

Multi-Point Environmental Analysis of Hazardous Air Pollutants

P E T E T R A Y N O R

An effective central monitoring system, based on either FTIR or EMS, can be used to provide comprehensive and actionable monitoring of a wide range of hazardous air-born pollutants.

Abstract

Environmental analysis of hazardous air pollutants (HAPs) fall into three categories: laboratory analysis of captured sample; broad-area real-time analysis (along a fence line for example); and point-specific real-time analysis. The latter might include point source emissions from stacks or fugitive emissions measured at strategically located test points. The preferred technologies for multi-component point-specific analysis include extractive FTIR and magnetic sector mass spectrometry. The FTIR analyzer takes advantage of the fact that most molecules absorb infrared radiation and the absorbance occurs in a characteristic pattern that is very reproducible. The modern process FTIR analyzer provides high spectral resolution for a quantitative breakdown of the composition of potentially contaminated air or stack gas. The different vibrational modes that result in the absorbance spectrum can be used to identify compounds from a library of standard spectra. On the other hand, the mass spectrometer identifies the trace components in air by fragmenting sample molecules in order to generate a mass spectrum that can also be used to quantify target compounds. This paper considers the advantages and disadvantages of these complimentary technologies and provides some guidelines to help with the selection of the most appropriate technology for a given environmental application.

Traditional Monitoring Methods

The monitoring method at a given site will depend upon a number of local unique factors such as the likelihood of a HAP release, the

risk to personnel posed by an accidental release and the local regulations in place at the site. It is often considered satisfactory to place a sample collection device, such as a summa canister, at a potentially hazardous location where it is left to collect an air sample over a period of hours or days. Once the integration interval has expired, the canister will be collected and shipped to an off-site

laboratory for analysis by gas chromatography/mass spectrometry (GC-MS). OSHA standards will typically specify the accuracy and repeatability of the measurement at a concentration equal to the "action level" for a given pollutant. In the event that the time-weighted average concentration exceeds this level then steps must be taken to identify the source of

release and in some circumstances, to reassign workers to areas where future exposure is unlikely. The obvious problem with this methodology is that a potentially dangerous toxic release isn't discovered until many days after

The monitoring system should provide many sampling points distributed throughout the manufacturing unit and product storage areas.

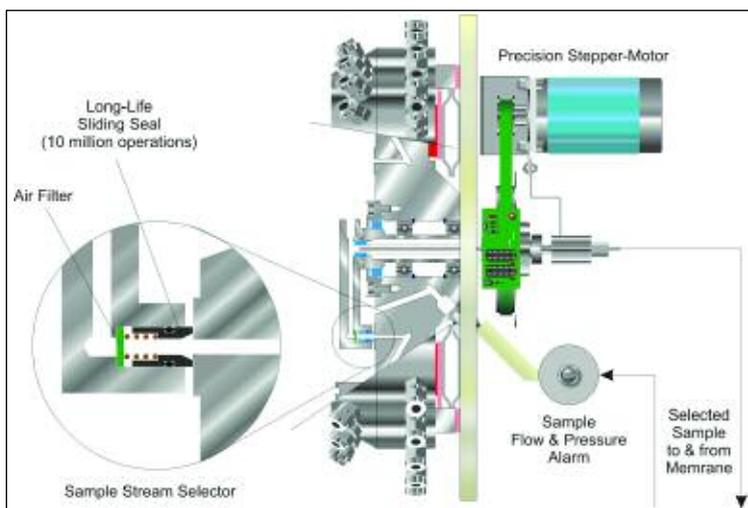


Figure 1 – Rapid Multistream Sampler (RMS)

the event. Even in situations where on-site analysis is available, the purge-and-trap type of device will only provide an average concentration for the duration of the test. Any potentially dangerous toxic spikes will be missed and there will be no information regarding the likely source of the pollutant.

