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APPLICATION NOTE

Thermo Scientific™ Prima PRO Process Mass Spectrometer

Improving ethylene oxide process control

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Keywords
- Selectivity
- Carbon Balance
- Oxygen Balance
- Organic chlorides
- Magnetic Sector
- Rapid Multistream Sampler

Introduction

Ethylene oxide (EO) is an important chemical intermediate with global production capacity around 30 million tonnes per year. It is extremely reactive because its highly strained ring structure can easily be opened, and is therefore one of the most useful and versatile chemical intermediates. Products derived from EO include:

Ethylene glycols: used to produce antifreeze, coolants, polyester and polyethylene terephthalate (PET)

Glycol ethers: used to produce brake fluids, hydraulic fluids, detergents, paints, lacquers and solvents

Ethanolamines: used to manufacture detergents, and to purify natural gas

Ethoxylates: used to manufacture detergents, dispersants, surfactants and emulsifiers

According to a 2016 report[1], overall demand for ethylene oxide is expected to grow at an average rate of 2.6% per year over the next 5 years, primarily fuelled by incremental demand for polyester products, antifreeze, polyurethanes, soaps, detergents, etc. in emerging regions. Around 75% of EO is converted to ethylene glycol; as the EO derivatives market is highly competitive, and feedstock prices are volatile, it is vital that EO process economics are optimized. At the same time, the EO process is inherently potentially hazardous, so great care must be taken to operate the plant safely. Process gas analysis plays an important part in both of these areas; this paper will describe the benefits of process mass spectrometry in general and the Thermo Scientific™ Prima PRO Process Mass Spectrometer in particular in improving process efficiency while maintaining process safety.

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The process

EO is produced commercially by the vapor-phase reaction of ethylene and oxygen over a silver-based catalyst. There are two possible reactions that can occur:

Main Oxidation Reaction

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow{Ag} C_2H_4O$$

Side Oxidation Reaction

$$C_2H_4 + 3O_2 \xrightarrow{Ag} 2CO_2 + 2H_2O$$

Both reactions are exothermic. The side reaction is not only completely inefficient, producing no EO, it is over 10 times more exothermic than the main reaction, so that large amounts of heat must be removed from the process to avoid the risk of explosion. The key process control strategy is therefore to maximize the primary partial oxidation reaction while minimizing or eliminating the competing side reaction to complete oxidation. This is defined as the selectivity, the number of moles of EO produced in the reactor per 100 moles of ethylene converted. The key role of the catalyst is to maximize this selectivity.

Process control must ensure that the catalyst maintains its activity for as long as possible, since this is costly and time consuming to replace. Selectivity is improved by adding various organic chloride inhibitors, designed to slow preferentially the side oxidation reaction. These must be maintained and monitored at low ppm levels in the reaction mixture.

As the process generates relatively low levels of EO, process gas is recycled to increase the EO concentration. In principle, the EO concentration could be increased by increasing the feed gas oxygen content. However, EO and oxygen can react explosively; the chances of this occurring are minimized by adding methane to the stream to make it “fuel rich”.

EO process: analytical requirements

Gas analysis plays an important part in optimizing the EO process; Figure 1 shows a simplified schematic of a typical EO process, with gas analysis sample points identified. Table 1 shows typical reactor inlet and outlet compositions that need to be measured.

