Sentinel PRO Process Mass Spectrometer

Continuous monitoring of vinyl chloride and ethylene dichloride in air

Keywords

Vinyl chloride monomer (VCM), ethylene dichloride (EDC), polyvinyl chloride (PVC), volatile organic compound (VOC), short term, exposure limit (STEL), threshold limit value (TLV), time weighted average (TWA), magnetic sector, rapid multistream sampler (RMS)

Thermo Scientific™ Sentinel PRO™ 710 Mass Spectrometer

Introduction

Vinyl chloride, also known as vinyl chloride monomer (VCM) or chloroethene, is an organochloride with the formula CH_2 = CHCl. It is an important industrial chemical, mainly used to produce polyvinyl chloride (PVC). Around 34 million tons of PVC and vinyl products are consumed globally[1], making it the third-most widely produced synthetic plastic polymer. Vinyl chloride is a highly flammable and potentially explosive gas. Almost all vinyl chloride is produced by reacting chlorine and ethylene, initially producing ethylene dichloride (EDC), also known as 1,2-dichloroethane (DCE).

$$CH_2 = CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$$

Ethylene dichloride is then cracked at high temperature and pressure to produce vinyl chloride and hydrogen chloride.

$$ClCH_2CH_2Cl \rightarrow CH_2 = CHCl + HCl$$

Workplace monitoring of vinyl chloride and ethylene dichloride

Early laboratory studies revealed that vinyl chloride can be a carcinogen, with the potential to cause angiosarcoma (cancer of the liver's blood vessels) and, in the 1970s, the first fatalities linked to exposure to VCM were reported.

Changes were made to production processes to protect workers, and governments around the world began to mandate maximum allowable industrial exposure levels. The most common short-term exposure limit for vinyl chloride is 5 ppm (12.8 mg/m3) 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 "No employee may be exposed to vinyl chloride at concentrations greater than 1 ppm (2.56 mg/m3) averaged over any 8-hour period"[2]. OSHA also specifies an "Action Level" for VCM of just 0.5 ppm as an 8-hour time-weighted average, to indicate the VCM level which requires medical surveillance, increased industrial hygiene monitoring, or biological monitoring. The US National Institute for Occupational Safety and Health (NIOSH) defines VCM as a 'Potential Occupation Carcinogen' and recommends that Recommended Exposure Limits (RELs) be minimized to the lowest feasible limit[3]. Table 1 shows the OSHA short-term and TWA limits for vinyl chloride and ethylene dichloride. EDC is not as dangerous a substance as VCM, but the VCM production process means there may be potential releases of EDC as well as VCM into the workplace. Any VCM monitoring systems must therefore be able to differentiate between VCM and EDC, to ensure there are no false VCM alarms caused by the release of levels of EDC that are relatively high, albeit below the permitted exposure level.

The detection limits for the Sentinel PRO MS 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 vinyl chloride and ethylene dichloride

Compound	MW	OSHA PEL 15-minute STEL ppm[2]	OSHA PEL 8-hour TWA ppm[2]	Sentinel PRO detection limit
Vinyl chloride	62	5	1	< 20 ppb
Ethylene dichloride	98	200	50	< 20 ppb

Area monitoring by mass spectrometry

We have supplied online mass spectrometers (MS) to provide fast, multi-component, multi-point gas analysis of VCM and EDC for over 30 years. One mass spectrometer can provide total plant coverage; our Sentinel PRO™ on-line mass spectrometer monitors a single sample point for VCM and EDC in just 12 seconds including stream settling time, so 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 priority, ensuring they are monitored more frequently.

To enhance the system's sensitivity to Volatile Organic Compounds (VOCs), we use a membrane inlet to increase the relative concentrations of VOCs inside the MS–VOCs have a higher permeability through the membrane relative to inorganic air gases. We then use Electron Ionization to both ionize and fragment the molecules. Each molecule produces a unique "fragmentation pattern;" this 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, for example Figure 1 shows the mass spectra fragmentation patterns of VCM and EDC from the National Institute of Standards and Technology (NIST) library.

It can clearly be seen that, although there are peaks at mass 98 and mass 100 that are unique to EDC, there is significant overlap at all of the main peaks. If the MS is to differentiate between high levels of relatively harmless EDC and low levels of carcinogenic VCM, it must be able to measure these interfering fragmentation patterns accurately. And if the MS is to have high availability these fragmentation patterns must be stable over time, otherwise the MS will need frequent recalibrations.

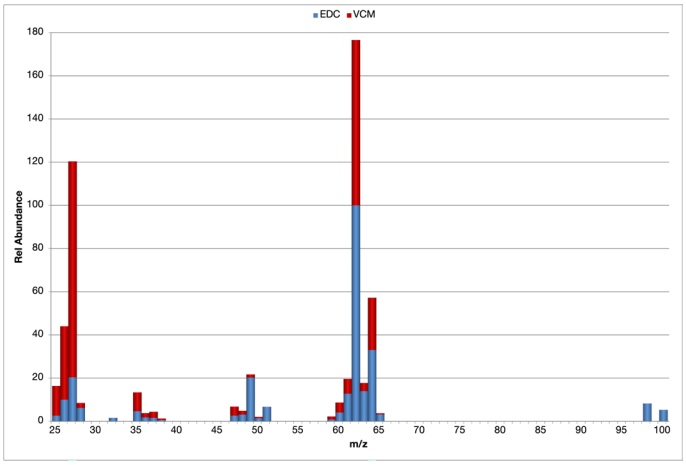

Figure 1. Composite mass spectrum of ethylene dichloride and vinyl chloride (NIST)

Advantages of magnetic sector mass spectrometry

There are two types of MS that have been used for process and 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.