An alternative that provides real-time analysis is Open Path Fourier Transform Infrared (OP-FTIR). These instruments provide real-time, continuous measurement of a broad range of volatile organic and inorganic compounds. An OP-FTIR system generally consists of an IR source, interferometer, a transmitting optical device, a receiving optical device, a detector, and computer for interpreting and recording the data. Any FTIR device will obey Beer's Law which states that for a constant path length the intensity of the incident light energy traversing an absorbing medium diminishes exponentially with concentration. A large uncertainty in the OP-FTIR measurements occurs due to the fact that measured concentrations are divided by the path length, based on the assumption that distribution of a toxic air pollutant is uniform throughout the path. In reality, plumes from emissions sources may be highly concentrated in a narrow cloud. The data provided are real-time but they don't localize the source or accurately represent the exposure experienced by an individual.

Multi-Point, Multi-Component Monitoring

Large-scale chemical processing units like the ones found in refineries and petrochemical plants can suffer from leaks that go undetected and contribute to a potentially hazardous local environment. These fugitive emissions need to be detected early before the damage they

cause becomes irreversible. Ideally, the monitoring system should provide many sampling points distributed throughout the manufacturing unit and product storage areas. The analytical methodology should provide accurate, sensitive, species-specific measurements so that appropriate actions can be taken immediately. 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. For many target HAPs, particularly volatile organics, the magnetic sector mass spectrometer is king. A monitoring system based on this technology will provide a very fast (typically 10-20 seconds per point) analysis with detection limits in the parts-per-billion range. Although this type of technology is relatively expensive, the comprehensive coverage that it can provide results in a very cost-effective installation, especially when compared with a GC-based system. 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 4

calibration ports (Figure 1). When dual-RMS inlets are provided, a single analyzer will measure as many as 100 sample points within 15 minutes so that short-term exposure levels can be accurately recorded for the entire facility. Table 1 details some of the VOCs that are routinely measured using environmental mass spectrometry (EMS).

Mass Spectrometer 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 ionization (EI) is used to both ionize and fragment the molecules. The source produces a high energy (1,000 electron Volts) beam that is accelerated into a perpendicular magnetic field produced by an electromagnet under the control of a microprocessor (Figure 2). The forces exerted on the individual ions effect 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 micro channel plate (MCP) detector. Interactions between the

Acetonitrile	Dimethylacetamide	Methyl tertiary-butyl ether
Acrylonitrile	Dimethyl formamide	Propylene oxide
Benzene	1,4 Dioxane	Perchloroethylene
Butadiene	Epichlorohydrin	Styrene
Carbon disulfide	Ethyl benzene	Tetrahydrofuran
Carbon tetrachloride	Ethyl lactate	Tetrachloroethylene
Chloroform	Hexamethyldisilane	Vinyl acetate
Chlorobenzene	Methyl bromide	Vinyl bromide
Cyclohexane	Methyl ethyl ketone	Vinyl chloride
Dichloromethane	Methyl iodide	Xylenes

Table 1: VOCs that are routinely measured using environmental mass spectrometry

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.

Extractive FTIR Principles of Operation

The mass spectrometer option works best when a fixed list of known target VOCs need to be monitored.

The multistream selector will be very similar to the one used with the mass spectrometer but the sample gas will be directed to a folded-path 10m gas cell (typically). FTIR instruments use a device called an interferometer (Figure 3) to improve sensitivity, speed and spectral resolution (the ability to differentiate different molecules). The interferometer includes an IR beam-splitter that sends the beam to both a fixed mirror and a laser-controlled moveable one. The infrared light is recombined at the beam-splitter, passed through the sample gas cell and then

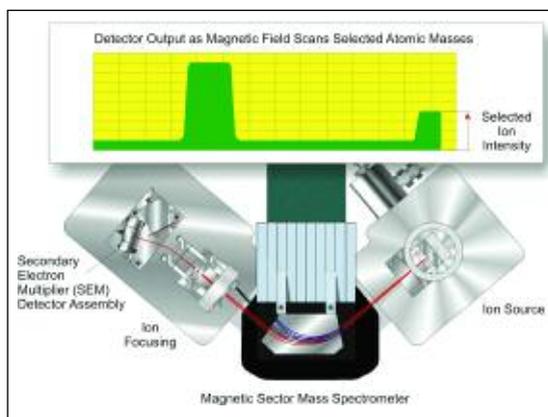


Figure 2 – Mass Spectrometer Operation

on to the detector. The resulting “interferogram” is transformed into a frequency domain signal by a mathematical technique termed Fourier Transformation. An absorbance spectrum is obtained by referencing the frequency-domain spectrum against a background measurement, providing information unique to the sample. This absorbance spectrum is further processed to report individual molecular concentrations.

