APPLICATION NOTE

Sentinel PRO Process Mass Spectrometer

Continuous analysis of Volatile Organic Compounds (VOCs) in water

Author: Graham Lewis, Thermo Fisher Scientific, Winsford, Cheshire, United Kingdom

Key Words

- Volatile Organic Compound (VOC)
- Ethylene Dichloride (EDC)
- Vinyl Chloride Monomer (VCM)
- Polyvinyl Chloride (PVC)
- Magnetic Sector
- Rapid Multistream Sampler
- Supported Capillary Membrane Sampler (SCMS)

Introduction

Mass spectrometry has been widely used for many years for multi-point, multi-component monitoring of a wide range of Volatile Organic Compounds (VOCs) in the workplace. A key application has been in the manufacture of Vinyl Chloride Monomer (VCM) from the reaction of chlorine and ethylene, initially producing ethylene dichloride (EDC), also known as 1,2-dichloroethane (DCE).[1]

Many companies also want to monitor the same VOCs in cooling water. The combination of Thermo Scientific™ Sentinel PRO's high precision magnetic sector MS with a proven sampling probe offers sensitive, selective analysis of a wide range of VOCs down to part per billion levels.

Monitoring ethylene dichloride in process water

Ethylene dichloride has frequently been detected in surface water in the µg/liter concentration range, particularly near industrialized areas, the highest levels often being near factories producing VCM.[2] Based on its known potential as a human carcinogen, the World Health Organization has established a guideline value of 30 µg/liter in drinking water, corresponding to 7.4 parts per billion.

During the manufacture of EDC, there is a risk of process cooling water becoming contaminated with trace levels of EDC through leakages, with the ensuing risk of contaminated plant effluent being released into local water sources. A monitoring system must be sensitive enough to detect these trace levels, and selective enough to differentiate EDC from the many other VOCs used on a typical chemical plant.

Supported Capillary Membrane Sampling

Originally developed and patented by Dow Chemical Company[3] and subsequently licensed to Global FIA Inc, the Supported Capillary Membrane Sampler (SCMS) was originally designed to interface with a gas-or liquid-chromatograph. However it can easily be interfaced with MS, taking advantage of its faster analysis speed.

The SCMS is shown in Figure 1. It consists of a metal body around which is wrapped a long (typically 2 meters), thin-walled membrane tubing. Dissolved VOCs permeate through the tube membrane wall into a carrier gas stream at a rate dependent on the concentration of the dissolved VOC. The SCMS is equivalent to head space and purge-and-trap sampling, but with a simpler, more direct sampling system.

Figure 1 SCMS Supported Capillary Membrane Sampler (Global FIA Solutions)

The carrier gas (typically air for the Sentinel PRO) enters the SCMS through 1/8" tubing from a mass flow controller, flows through the silicone rubber permeation tubing, and exits the SCMS through a second 1/8" tube which is connected to the Sentinel PRO's Rapid Multistream Sampler (RMS). The typical carrier gas flow through the device is 40 ml/min. The output of the device is connected directly to the Sentinel PRO by around 4 meters of stainless steel tube, which should be trace-heated to at least 50°C.

A typical installation schematic is shown in Figure 2. The SCMS can be installed in a flow cell, also available from Global FIA Inc.

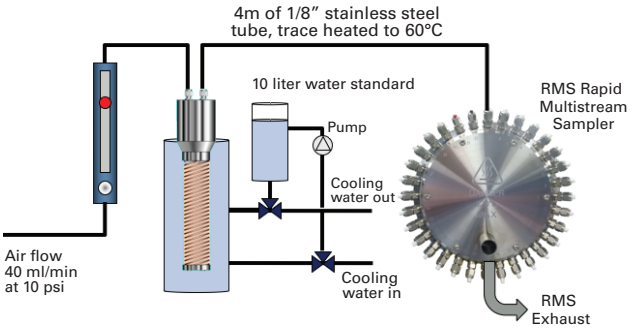

Figure 2 Typical SCMS probe installation

Calibration

Sentinel PRO is calibrated using cylinders containing 10 ppm of each VOC in a separate cylinder. Known concentrations of the VOCs in water are then used to determine the conversion factor for concentration in the air carrier gas (molar ppm) to the actual concentration in the water flowing through the probe cell (ppm by weight). As with other membrane sampling devices, the permeation rate of the SCMS is known to vary with temperature. In order to provide compensation for the effect of sample temperature on the MS results, a study was made to determine the effect of sample temperature on target VOC species and implement correction factors in Sentinel PRO's analysis method.

