Application note | 1535

Sentinel PRO process mass spectrometer

Continuous monitoring of benzene, toluene, ethyl benzene, and xylenes (BTEX) in air

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Keywords

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Introduction

Benzene is an aromatic hydrocarbon produced by the incomplete combustion of many materials and is naturally found as a trace level component of crude oil, petroleum and coal. It is used to manufacture plastics, detergents, pesticides, and other chemicals such as ethyl benzene, cyclohexane, nitrobenzene, chlorobenzenes and maleic anhydride. It is a known leukemia-causing carcinogen and people who work with or are exposed to benzene over a long period of time have a high risk of developing benzene-related illnesses, ranging from anemia to cancer. Research has shown that individuals have developed, and died from, leukemia when exposed to benzene for periods varying from five years to thirty years. Long-term (chronic) exposure can affect bone marrow and blood production. Unfortunately, the odor of benzene does not provide adequate warning of its hazard and many blood disorders related to benzene exposure can occur without symptoms. Short-term exposure to high levels of benzene can cause drowsiness, dizziness, unconsciousness, and even death. For these reasons, governments around the world mandate maximum allowable industrial exposure levels of benzene.

The most common short-term exposure limit is 5 ppm (16 mg/m^3) for any 15 minute period, developed by the US Occupational Safety and Health Administration (OSHA) as a Permissible Exposure Limit (PEL). OSHA also specifies that “the employer shall assure that no employee is exposed to an airborne concentration of 1 ppm benzene in air as an 8-hour time-weighted average.” They also use “Action Levels” to indicate the level of a harmful or toxic substance which requires medical surveillance, increased industrial hygiene monitoring, or biological monitoring. The Action Level for benzene is just 0.5 ppm as an 8-hour time-weighted average (TWA). The US National Institute for Occupational Safety and Health (NIOSH) has even lower recommended exposure limits (RELs) of just 1 ppm over a 15 minute period and 0.1 ppm over 8 hours[1].

Table 1 shows the typical short-term and TWA limits for the aromatic compounds commonly grouped together as “BTEX” – benzene, toluene, ethyl benzene and xylene. The detection limits for the Thermo Scientific™ Sentinel PRO Environmental Mass Spectrometer are shown as a comparison; they are significantly lower than the legal requirements so leaks can be identified and corrected long before the mandated action limits are reached or exceeded.

Table 1. Typical exposure limits and Sentinel PRO detection limits for BTEX

Compound	MW	OSHA PEL STEL ppm	OSHA PEL 8-hour TWA ppm	NIOSH REL STEL ppm	NIOSH REL 8-hour TWA ppm	Sentinel PRO detection limit
Benzene	78	5	1	1	0.1	< 5 ppb
Toluene	92	300	200	150	100	< 5 ppb
Ethyl benzene	106		100	125	100	< 5 ppb
Xylene	106		100	150	100	< 5 ppb

Traditional monitoring methods for benzene

Employers have an obligation to select a monitoring method which meets the accuracy and precision requirements of the prevailing standard taking into account the unique local field conditions. The OSHA standard, for example, requires that the method of monitoring must have an accuracy, to a 95% confidence level, of not less than ±25% for concentrations of benzene greater than or equal to 0.5 ppm.

The traditional method of achieving this was to use field-deployed Summa canisters that were collected, once per shift, for laboratory analysis by gas chromatography/mass spectrometry[2, 3]. These six-litre, stainless-steel vacuum cylinders are so-called because their internal surfaces are passivated using a “Summa” process. This method may comply with the law when the maximum exposure remains below the action level (0.5 ppm), but it cannot be relied on if this level can potentially be exceeded. In such cases, workers’ “breathing zones” must be monitored to protect them at the short-term exposure limit (STEL), which is typically set at 5 ppm. One method for measuring personal exposure is to wear adsorbent tubes for several days. These are then returned to the laboratory for analysis, but the results can take several days to come back. Clearly, neither of these methods is able to provide immediate warning of an accidental release.

In the past, online gas chromatography was sometimes used, but the combined sampling and analysis times can be 15 minutes or more. This indicated a need for analyzers to provide an effective area monitoring system for a large industrial complex. Furthermore, benzene may not be the only volatile organic compound (VOC) in the air around an oil refinery or petrochemical complex—there will almost certainly be the other BTEX aromatics–toluene, ethyl benzene and xylenes. As can be seen from Table 1, these are not as harmful as benzene but they still need to be monitored, and if using a gas chromatograph (GC), it is vital that the GC separates them from benzene to avoid spurious false alarms. This separation requirement will only increase the GC’s analysis cycle time.