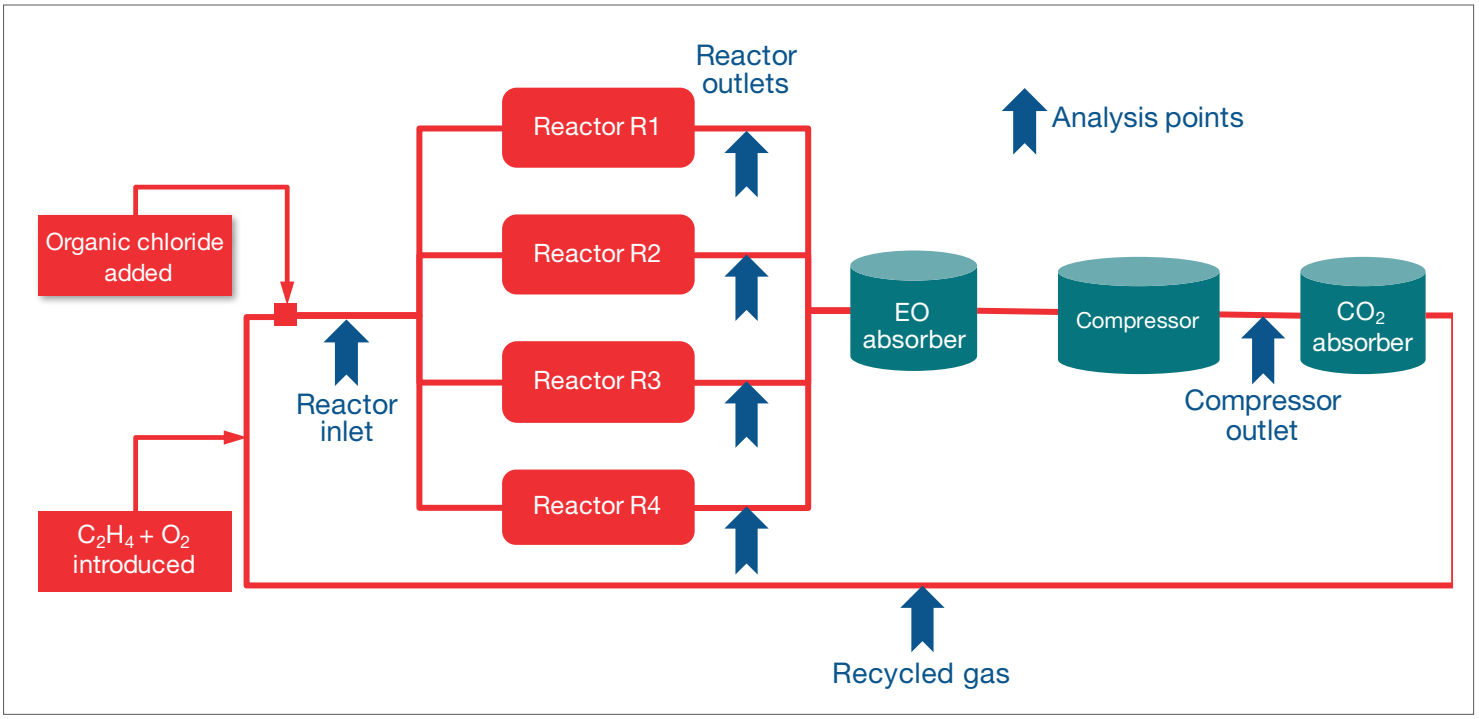

Figure 1 Schematic of typical EO process

Table 1 Typical stream compositions for EO inlet & outlet stream

Component	Typical Reactor Inlet Concentration %mol	Typical Reactor Outlet Concentration %mol
Methane	47	48
Water	0.3	0.8
Nitrogen	1	1
Ethylene	30	28
Ethane	1	1
Oxygen	7.6	5.8
Argon	12	12
Ethylene Oxide	0	2.2
Carbon Dioxide	1	1.5
Organo-chlorides	ppm	ppm

By measuring the inlet and outlet gases, important parameters such as Selectivity, Carbon Balance and Oxygen Balance can be derived. Analysis speed is critical, as is a wide dynamic range. Additionally, the analyzers must be able to cope with two different balance gases— during normal operation methane is used as the bulk gas, but for enhanced safety during plant start-up and shut-down this is replaced by nitrogen.

Advantages of mass spectrometry

Mass spectrometers offer fast, complete stream analysis; typical analysis time including stream switching time is less than 30 seconds per stream for all components including trace chlorides.

Advantages of Prima PRO process MS

The ethylene oxide process presents a series of challenges to the Process MS. Prima PRO has been designed to meet and beat these challenges.

Rapid multistream sampling

If the MS is to monitor all EO process streams then a fast, reliable means of switching between streams is required. Solenoid valve manifolds have too much dead volume and rotary valves suffer from poor reliability so we developed the unique RMS Rapid Multistream Sampler. It offers an unmatched combination of sampling speed and reliability and allows sample selection from 1 of 32 or 1 of 64 streams. Stream settling times are application dependent and completely user configurable. The RMS includes digital sample flow recording for every selected stream. This can be used to trigger an alarm if the sample flow drops, for example if a filter in the sample conditioning system becomes blocked.

