Application Note

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Ethylene Oxide and Propylene Oxide Analysis Using the Agilent 990 Micro GC

Authors

Fang Yue and Jiang Fei
Agilent Technologies
(Shanghai) Co. Ltd.

Abstract

This application note presents a method for the analysis of ethylene oxide (EO) and propylene oxide (PO) in their synthesis using an Agilent 990 Micro GC. Raw materials and products of interest (hydrogen [H_2], oxygen [O_2], nitrogen [N_2], carbon monoxide [CO], carbon dioxide [CO_2], ethylene, EO, propylene, and PO) before and after the reaction can all be separated and quantified on the Agilent J&W CP-Molsieve 5Å and Agilent J&W PoraPLOT U channels with excellent repeatability and a short analytical cycle time (less than 4 minutes). The lower detection limit (LDL) for EO and PO can be as low as parts per million (ppm).

Introduction

1,2-Epoxy compounds, abbreviated as epoxides, are a class of compounds with a ternary cyclic ether structure. The main epoxides in industry are EO and PO. Both are important chemical intermediates in the production of various solvents, surfactants, and polymer precursors, and they have a wide range of applications in the chemical, pharmaceutical, construction, pesticide, and other sectors.[1–3]

The traditional synthesis of epoxides is carried out under high temperature and pressure, and the oxygen for epoxidation comes from the oxygen supply in the feed. In this situation, ethylene is prone to peroxidation, generating constant amounts of CO_2 and CO.[1–3] Thus, both raw materials and products are mostly constant components, and accurate analysis does not require high chromatographic performance.

However, in the electrocatalytic synthesis of epoxides, such as halogen-mediated indirect oxidation processes, the oxygen for epoxidation comes from water. The amount of free oxygen in the system, which is a byproduct of side reactions, is much less than that in traditional one. Furthermore, due to its mild reaction conditions, the peroxidation reaction of ethylene is significantly inhibited, and the yields of CO and CO_2 byproducts are much lower.[1,3] Currently, this direction is still in the laboratory research stage. The overall reaction scale is small, with low current and yield, which puts high demands on the analytical equipment's detection limit and sample consumption.[1–3] At the same time, exploring reaction mechanisms efficiently and batch screening of catalysts requires rapid online analysis.

The Agilent 990 Micro GC can perform quick and accurate analysis of ppm-level EO, PO, and other related components from both traditional and/or electrocatalytic reaction systems. Its low consumption of power and carrier gas make it an ideal tool for online analysis, bringing value to both industrial production and laboratory research. Automatic sequential analysis of multiple samples and calibrations can also be achieved on one machine to accelerate batch screening by adding stream selection valves.

In this application note, two analytical channels of the 990 Micro GC were used, namely the 3+10 m Agilent J&W CP-Molsieve 5Å and the 1+10 m Agilent J&W PoraPLOT U. The 3+10 m Molsieve 5Å enabled the separation of permanent gases, while the 1+10 m PoraPLOT U enabled the separation of CO_2, ethylene, and EO, or CO_2, propylene, and PO under corresponding conditions.[4] Each run took less than 4 minutes to complete, with excellent repeatability for multiple analyses.

Experimental

The 990 Micro GC was equipped with a 3+10 m Molsieve 5Å backflush channel (retention time stability configuration), and a 1+10 m PPU backflush channel. Table 1 shows the experimental conditions for the analysis. Standard gases were purchased from Air Liquide, Inc. (Shanghai, China). Table 2 shows the composition of the standard gases.

Table 1. Experimental conditions for EO and PO synthesis analysis using the 990 Micro GC.