The study consisted of circulating a 1 ppm by volume sample of each VOC in water through a sample system containing the SCMS, to characterize Sentinel PRO's response at a range of temperatures. The effect of sample temperature is significant — the recorded concentration was 47% higher for EDC and 28% higher for VCM at 40°C than at 30°C. Figure 3 shows the response for EDC generated from the study.

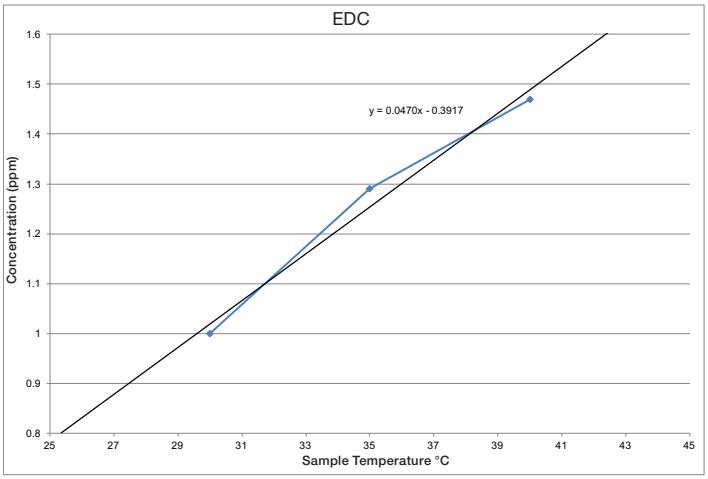

Figure 3 Effect of temperature on response of EDC

The VOC correction factors can be set up in GasWorks™ software, including temperature from analog inputs. This enables real time compensation for water temperature effects. Typical conversion factors are between 0.01 and 0.1, depending on the probe, the VOC and the temperature.

Magnetic Sector Mass Spectrometry

To further enhance Sentinel PRO's sensitivity to VOCs, we use a membrane inlet to increase the relative concentrations of VOCs inside the MS – as with the SCMS membrane, VOCs have a higher permeability through the Sentinel PRO membrane relative to inorganic air gases. We then use Electron Impact 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 the various VOCs is a complex composite spectrum, for example Figure 4 shows the mass spectra fragmentation patterns of VCM and EDC from the National Institute of Standards and Technology (NIST) library.

It can be seen that, although there are peaks at mass 98 and mass 100 that are unique to EDC, there is significant overlap at all the main peaks. If the MS is to differentiate between the two VOCs it must be able to measure the 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.

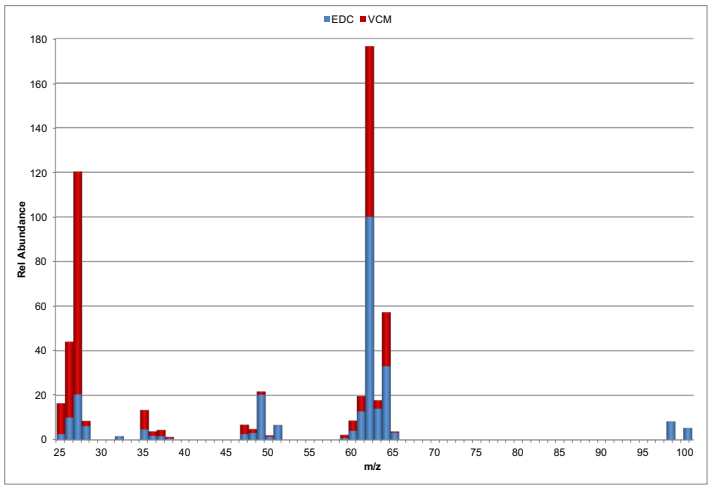

Figure 4 Composite mass spectrum of ethylene dichloride and vinyl chloride (NIST)

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. We manufacture 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.

Figure 5 shows the Sentinel PRO's magnetic sector analyzer with its characteristic flat-top peaks. As the height of the peak is directly proportional to concentration, we can measure peak height anywhere across the peak top to obtain the correct result; the magnetic sector analyzer is therefore inherently fault tolerant.