Precision of analysis

The MS is required to monitor a complex mixture of inorganic and organic compounds over a wide range of concentrations; if the results are to be used as part of a dynamic plant control strategy they must be reliable and available.

At the heart of the Prima PRO is a magnetic sector analyzer which offers unrivalled precision and accuracy compared with other mass spectrometers. We produce both quadrupole and magnetic sector mass spectrometers; over thirty years of industrial experience have shown the magnetic sector analyzer offers the best performance for industrial on line 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 Prima PRO magnet is that it is laminated. Its analysis times are similar to a quadrupole analyzer, 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 24-bit precision using a magnetic flux measuring device for extremely stable mass alignment.

Our enclosed ion source provides high sensitivity, minimum background interference and maximum contamination resistance. The high-energy (1000 eV) analyzer offers extremely rugged performance in the presence of gases and vapors that have the potential for contaminating the analyzer.

Software

Thermo Scientific™ GasWorks™ software supports the analysis of an unlimited number of components per stream, and an unlimited number of user defined calculations (called Derived Values), such as Selectivity, Oxygen Balance and Carbon Balance. An unlimited number of analytical methods can be set up, so different analyses can be defined for different process streams. Analog signals, from temperature and pressure sensors for example, can also be logged, displayed and used in Derived Value calculations. A range of industry standard protocols are available for communicating with plant process control systems.

Prima PRO performance

Table 2 shows Prima PRO's typical performance specification, covering both methane-rich and nitrogen-rich process conditions. Analysis time including stream switching time is approximately 25 seconds per stream for all 14 components. This reduces to 15 seconds if measurement of the chlorides is omitted.

Table 2 Typical Prima PRO performance specification for EO inlet and outlet streams

Measurement	Concentration range %mol	Typical Reactor Inlet Concentration %mol	Typical Reactor Outlet Concentration %mol	Prima PRO Standard Deviation (8 hours)
Methane	0 - 70	47	48	≤0.03 %mol or 0.1 % relative*
Water	0 - 4	0.3	0.8	≤0.01 %mol
Nitrogen	0 - 100	1	1	≤0.03 %mol or 0.1 % relative*
Ethylene	0 - 40	30	28	≤0.03 %mol or 0.1 % relative*
Ethane	0 - 5	1	1	≤0.005 %mol
Oxygen	0 - 10	7.6	5.8	≤0.005 %mol or 0.1 % relative*
Argon	0 - 20	12	12	≤0.005 %mol or 0.1 % relative*
Ethylene Oxide	0 - 4	0	2.2	≤0.005 %mol
Carbon Dioxide	0 - 10	1	1.5	≤0.01 %mol or 0.1 % relative*
Methyl Chloride	0 - 5 ppm	1 ppm	1 ppm	≤0.2 ppm
Vinyl Chloride	0 - 5 ppm	1 ppm	1 ppm	≤0.2 ppm
Ethyl Chloride	0 - 5 ppm	1 ppm	1 ppm	≤0.2 ppm
Allyl Chloride	0 - 5 ppm	1 ppm	1 ppm	≤0.2 ppm
1,2 Dichloroethane	0 - 5 ppm	1 ppm	1 ppm	≤0.2 ppm
				whichever is greater

Figure 2 shows 10 hours' data from an EO reactor outlet, displayed in log scale in Thermo Scientific GasWorks Data Review software. EO output is just 2%, demonstrating the need to recycle the output to increase yield.