Application Scope	EO and PO Synthesis	EO Synthesis	PO Synthesis
Channel Type	3+10 m Molsieve 5Å, backflush	1+10 m PoraPLOT U, backflush	1+10 m PoraPLOT U, backflush
Carrier Gas	Helium	Helium	Helium
Column Pressure	150 kPa	150 kPa	125 kPa
Injector Temperature	65 °C	70 °C	70 °C
Column Temperature	65 °C	70 °C	110 °C
Injection Time	40 ms	40 ms	40 ms
Backflush Time	15.8 s	14.0 s	17.8 s
Sample Time	60 s	60 s	60 s

Table 2. Composition of the standard gases.

Standard Gas 1		Standard Gas 2	
Component	Concentration	Component	Concentration
N_2	Balance	N_2	Balance
Ethylene	75.0%	Propylene	74.7%
H_2	390 ppm	H_2	410 ppm
O_2	194 ppm	O_2	200 ppm
EO	90.0 ppm	PO	114 ppm
CO	50.9 ppm	CO	52.0 ppm
CO_2	49.8 ppm	CO_2	47.5 ppm

Results and discussion

The Molsieve 5Å is used for the separation of permanent gases. To adapt to different sample compositions, especially for high-concentration CO_2 analysis in traditional synthesis processes, a 3-meter-long precolumn is preferred for the Molsieve 5Å channel to ensure that CO_2 will not enter the analysis column. Based on the actual sample system, other Molsieve 5Å configurations may also be selected. Helium is applied as the carrier gas to elicit a higher response in components other than H_2, and the actual content of H_2 in the sample is unlikely to exceed 10%, so there is no need to worry about peak inversion brought on by the abnormal thermal conductivity of the H_2/He mixture.[5] However, due to the close thermal conductivity between He and H_2, analysis of H_2 component with a concentration lower than 50 ppm is unlikely.

The PoraPLOT U channel is used for the separation of permanent gas, CO_2, olefin raw materials, and the target product (EO or PO). A straight configuration can also be chosen. The use of backflush configuration is recommended here to allow any possible higher-boiling components in these complex practical systems to be vented out from the column, keeping analysis time short. Since the synthesis of EO and PO is generally independent of each other, and the retention time (RT) of EO and PO on the PoraPLOT U under the same conditions differs greatly, different analysis conditions were applied for EO and PO to shorten analysis time, enhance sensitivity, and improve separation. Due to the significantly stronger retention of epoxides on the PoraPLOT U, the overall principle for adjusting analysis conditions is to minimize the RT of epoxides while ensuring the effective separation of other components. The separation of CO_2 and ethylene in the EO system and the separation of permanent gas and CO_2 in the PO system are critical for the respective analyses.

The analysis results of the EO synthesis were as follows. Figure 1A shows the chromatogram of Standard Gas 1 on the 3+10 m Molsieve 5Å backflush channel. H_2, O_2, N_2, and CO were well resolved. On the 1+10 m PoraPLOT U backflush channel, permanent gas composite, CO_2, ethylene, and EO were separated as shown in Figure 1B. EO had a good peak shape.

The analysis results of the PO synthesis were as follows. Figure 2A shows the chromatogram of Standard Gas 2 on the 3+10 m Molsieve 5Å backflush channel. H_2, O_2, N_2, and CO were well resolved, as expected. On the 1+10 m PoraPLOT U backflush channel, permanent gas, CO_2, ethylene, and PO were separated as shown in Figure 2B. PO also had a good peak shape.

The maximum analytical cycle time was less than 4 minutes for both the EO and PO methods.