Area monitoring by mass spectrometry

An effective alternative to a GC is to use online mass spectrometry, which provides fast, multi-component gas analysis. One mass spectrometer (MS) can provide total plant coverage; our Sentinel PRO monitors a single sample point for benzene, toluene, ethyl benzene and xylenes (BTEX) in just 12 seconds, including stream settling time. Therefore, 60 sample points can be monitored in just 12 minutes, assuming all points are assigned equal priority. If some sample points are more important than others (because of a higher level of personnel activity or a higher risk of leaks) these can be assigned higher levels of priority, ensuring they are monitored more frequently.

Advantages of magnetic sector mass spectrometry

The MS is required to monitor a wide range of volatile organics in air; if this data is to be used as part of a site monitoring strategy it must be accurate and reliable. The MS uses electron ionization to both ionize and fragment the molecules. Each molecule produces a unique “fragmentation pattern,” which can be used to identify and quantify the numerous gas components in a typical chemical plant atmosphere. The result of all the various fragmentation and isotope possibilities that exist for all the volatile organics present in a typical plant environment is a complex composite spectrum. As an example, Figure 1 shows the mass spectra fragmentation patterns of benzene, toluene, ethyl benzene and o-xylene from the National Institute of Standards and Technology (NIST) library[4].

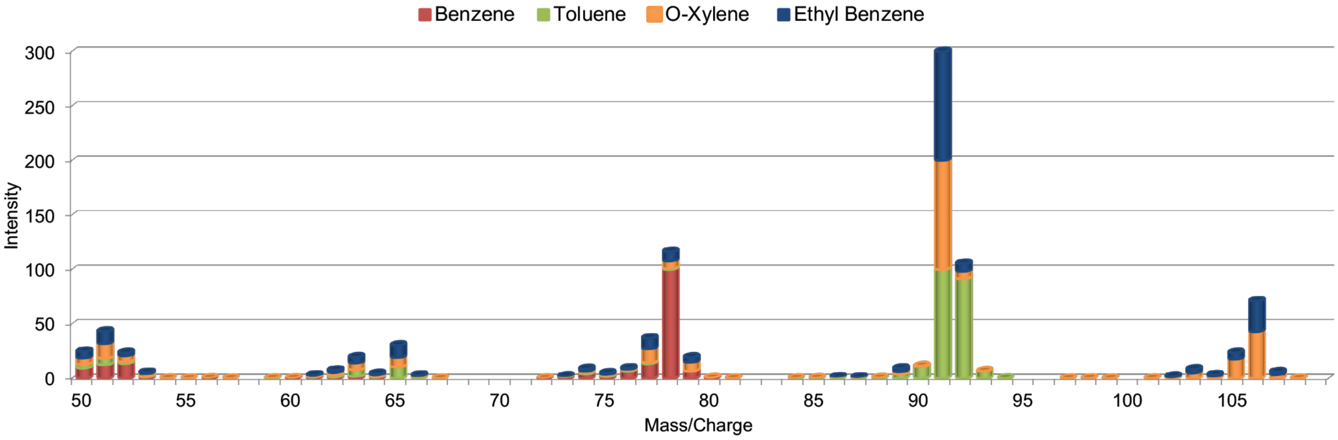
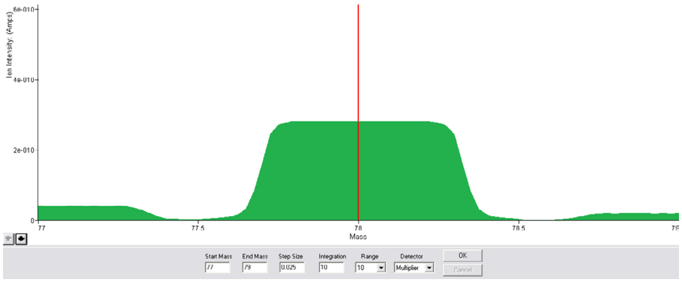


Figure 1. Composite mass spectrum of benzene, toluene, ethyl benzene and o-xylenes (NIST)

If the MS is to differentiate between high levels of a relatively harmless VOC and low levels of a toxic or carcinogenic VOC, it must be able to measure these fragmentation patterns accurately. Also, if the MS is to have high availability, these fragmentation patterns must be stable over time, otherwise the MS will need frequent recalibrations. There are two types of MS that have been used for environmental monitoring, quadrupole and magnetic sector. Thermo Fisher Scientific manufactures both types; over thirty years of industrial experience have shown the magnetic sector based analyzer offers the best performance for both process and environmental industrial gas analysis.

Key advantages of magnetic sector analyzers include improved precision, accuracy, long intervals between calibrations and resistance to contamination. Typically, analytical precision is between 2 and 10 times better than a quadrupole analyzer, depending on the gases analyzed and complexity of the mixture.