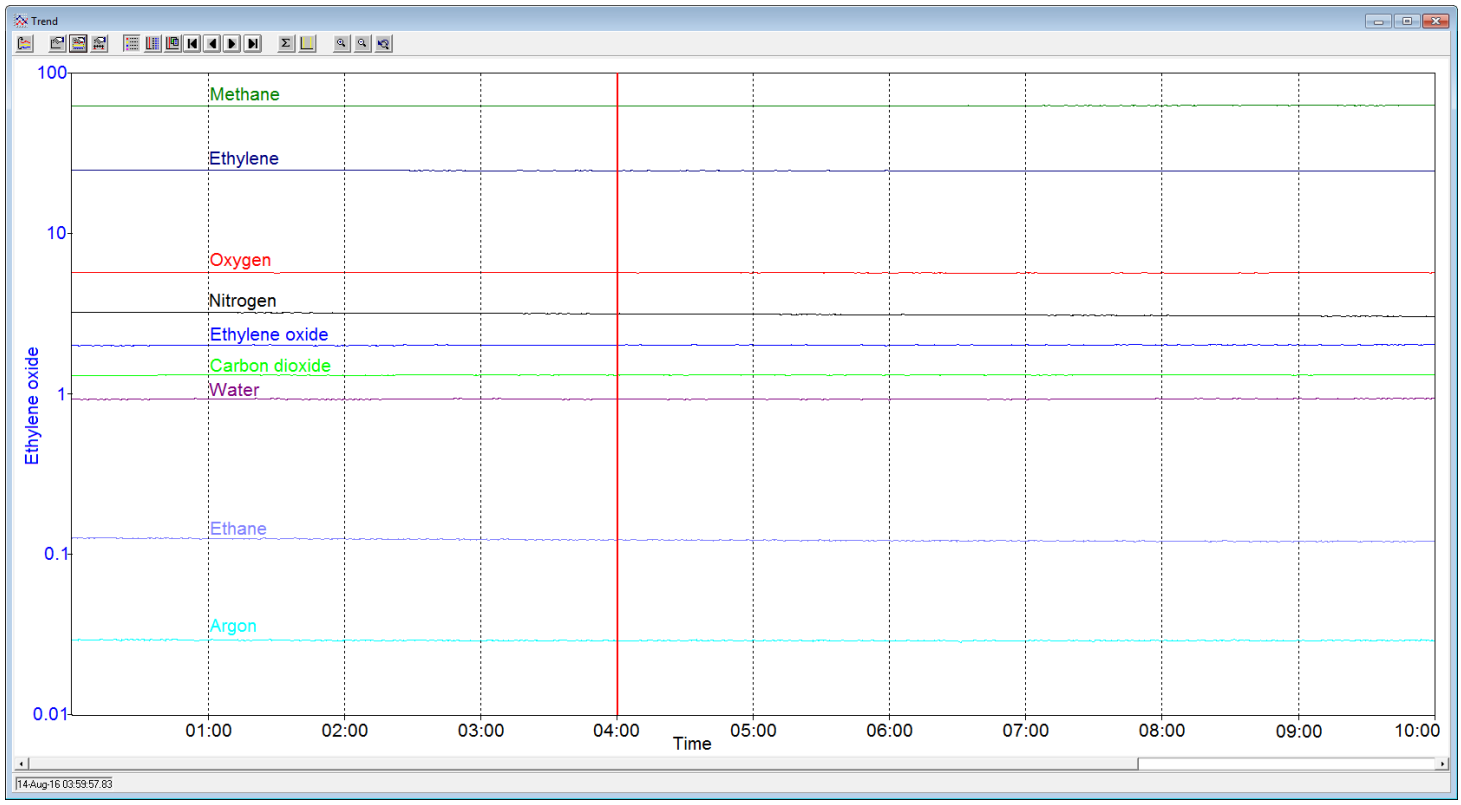

Figure 2 EO process reactor outlet concentrations over 10 hours

Carbon and oxygen balances

If the gas analyzer together with its associated sample conditioning system is to be used as part of the plant's control strategy, it must be able to measure all the carbon and oxygen-containing compounds in the streams with high accuracy. This can be defined by the Carbon Balance and Oxygen Balance respectively, the certainty that the analyzer is measuring accurately all the carbon and oxygen atoms in the reactor inlet and outlet streams. Theoretically both of these should be 100%. Prima PRO's combination of high performance RMS and high precision magnetic sector analyzer achieve balances of close to 100%, depending on the accuracy of the calibration gases. MS provides a considerable improvement on GC analyzers that provide a slower, partial stream composition — GCs do not measure oxygen, so the Oxygen Balance calculation is not possible with GC alone.

Table 3 shows how these balances can be set up in GasWorks software using the Derived values feature.