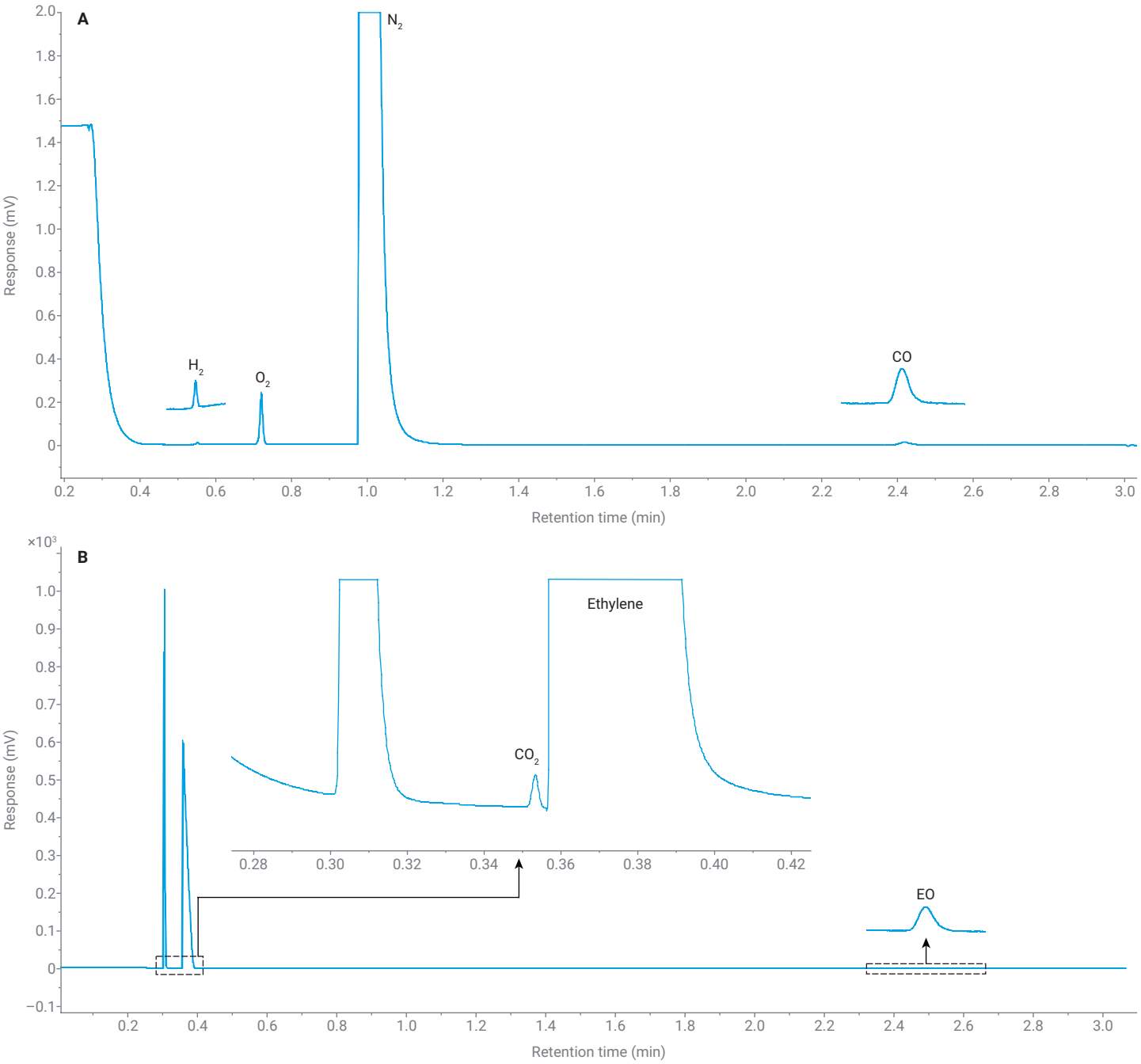

Figure 1. (A) Chromatogram of the Standard Gas 1 (EO synthesis) on the 3+10 m Agilent J&W CP-Molsieve 5Å backflush channel. (B) Chromatogram of the Standard Gas 1 (EO synthesis) on the 1+10 m Agilent J&W PoraPLOT U backflush channel.