The standard process FTIR employs a deuterated triglycine sulfate (DTGS) type of detector. These have the advantage of being maintenance-free since they operate at room temperature. Alternative detectors are available for improved signal to noise ratio and faster analysis times. Mercury cadmium telluride (MCT) is the most common, and like all quantum detectors, these must operate at liquid nitrogen temperatures or they get swamped by thermal noise. A liquid nitrogen dewar can be provided but these require regular filling; a procedure that is inappropriate for a process environment. An alternative is to use a closed-loop Cryostat that operates from a high pressure nitrogen cylinder. These are intrinsically safe devices but they still require a 6,000 psi cylinder replacement every week or so.

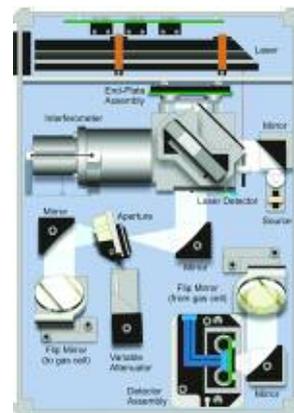


Figure 3 – FTIR Optical Bench Layout

Choosing the Most Effective Technology

The mass spectrometer option works best when a fixed list of known target VOCs need to be monitored. For example: benzene, toluene, ethyl benzene and xylenes (BTEX) on a refinery or petrochemical unit. Other examples include acrylonitrile, butadiene and styrene (ABS) on a resins plant or vinyl chloro-

Ammonia	Hydrogen cyanide
Acrolein	Phosgene
Acetaldehyde	Sulfur hexafluoride
Carbon monoxide	Perfluoromethane
Formaldehyde	Perfluoroethane
Hydrogen bromide	Perfluoropropane
Hydrogen chloride	Perfluorocyclobutane
Hydrogen fluoride	Perfluorocyclopentane

Table 2: HAPs appropriate for monitoring by multi-point FTIR

ride monomer and ethylene dichloride (VCM and EDC) on a PVC plant. The reason for this is that the ion-optics of a mass spectrometer need to be “tuned” occasionally therefore each instrument must be calibrated for each gas species being measured following such a tuning event. The calibration is infrequent but the binary mixtures that are used to measure the fragmentation patterns need to be provided at the time of

installation. In situations where a complete list of potential HAPs is not available, then extractive FTIR can prove to be a better option. A typical process FTIR will include very repeatable pinned-in-place optics that provide a fully transferable calibration. As a result



Figure 4: Thermo's Environmental Monitoring System Configured Either with EMS (VG Sentinel_B) or FTIR (InterceptIR).

of this, most analyzers will include a calibrated library of spectra allowing the use of a single validation mixture to confirm instrument performance. A second problem with the EMS is that they tend to rely on a membrane inlet to enrich the VOC content of the sample gas. Inorganic species will see no benefit from this type of inlet

system and their lower limits of detection will be significantly higher than those for VOCs. An installation based on FTIR technology is well suited to air monitoring for a wide range of both organic and inorganic HAPs. The downside is that for a typical installation, the FTIR unit will be about 10 times slower than the mass spectrometer and so will only be used to monitor maybe 10 – 15 sample points. Such an installation will provide a more comprehensive analysis of the environment than the open-path alternative.

Conclusions

An effective central monitoring system, based on either FTIR or EMS, can be used to provide comprehensive and actionable monitoring of a wide range of hazardous air-borne pollutants. The environmental mass spectrometer is usually the best option for rapid detection of tar-

geted VOCs whereas the extractive FTIR works best for general volatile organic and inorganic pollutants. Both systems have the necessary speed, sensitivity and multipoint capability for the detection of leaks, usually before a toxic hazard develops. It should be noted that a relatively high number of alarms can be expected once a system is first commissioned but remedial action tends to create a more efficient leak-free process unit and a much safer environment for the workplace and the neighborhood.

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