Table 3 Carbon balance, & oxygen balance derived values in GasWorks software

Carbon Balance:

$$\frac{100 \times \{CH_4 + CO_2 + 2 \times (C_2H_4 + C_2H_6 + EO)\}[outlet] \times 100}{\{CH_4 + CO_2 + 2 \times (C_2H_4 + C_2H_6 + EO)\}[inlet] \times (100 + 0.5EO[outlet])}$$

Oxygen Balance:

$$\frac{100 \times \{2 \times (O_2 + CO_2) + EO + H_2O\}[outlet] \times 100}{\{2 \times (O_2 + CO_2) + EO + H_2O\}[inlet] \times (100 + 0.5EO[outlet])}$$

Figure 3 shows Carbon and Oxygen Balances measured over 10 hours with Prima PRO. Both are close to the theoretical perfect value of 100, with excellent precision, verifying the high degree of confidence that can be placed in Prima PRO's results.

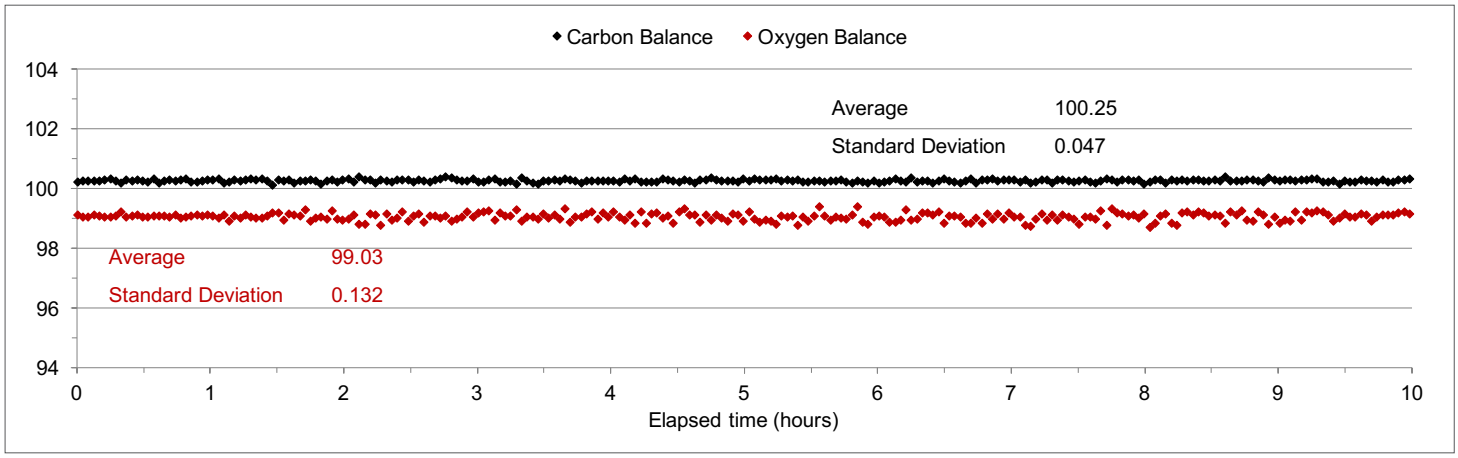

Figure 3 Carbon & oxygen balances on EO process stream over 10 hours

In practice, the oxygen concentration is such a critical safety measurement that dedicated paramagnetic oxygen analyzers will be used in addition to the MS.

Selectivity

Selectivity, the number of moles of EO produced in the reactor per 100 moles of ethylene converted, can also be calculated and displayed using GasWorks Derived Values. This is shown in Table 4 below.

Table 4 EO selectivity derived value in GasWorks software

Selectivity:

$$\frac{100 \times (EO[outlet] \times 100/(100 + 0.5 \times EO[outlet]) - EO[inlet])}{\{C_2H_4[inlet] - C_2H_4[outlet] \times 100/(100 + 0.5 \times EO[outlet])\}}$$

Figure 4 shows the selectivity of an EO process stream measured over 10 hours.

