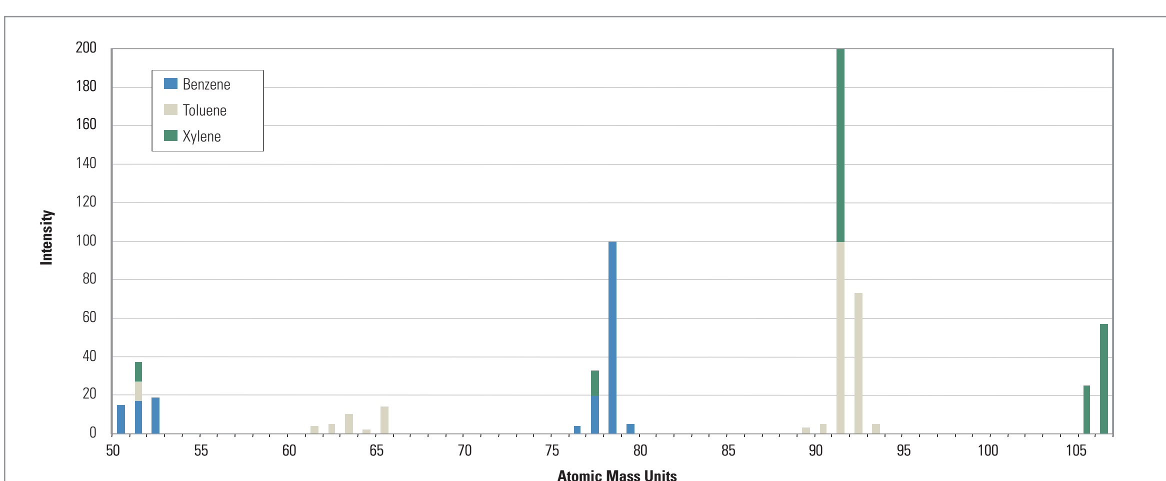


figure 4 - Composite Spectrum

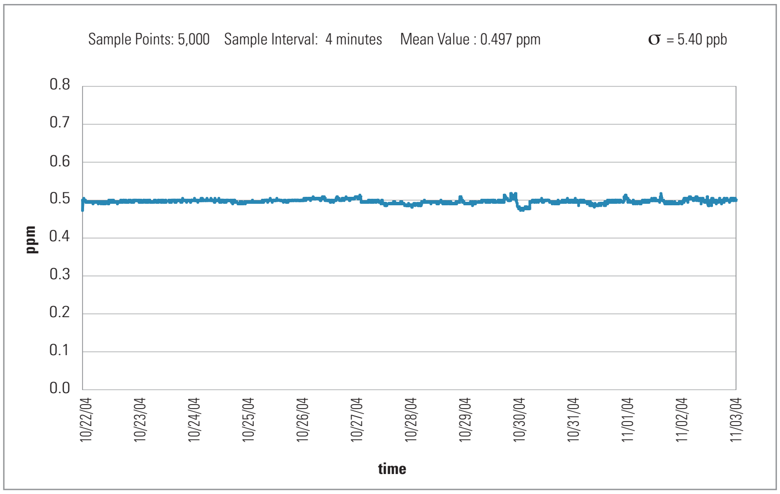


figure 5 - Benzene in Air Calibrated at the OSHA Action Level of 0.5 ppm

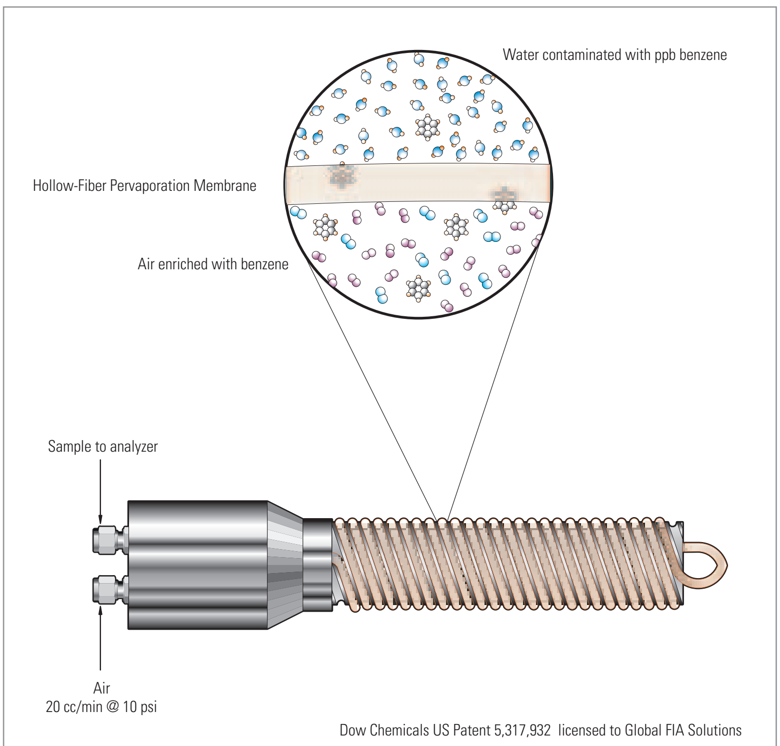


figure 6 - Supported Capillary Membrane Sampler (SCMS)

The typical gas flow through the device is 20 cc/min which is controlled by a simple flow meter and needle valve. When the probe is installed in a flow cell the 2 m length of silicone rubber capillary tube is in direct contact with the process water. Organic solvents permeate through the membrane into the carrier fluid. Initial calibration of the device requires a known concentration of benzene and a known temperature. The SCMS is typically calibrated at 5 ppb—the EPA maximum contaminate level (MCL) for benzene.

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