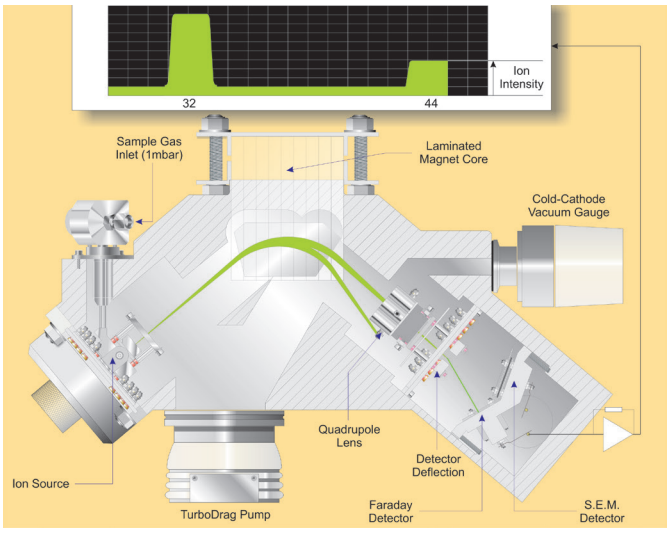

Figure 5 Sentinel PRO's magnetic sector analyzer showing characteristic flat-top peaks

Dynamic Range

The system must detect traces of the designated VOCs, and yet have a sufficiently wide dynamic range to handle much higher levels in the event of a major leak. Figure 6 demonstrates the wide dynamic range of the Sentinel PRO with SCMS for EDC; the system was challenged with four decades of EDC concentrations, from 10 ppb to 10 ppm.

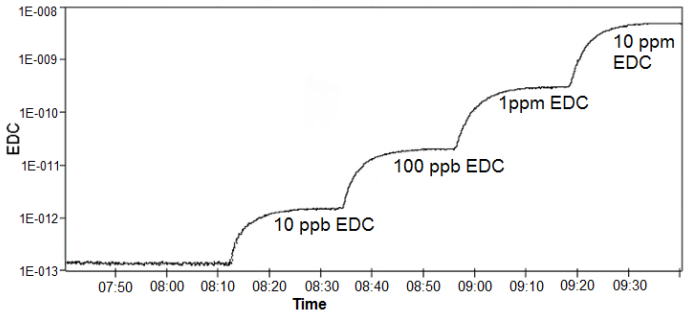

Figure 6 EDC dynamic range with Sentinel PRO and SCMS

Selectivity & Flexibility

Although EDC is the most common VOC measured by Sentinel PRO, there are processes that require other chlorinated compounds to be monitored. For example, Table 1 shows the analysis specification for vinyl chloride, ethylene dichloride and chloroform.

Table 1 Analysis specification for VCM, EDC and Chloroform

Component	Air	VCM	EDC	Chloro-form
Molecular Weight		62.50	98.95	119.37
Typical Relative Sensitivity	1	15,000	50,000	70,000
m/z 34	100			
m/z 62		100	100	0.1
m/z 83				100
m/z 98			30	0.1
Sentinel PRO/ SCMS detection limit in isolation (ppb by weight)		10	10	10

Analysis time for the three VOCs is typically 12 seconds, while the settling time required when switching between different inlets is just 100 seconds.

Thermo Scientific™ GasWorks™ software supports an unlimited number of analysis methods and can apply different methods to different sample streams. So Sentinel PRO can be configured to measure different sets of VOCs at different sample locations. Figure 7 shows two example analysis configurations for different cooling water streams,

thermo scientific

one measuring five VOCs, the other measuring just three.