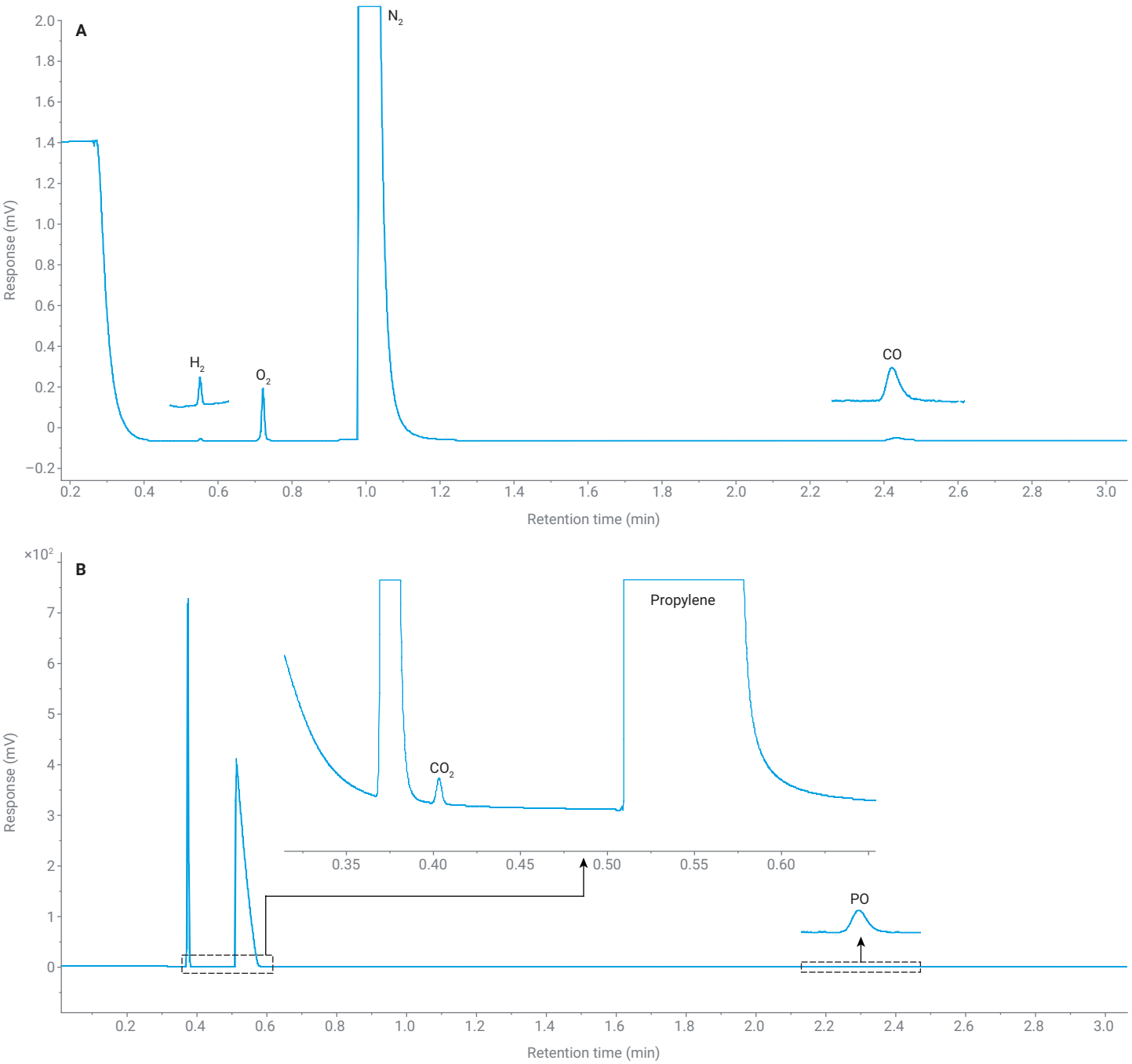

Figure 2. (A) Chromatogram of the Standard Gas 2 (PO synthesis) on the 3+10 m Agilent J&W CP-Molsieve 5Å backflush channel. (B) Chromatogram of the Standard Gas 2 (PO synthesis) on the 1+10 m Agilent J&W PoraPLOT U backflush channel.