Earlier systems monitoring VCM in air used Quadrupole MS; however these were susceptible to interference effects between VCM and EDC. The effect of membrane selectivities, combined with different MS sensitivities, gives a response ratio of 10:1 for EDC:VCM on a quadrupole MS. The equivalent response ratio for magnetic sector MS is 3:1; the magnetic sector's selectivity towards VCM is therefore more than three times better than a quadrupole.

Other 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.

Figure 2 shows the Sentinel PRO's magnetic sector analyzer with its characteristic flat-top peaks. 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.

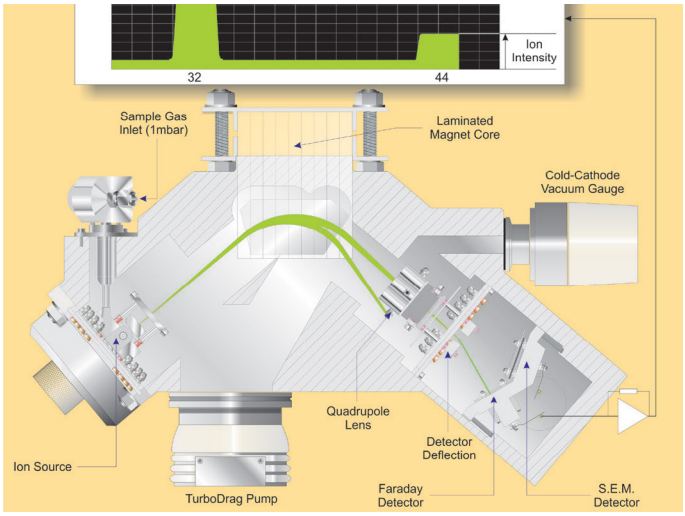

Figure 2. Sentinel PRO's magnetic sector analyzer showing characteristic flat-top peaks

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. We developed the original RMS Rapid Multistream Sampler 35 years ago to meet these requirements; this highly reliable device is now on its 3rd generation and is virtually maintenance-free.

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

The selected sample from the RMS is diverted past the 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. The resulting positively charged ions are then accelerated into the scanning magnetic sector; this 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 MS 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 reached or exceeded.

Stability

Figure 3 shows a 24 hour stability check on a cylinder nominally containing 5 ppm VCM in air. The readings are extremely stable with a Standard Deviation of just 18 ppb absolute (0.36% relative). The data are reviewed using Thermo Scientific™ GasWorks Data Review facility.

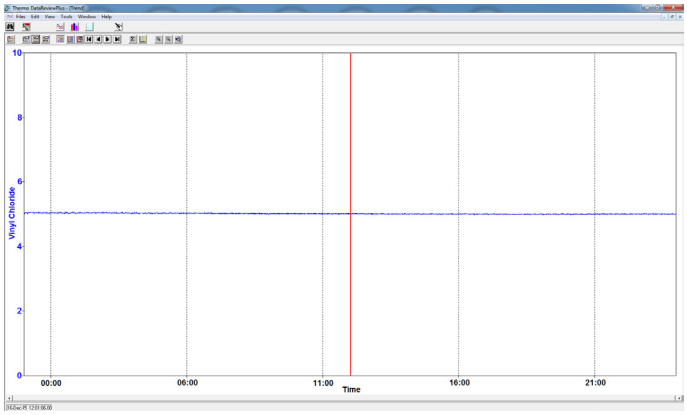

Figure 3. 24 hour stability run on 5 ppm VCM

Selectivity and flexibility

Although VCM and EDC is the most common combination of VOCs measured by Sentinel PRO, there are processes that require a different set of chlorinated compounds to be monitored. For example, Table 2 shows the analysis specification for ambient air multi-point monitoring of ppm levels of Vinyl Chloride, Ethyl Chloroformate and Vinyl Acetate.

Table 2. Analysis specification for VCM, ECF and VA

Component	Vinyl chloride (VCM)	Ethyl chloroformate (ECF)	Vinyl acetate (VA)
Molecular weight	62	108	86
Formula	C_2H_3Cl	$C_3H_5ClO_2$	$C_4H_6O_2$
Sentinel PRO lower detection limit (LDL)	20 ppb	20 ppb	20 ppb

Table 3 shows the analysis configuration used to achieve this specification. Sentinel PRO's GasWorks software supports an unlimited number of analysis methods and can apply different methods to different sample streams. So Sentinel PRO MS can be configured to measure VCM & EDC at some sample locations and VCM, ECF and VA at others, providing total site coverage.

Table 3. Analysis configuration for VCM, ECF and VA

Component	Air	VCM	ECF	VA
Detector	Multiplier	Multiplier	Multiplier	Multiplier
Typical relative sensitivity (compared with air measured at mass 34)	1	8,000	25,000	10,000
Measurement masses				
m/z 34	100			
m/z 62		100		
m/z 63		20	100	
m/z 86				100

Summary

Sentinel PRO MS 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 leads 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 VCM and other chlorinated hydrocarbons with ppb repeatability ensures that future environmental regulations will not compromise the installation.

References

1. British Plastic Federation web site: http://www.bpf.co.uk/
2. US Department of Labor, Occupational Safety & Health Administration Standards 29 CFR 1910.1017 (VCM) and 1910.1000 (EDC)
3. NIOSH Pocket Guide to Chemical Hazards (http://www.cdc.gov/niosh/npg/npgd0658.html)

- 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
  - Best selectivity against ethylene dichloride
  - 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

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