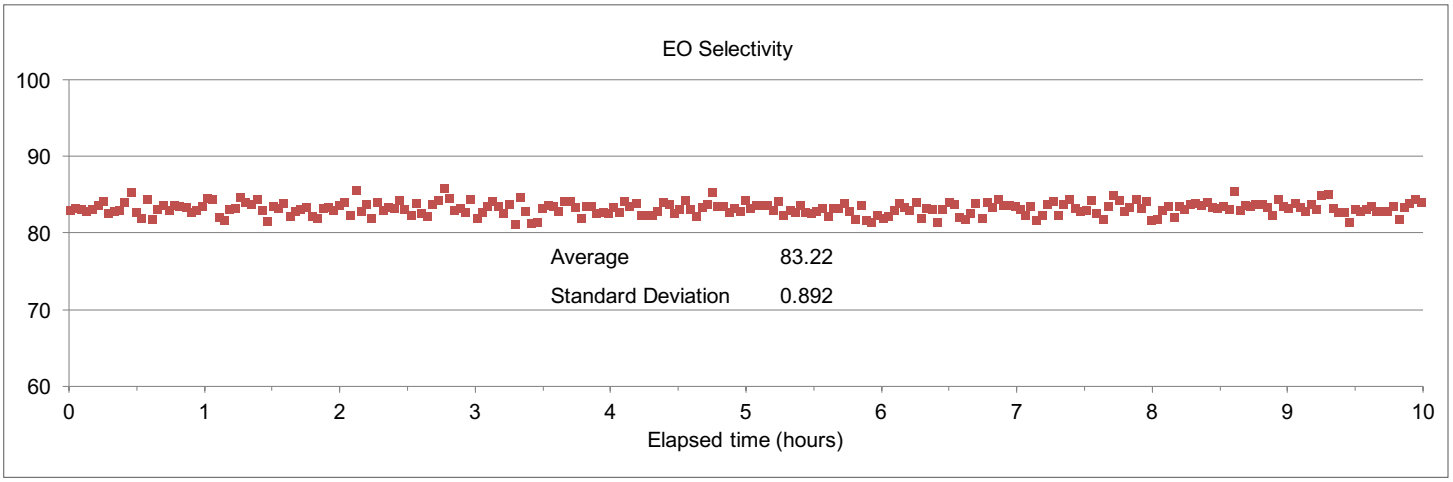

Figure 4 EO selectivity on process stream over 10 hours

Accuracy of MS during start-up with nitrogen balance

During normal plant operation, methane is used as the balance gas to ensure the process streams are 'fuel rich', thereby minimizing the explosion risk. However, for maximum plant safety, methane is replaced by nitrogen during plant start-up and shut-down. The gas analyzer is therefore required to analyze two very different stream compositions. Many analyzers do not have the dynamic range to cope with this requirement without being calibrated for both balance gases.

Prima PRO has excellent linearity, and can measure both stream types when calibrated for one balance gas. Table 5 shows an example of a Prima PRO calibrated with methane as the bulk gas, then analyzing two cylinders representing methane and nitrogen balance process streams. The observed differences in measured and certificate values are consistent with the uncertainties of the cylinder certificate values.

Table 5 Prima PRO's ability to measure methane- and nitrogen-balance streams with single calibration

	Methane balance		Nitrogen balance	
	Prima PRO	Certificate	Prima PRO	Certificate
Methane	56.4767	56.44 ±1.13	4.9252	5.17 ± 0.1
Nitrogen	5.8252	5.88 ± 0.12	52.13	51.99 ± 1.04
Ethylene	26.2369	26.2 ± 0.52	25.7779	25.6 ± 0.51
Ethane	0.2014	0.2 ± 0.01	0.1966	0.21 ± 0.01
Oxygen	0.8624	0.87 ± 0.02	5.2183	5.15 ± 0.1
Argon	4.9466	4.95 ± 0.10	4.8151	4.92 ± 0.1
Carbon dioxide	4.9808	4.99 ± 0.10	4.8682	4.96 ± 0.1
Ethylene oxide	0.4697	0.47 ± 0.01	2.07	2 ± 0.08

Trace chloride analysis

The analysis of ppm levels of organic chlorides in the complex matrix of components present at percentage levels in the EO process presents challenges even to the best gas analyzer. For example, ethylene glycol can be produced in the reactor outlet stream by the reaction of EO and water; this produces a peak at mass 62, where vinyl chloride is measured. The effect must be minimized by operating the sampling system, inlet system and MS ion source at high temperatures (80-100 °C for the RMS, 140-180 °C for the ion source) and eliminating cold spots in the sampling system (the minimum temperature at any point between the process take-off point and the RMS should be 80 °C).

