

The battle against benzene

Pete Traynor, Thermo Electron Corporation, USA, compares different methods open to employers for the environmental monitoring of benzene in a refinery scenario.

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. It is used in the manufacture of plastics, detergents, pesticides, and other chemicals such as ethyl benzene, cyclohexane, nitrobenzene, chlorobenzenes and maleic anhydride.

Benzene is a known leukemia causing carcinogen, which commonly has a mandated maximum average shift exposure of 1 ppm. The most common short term exposure limit is typically set at 5 ppm for any 15 minute period. People who work with benzene, or who are exposed to it over a long period of time, are at the highest risk of developing benzene related illnesses ranging from anemia to cancer. Research has shown that individuals have developed and died from leukemia with exposure to benzene over periods ranging from 5 - 30+ years. Long term (chronic) exposure may affect bone marrow and blood production. Short term exposure can cause drowsiness, dizziness, unconsciousness and death. Unfortunately, the odour of benzene does not provide adequate warning of its hazard - the odour threshold for recognition is approximately 100 ppm, which is 100 times the threshold limit value (TLV). Many blood disorders associated with benzene exposure may occur without symptoms.

For these reasons, governments around the world mandate maximum allowable industrial exposure. For example, in 1987 the US Occupational Safety and Health Administration (OSHA) set the 8 hour shift maximum to 1 ppm, but recent studies suggest that this level may be too high. Studies published in 1984 (Crump and Allen) and 1992 (Paustenbach et al) have predicted 3 - 5 lifetime risks per 1000 workers exposed to an average of 1 ppm (3.2 mg/m^3).

As a result of these model based predictions, benzene was the first carcinogen to be regulated by the European Union (EU) in their air quality directives initiative. In the 2nd December 2004 journal, *Science*, researchers reported 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 be likely to force a reduction in the OSHA 'Action Level', which is currently set to 0.5 ppm. The National Institute of Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for benzene is 0.1 ppm (8 hour time weighted average concentration) and 1

ppm for any 15-minute exposure.

Industrial exposure to benzene

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

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. This 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 that meets the accuracy and precision requirements of the prevailing standard, taking into account the local unique field con-



Figure 1. The VG Sentinel δB .

Table 1: 130 hour stability test of 0.5 ppm benzene standard	
Start date/time	22/10/04, 2:00 PM
End date/time	27/10/04, 11:59 PM
Elapsed time (H:M:S)	129:59:47
Records	7822
Sample time seconds	12:00
Sample interval seconds	57:00
Mean value (ppm)	0.497
Standard deviation (ppb)	4.63

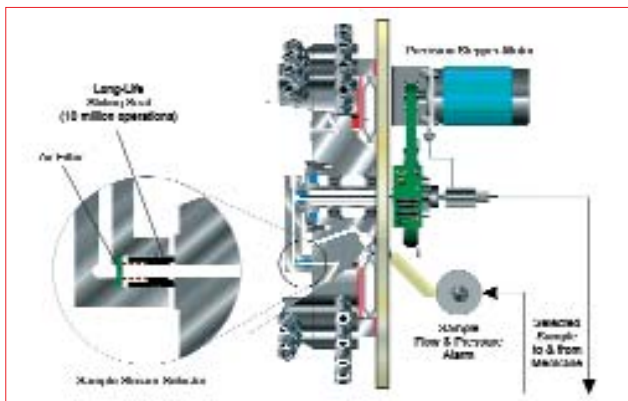


Figure 2. RMS Inlet.

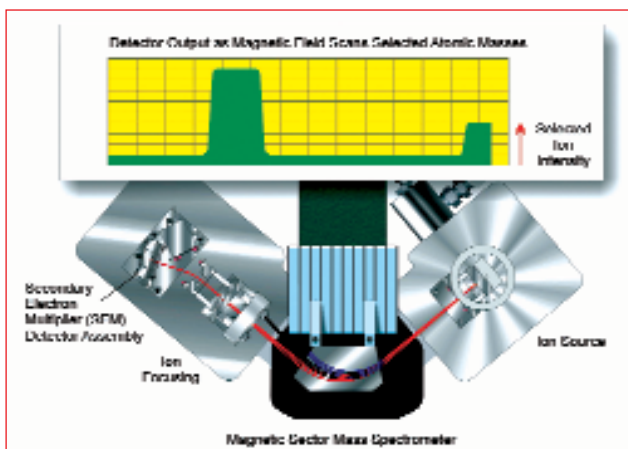


Figure 3. Scanning Magnetic Sector with EI Source.

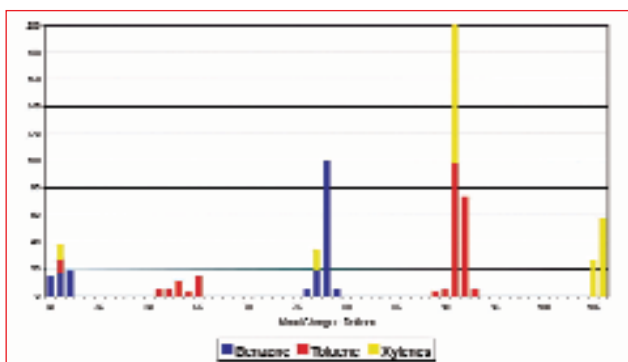


Figure 4. Linear peak superposition of overlapping spectra.

ditions. The OSHA standard, for example, requires that the method of monitoring must be accurate up to a 95% confidence level: no less than +/- 25% 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 and replaced at an interval that can vary from once a

shift to once a week, or even longer. These six litre stainless steel vacuum cylinders are so called because their internal surfaces are passivated using a 'Summa' process. This electro-polish chemical treatment ensures that a surgically clean internal surface can be provided such that any contaminants detected in the captured gas can safely be assumed to represent the atmosphere at the test site. When the canisters are first located at the test site, they are under high vacuum and free from gaseous impurities. A leak valve is set to allow a steady rise in pressure to occur over the period of the test. When the test interval has expired, the canisters are collected and shipped to the laboratory for analysis by gas chromatography/mass spectrometry (EPA Method TO-15).