Table 3 and Table 4 show the performance for a sequence of 10 runs of these two standard gases. The RT and area relative standard deviations (%RSDs) for these components are less than 0.2% and 2.5%, respectively. These low %RSD values demonstrate the excellent performance of the 990 Micro GC and its ability to provide quantitative results with a high level of confidence, repeatability, and quality.

Table 5 shows the estimated LDL of related components on the 3+10 m Molsieve 5Å backflush and 1+10 m PoraPLOT U backflush based on the calculation of current results or historical data that was obtained under similar experimental conditions described in Table 1.

Table 3. Retention time, area, and repeatability (%RSD) of these measures for 10 runs of the Standard Gas 1 (EO synthesis).

Component	Concentration	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analysis Channel
H_2	390 ppm	0.552	0.011	0.005	2.428	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
O_2	194 ppm	0.720	0.005	0.125	0.526	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
N_2	Balance (~25%)	0.985	0.012	156.582	0.017	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
CO	50.9 ppm	2.419	0.040	0.032	2.137	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
CO_2	49.8 ppm	0.354	0.040	0.034	0.141	1+10 m Agilent J&W PoraPLOT U, backflush
Ethylene	75.0%	0.359	0.000	516.881	0.093	1+10 m Agilent J&W PoraPLOT U, backflush
EO	90.0 ppm	2.493	0.037	0.067	1.691	1+10 m Agilent J&W PoraPLOT U, backflush

Table 4. Retention time, area, and repeatability (%RSD) of these measures for 10 runs of the Standard Gas 2 (PO synthesis).

Component	Concentration	RT (min)	RT RSD (%)	Area (mV × s)	Area RSD (%)	Analysis Channel
H_2	410 ppm	0.553	0.005	0.005	2.540	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
O_2	200 ppm	0.722	0.003	0.132	0.174	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
N_2	Balance (~25%)	0.986	0.006	163.553	0.018	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
CO	52.0 ppm	2.433	0.047	0.032	2.556	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
CO_2	47.5 ppm	0.404	0.004	0.037	0.102	1+10 m Agilent J&W PoraPLOT U, backflush
Propylene	74.7%	0.513	0.000	717.113	0.041	1+10 m Agilent J&W PoraPLOT U, backflush
PO	114 ppm	2.309	0.041	0.078	0.940	1+10 m Agilent J&W PoraPLOT U, backflush

Table 5. Lower detection limit (LDL) of this configuration.

Component	LDL (ppm)	Analysis Channel
H_2	50	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
O_2	10	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
N_2	10	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
CO	5	3+10 m Agilent J&W CP-Molsieve 5Å, backflush
CO_2	1	1+10 m Agilent J&W PoraPLOT U, backflush
Ethylene	2	1+10 m Agilent J&W PoraPLOT U, backflush
EO	5	1+10 m Agilent J&W PoraPLOT U, backflush
Propylene	2	1+10 m Agilent J&W PoraPLOT U, backflush
PO	5	1+10 m Agilent J&W PoraPLOT U, backflush

Conclusion

This application note demonstrates the chemical performance of Agilent 990 Micro GC for the analysis of ethylene oxide (EO) and propylene oxide (PO) synthesis. The 3+10 m Agilent J&W CP-Molsieve 5Å and the 1+10 m Agilent J&W PoraPLOT U channel on the 990 Micro GC can analyze H_2, O_2, N_2, CO, CO_2, ethylene, EO, propylene, and PO with excellent repeatability, a short analytical cycle time, and sufficient LDL at ppm levels. The 990 Micro GC is well suited for the fast and precise analysis of EO, PO, and their synthesis-related components.

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DE-008645

Printed in the USA, August 18, 2025
5994-8539EN

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