A unique feature of the Sentinel PRO magnet is that it is laminated. Our analyzer scans at speeds similar to that of quadrupole analyzers, offering the unique combination of rapid analysis and high stability. This allows the rapid and extremely stable analysis of an unlimited number of user-defined gases. The scanning magnetic sector is controlled with a precise magnetic flux measuring device for extremely stable mass alignment. Figure 2 shows the molecular ion peak for benzene at 78 atomic mass units (AMU) measured with Sentinel PRO, showing the magnetic sector analyzer's characteristic flat-top peak. As the height of the peak is directly proportional to the concentration of the molecule, we can measure the peak height anywhere across the peak top to obtain the correct result; the magnetic sector analyzer is therefore inherently fault tolerant.



Start Mass 77
End Mass 79
Step Size 0.025
Integration 10
Range 10
Detector Multiplier

Figure 2. Analog scan of benzene's mass 78 peak with Sentinel PRO's magnetic sector analyzer showing characteristic flat-top peak

Multistream sampling

If the MS is to provide total plant coverage it must have a rugged multi-stream sampling system that offers fast, reliable stream switching with no cross-contamination between streams. Thermo Fisher Scientific developed the original Rapid Multistream Sampler (RMS) 35 years ago to meet these requirements; this highly reliable device is now on its 3rd generation and is virtually maintenance-free. A cross section of the RMS is shown in Figure 3. The stepper-motor driven device diverts one sample stream at a time to the mass spectrometer and records the flow for each stream in turn.

The RMS is available with either 32 or 64 sample points; if more sample points are required then two RMS units can be used in series, giving a total of 127 sample points.

There are hundreds of these stream selectors around the world on a wide range of process and environmental applications and the RMS remains the only multi-stream sampling system with a standard 3-year warranty.

The selected sample from the RMS is diverted past a membrane inlet through which sample gas permeates into the mass spectrometer ion source, where it is ionized by collisions with a high-energy electron beam. A key feature of the membrane inlet is that organic compounds have much higher permeation rates than the main inorganic air gases (N_2, O_2, Ar and CO_2), and are therefore detected with much higher sensitivity. The resulting positively charged ions are then accelerated into the scanning magnetic sector that sequentially separates the ions 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 in the parts per billion (ppb) range are routinely achieved when the Sentinel PRO is configured for fugitive emissions monitoring.

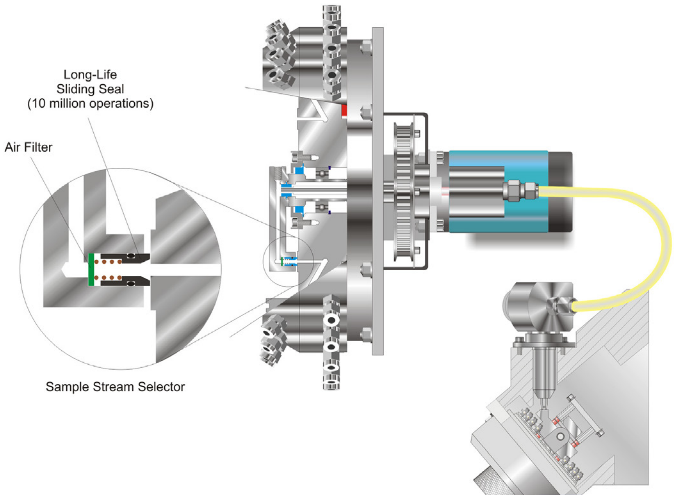


Figure 3. Rapid multistream sampler (RMS) cross section

Total plant monitoring

The Sentinel PRO is able to monitor a wide range of VOCs at ppb and ppm level, however there are some compounds that are not particularly suited to MS analysis, or may be present at higher concentration ranges than the MS can handle. For example, monitoring for explosion risks requires the measurement of total hydrocarbons (THC) with a Flame Ionization Detector (FID). The RMS has an optional Remote Analyzer Connection which enables the selected stream from the RMS to be fed to another analyzer; this is shown in Figure 4. The output from the THC is combined with the MS data to monitor both trace levels of target toxic & carcinogenic compounds and higher levels of flammable organics, providing fast location of emissions and resulting in a more leak-tight plant.