Whereas this method often complies with the law in cases where the maximum benzene concentration remains below the 0.5 ppm action level, 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) currently set at 5 ppm in the USA. Current methods for measuring personal exposure include adsorbent tubes (coconut shell based activated charcoal material), which are worn for the duration of the shift. These sensors are periodically sent to the lab for testing in order to provide a historical record of exposure for each individual worker. In the event that the STEL is exceeded, the individual must be re-assigned to duties that avoid further exposure. As the results can take several days to come back from the lab, neither of these methods is able to provide immediate warning of an accidental benzene 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 analysers 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 (EMS) (Figure 1). A magnetic sector based system such as the VG Sentinel δ B (Thermo Electron Corporation) can provide rapid measurement of many toxic volatile organic compounds (VOCs) in a fully software configurable system. The EMS 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. A typical refinery analysis would include measurements of benzene, toluene, ethyl benzene and xylenes (BTEX) with additional site specific VOCs added as required. A typical installation will include the mass spectrometer configured to operate in the potentially hazardous area, having at least one 64 port Rapid Multistream Sampler (RMS), providing 60 sample streams and four calibration ports (Figure 2). Such a system can accurately monitor a single point in approximately 12 seconds so that each of the 60 sample points is measured every 12 minutes, protecting workers at the STEL.

Principles of operation

The RMS continually draws on all the sample lines, and diverts one sample at a time into a heated membrane probe where the pressure is dropped and the organic molecules are preferentially leaked into the mass spectrometer ion source. Electron ionisation (EI) is used to both ionise and fragment the molecules (Figure 3). The source produces a high energy (1000 eV), which

is accelerated into a perpendicular magnetic field produced by an electromagnet under the control of a microprocessor. The forces exerted on the individual ions affect the curved trajectory such that only ions with the selected mass to charge ratio make it through the resolving slit where they are detected by a microchannel plate (MCP) detector. Interactions between the sample molecules and the energetic electrons of the ion source produce different results depending upon the nature of each individual interaction. A statistically stable proportion of these interactions will result in the loss of a single electron. A proportion of the many collisions 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 concentrations. The EMS software, which operates under a real time operating system, 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. When combined, the overlapping peaks 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 that correspond linearly to the individual concentrations of the contributing components in the mixture. This could be represented as:

$$i_1 = s_1f_1c_1 + s_2f_2c_2 + s_3f_3c_3 + \dots + s_nf_1c_n -$$

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' 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, with calculations 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 determine the values of f and s above with accuracy, so that overlaps are accurately dealt with and concentration values can be accurately determined. The high energy scanning magnetic sector mass spectrometer provides a virtually drift free analysis (Table 1). 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%.

Benzene in water

One or more of the EMS sample ports can be hooked up to a

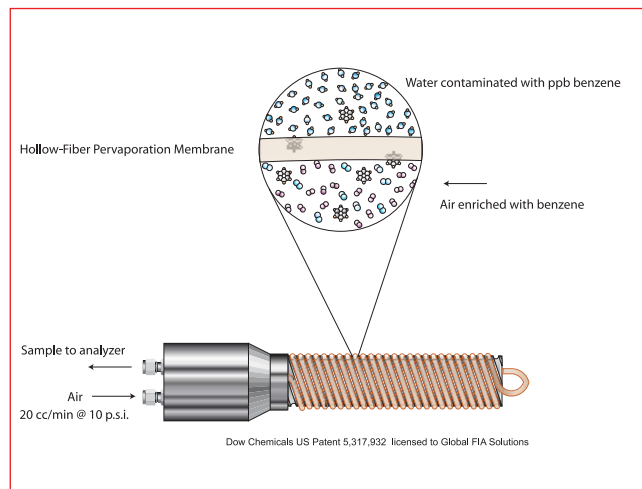


Figure 5. A schematic diagram of the SCMS.

Supported Capillary Membrane Sampler (SCMS) for measuring benzene and other volatile organic compounds (VOCs) 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 5. In operation, a carrier gas of either air or nitrogen enters the probe through a standard compression fitting. 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 contaminates level (MCL) for benzene.

Conclusion

A modern environmental mass spectrometer installation can provide broad coverage and rapid response when configured to monitor fugitive and point source emissions. Experience has shown that the incidence of alarms tends to be high when the equipment is first installed, but correction of accumulated leaks and improvements to standard operating procedures leads to a significant reduction in toxic emissions at the facility. The reliable nature of the technology and the flexible configuration options ensure that cost of ownership remains low. The ability to measure benzene with ppb repeatability ensures that future environmental regulations for benzene will not compromise the installation. ■

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