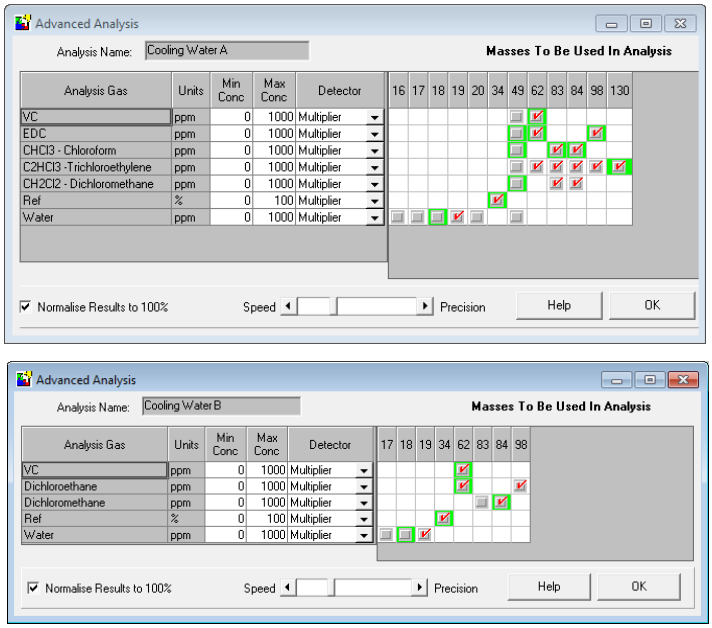

Figure 7 GasWorks analysis configurations for two different cooling water streams

Note that mass 19 is used to measure water, as an indication of the state of the SCMS membrane. If it is damaged, then carrier gas can bring water into the MS, but a high water alarm can be configured to disable analysis on that particular stream. The isotopic ion at mass 19 is used rather than the molecular ion at mass 18 to avoid overloading the MS detector — the relative intensity of the mass 19 peak is just 0.1% of the mass 18 peak, more than enough to act as an alarm indicator.

Figure 8 shows 30 days' data using method 'Cooling Water A', monitoring vinyl chloride, ethylene dichloride, chloroform, trichloroethylene & dichloromethane. The data are reviewed using GasWorks' Data Review facility.

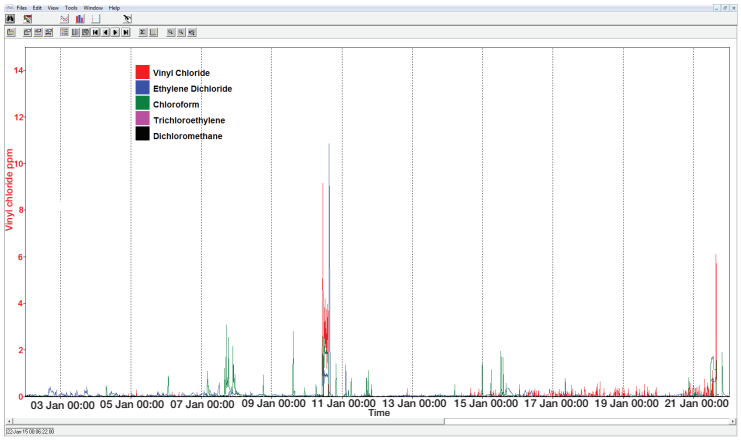

Figure 8 30 days process data for five VOCs

Summary

Sentinel PRO has a proven track record for monitoring fugitive and point source VOC emissions in a wide variety of industrial plant atmospheres. Adding a proven supported capillary membrane sampler extends Sentinel PRO's range of applications to VOCs in process water at ppb and ppm levels.

- Membrane inlet for high sensitivity
- Magnetic sector MS for highest precision and stability
- Multiple compounds monitored by one system
- GasWorks software's Derived Value facility enables real time compensation for water sample temperature
- Standard three year warranty

More information on the SCMS probe is available at http://www.globalfia.com/.

References

1. Thermo Scientific Application Note AN_SP_0716, 'Continuous Monitoring of Vinyl Chloride and Ethylene Dichloride in Air'
2. 1,2-Dichloroethane in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality
3. US Patent 5,317,932 dated June 7, 1994

USA
27 Forge Parkway
Franklin, MA 02038
Ph: (800) 437-7979
Fax: (508) 520-1460
orders.process.us@thermofisher.com

India
C/327, TTC Industrial Area
MIDC Pawane
New Mumbai 400 705, India
Ph: +91 22 4157 8800
india@thermofisher.com

China
+Units 702-715, 7th Floor
Tower West, Yonghe
Beijing, China 100007
Ph: +86 10 84193588
info.eid.china@thermofisher.com

Europe
Ion Path, Road Three,
Winsford, Cheshire CW73GA UK
Ph: +44 1606 548700
Fax: +44 1606 548711
sales.epm.uk@thermofisher.com

Find out more at **thermofisher.com/sentinel**

ThermoFisher SCIENTIFIC

For Research Use Only. Not for use in diagnostic procedures. © 2016 Thermo Fisher Scientific Inc. All rights reserved.
All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified.**AN_SP_0816**