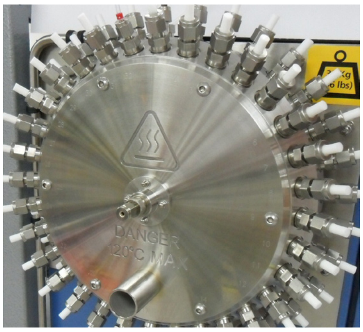


Figure 4. Rapid multistream sampler (RMS) with remote analyzer connection

System linearity

It is vitally important that the system's response is linear as the benzene level rises from zero to an early warning level and then, if corrective action is not taken, on to the high alarm level. Figure 5 shows a benzene linearity test designed to prove this performance for a customer. The system had to analyze a calibration cylinder of 3 ppm benzene within ± 0.15 ppm; the sample was then diluted to the high alarm level of 1.5 ppm, then to the early warning alarm level of 0.5 ppm. The benzene reading had to be within ± 0.08 ppm for the high alarm and ± 0.03 ppm for the early warning alarm level. The system was also set up to look for methyl cyclopentadiene, styrene and vinyl toluene, also present in the plant atmosphere. The system read zero for all three interfering compounds and easily met the benzene linearity specification.

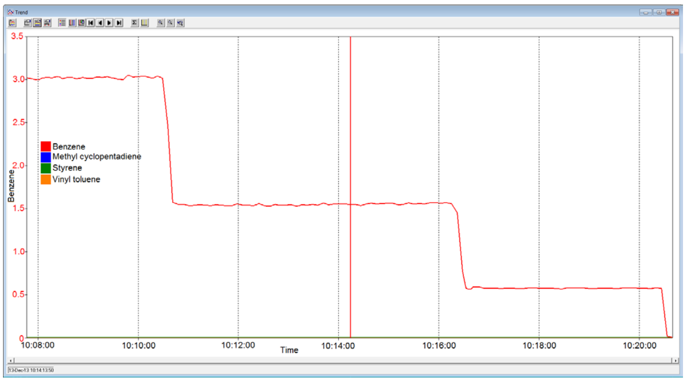


Figure 5. Benzene linearity check

Stability and selectivity

Figure 6 shows a 56 hour stability check on a cylinder nominally containing 3 ppm benzene in air. The readings are extremely stable with a Standard Deviation of just 20 ppb (0.75% relative) over more than two days. At the same time the system was set up to look for vinyl toluene and styrene. Both of these VOCs read zero concentration, once again demonstrating the system's inherent selectivity.

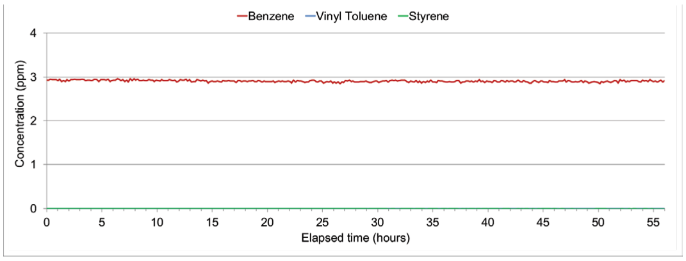


Figure 6. 56 hour stability run on 3 ppm benzene

Figure 7 shows data from a customer experiment. The system was challenged with high levels of toluene while benzene was held at 100 ppm, xylene and ethyl benzene at 0 ppm. There is no measurable interference from these high toluene levels, even when toluene level exceeded 1,600 ppm.

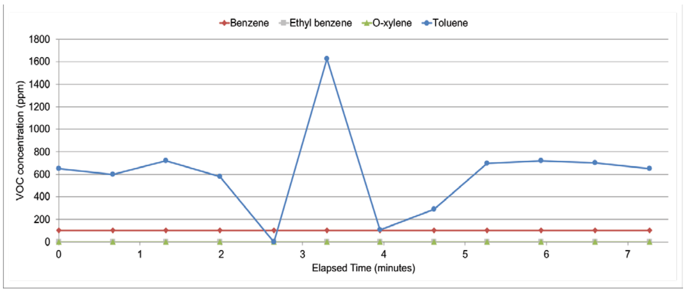


Figure 7. Benzene selectivity test

Summary

Sentinel PRO provides 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 lead to a significant reduction in toxic emissions at the facility. The reliable nature of the technology and the flexible configuration options ensure that the cost of ownership remains low. The ability to measure benzene and other aromatics with ppb repeatability ensures that future environmental regulations for benzene will not compromise the installation.

- **RMS inlet for fast, reliable multipoint sampling**
  - Up to 127 sample points
- **Membrane inlet for high sensitivity**
  - Detection limits much lower than legal exposure limits
- **Magnetic sector MS for highest precision and stability**
  - Ensures trace components are identified even in complex mixtures
  - Infrequent calibration for maximum availability
- **Multiple compounds monitored by one system**
  - Other VOCs can be added with no additional hardware
  - Remote analyzer connection option for other gas analyzers
- **Standard three year warranty**

References

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3. EPA Method TO-15, Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)
4. NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/)

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