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Percentage level components are measured on the Prima PRO's Faraday detector; ppm level components are measured using a Secondary Electron Multiplier (SEM) detector. The ion beam is directed to the appropriate detector by GasWorks software. Prima PRO uses two Micro Channel Plate (MCP) detectors as the SEM to measure the ppm level chlorides; this minimizes noise and maximizes signal to optimize performance

Figure 5 shows an 8 hour run on four typical organic chlorides measured in an EO calibration gas. Table 6 shows the standard deviations achieved during the test. These are all well within the specifications detailed in Table 2.

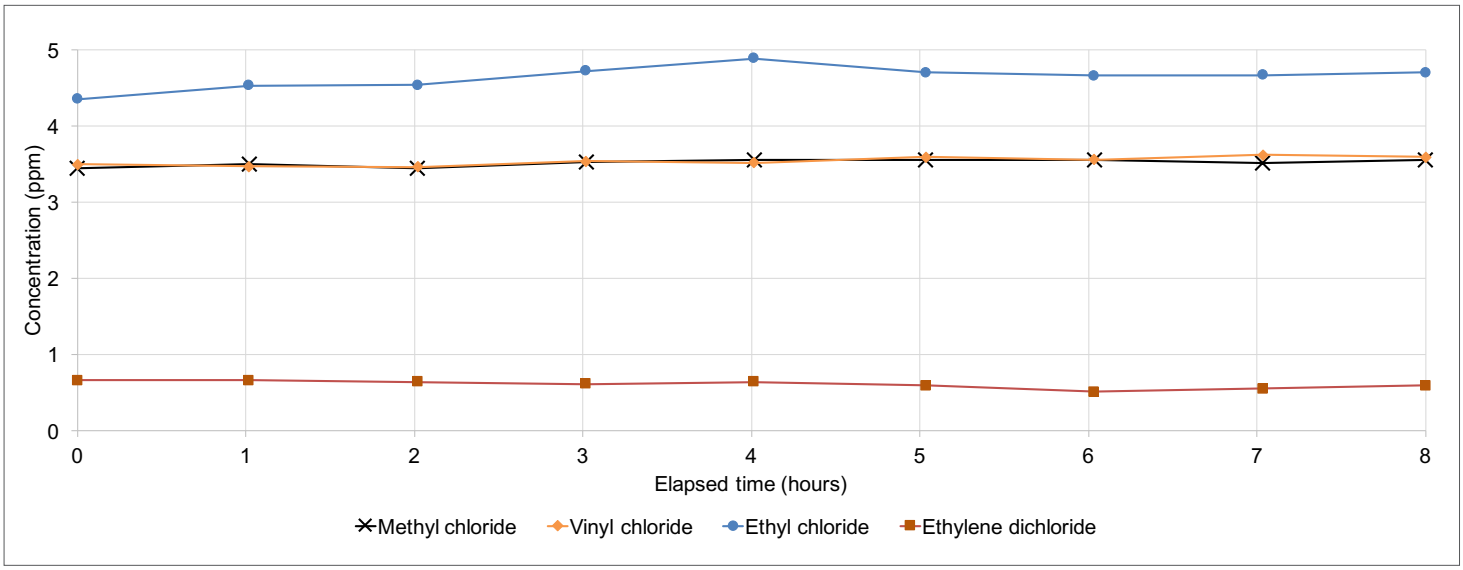

Figure 5 Repeatability test on four organic chlorides in calibration gas over 8 hours

Figure 6 Standard deviations on four organic chlorides in calibration gas over 8 hours

	Methyl chloride	Vinyl chloride	Ethyl chloride	Ethylene dichloride
Mean	3.51	3.53	4.63	0.61
Standard deviation	0.04	0.06	0.16	0.05

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Summary

Prima PRO is the optimal gas analysis solution for both EO process monitoring and EO catalyst research & development.

- Enables process optimization by fast, accurate selectivity measurement
- System accuracy is validated by measuring carbon and oxygen balances between 99 and 101%
- Inorganic and organic components are monitored on one instrument
- Dynamic range enables monitoring of component concentrations from ppm to 100 %

Prima PRO's precision of analysis ensures plant operation and catalyst performance are optimized and plant safety is maximized.

Reference

1. Chemical Economics Handbook – Ethylene Oxide, September 2016.

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