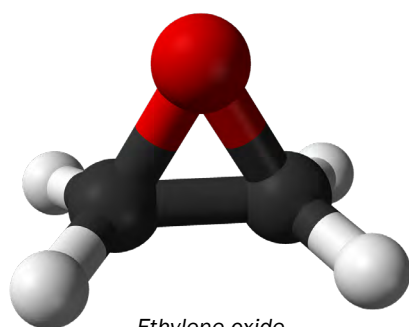


## Application Note 176

# Measurement of ethylene oxide with other air toxics from fugitive and area sources

### Summary

This application note covers the analysis of ethylene oxide as part of an air toxics study in compliance with US EPA Method 327. The note outlines the steps for evaluating method performance and testing system capability, with an emphasis on eliminating the use of liquid cryogen during the analysis. When sampling 500 mL, a method detection limit of 10 ppt was achieved, with a signal-to-noise ratio of 10:1 for the ethylene oxide peak.



### Introduction

Ethylene oxide is harmful to human health, and in 2016 was re-categorised as having a 100-in-1-million cancer risk level of 11 ppt.<sup>1</sup> This extreme low-level toxicity led to it being incorporated into the list of compounds measured at US EPA National Air Toxics Trends Stations (NATTS) in 2019.<sup>2</sup> However, to accurately monitor ethylene oxide, there are many analytical challenges to overcome such as:

- Sampling bias from formation of ethylene oxide in canisters of all types
- Chromatographic interferents
- Sensitivity due to the molecule's small size

Monitoring at NATTS sites was a first step towards a broader understanding of the presence of these species in ambient air but it did not address the risks to the public and workers from releases of ethylene oxide at industrial sites.

In response to the analytical challenges and the need to expand monitoring, the US EPA published Method 327 in 2024.<sup>3</sup> Method 327 provides analysts with a standard method for the measurement of selected hazardous volatile organic air pollutants for fugitive and area source measurements using canisters. It is based around the TO-15A guidance document for measurement of air toxics, described in Markes' [Application Note 169](#).

In this application note Markes' UNITY-CIA Advantage-xr™ with Kori-xr™ was used to generate data in line with the draft Method 327, demonstrating improved sensitivity, ease of method transfer between labs, and productivity without the need for cryogenic cooling.

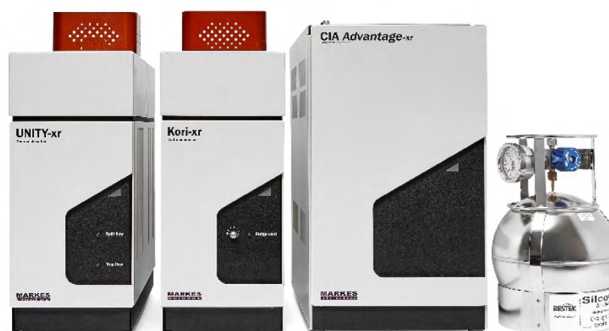
### Experimental

Standards were generated in canisters using a liquid ethylene oxide standard at 50 mg/mL and a 65 ppm TO-15 gas standard. The interferents investigated were acetaldehyde, methanol and trans-2-butene. These were added to the standards from two additional gas standards. Gas standards were at a concentration of 1 ppm. Canisters were humidified using HPLC grade water.

*Note: While excellent results were achieved using a liquid standard for generating standards, a traceable gas standard is recommended.*

The analytical system was Markes' UNITY-CIA Advantage-xr HL canister autosampler (with 14 positions and automated internal standard addition functionality) and preconcentration system coupled with Kori-xr for water management. Markes' Kori-xr works in tandem with UNITY-xr™ to remove water using the Dry-Focus 3™ three-stage focusing, which uses the Kori-xr water management module for the removal of the bulk which enables simultaneous analysis of all VOCs, including polar, in humid air. The UNITY-xr uses electrical cooling and backflush trapping to enable large volumes of sample to be concentrated and to enable rapid injections into the GC.

Before this work, to achieve sufficient separation, cooling the GC column with liquid cryogen had been publicised as the only option to carry out Method 327. To reduce routine laboratory operational costs, a cryogen-free program for the GC has been developed alongside the TD method.

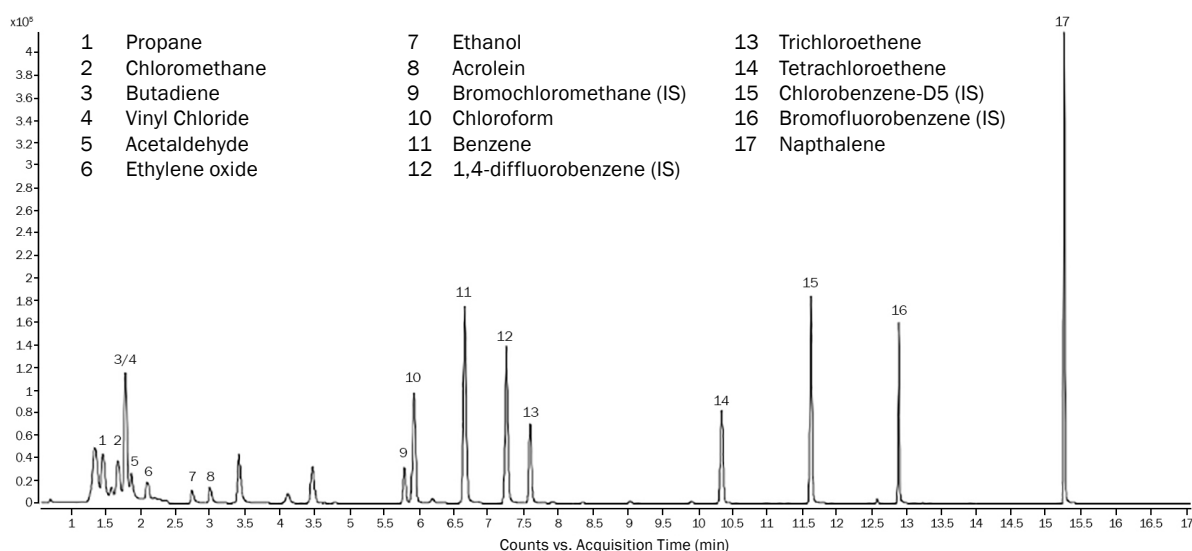


**Figure 1:** UNITY-CIA Advantage-xr coupled with Kori-xr is a modular system which can be upgraded in the field to add further capabilities as required.

**TD-GC-MS method parameters:**

Flow path: 120 °C  
 Sample: 500 mL @ 50 mL/min  
 (10 minutes)  
 Focusing trap: U-T015KXR  
 Kori trap temperature: -30 °C/300 °C  
 Focusing trap: -30 °C to 280 °C  
 Trap purge: 3 mins at 50 mL/min elevated  
 to 25 °C  
 Trap desorb time: 5 minutes  
 Trap heating rate: 40 °C/sec  
 Outlet split: 2 mL/min

Column: DB-624UI  
 (60 m x 320 µm x 1.8 µm)  
 Carrier gas: Helium  
 Column flow: 2 mL/min  
 GC oven: 35 °C (3 mins),  
 8 °C/min to 100 °C,  
 30 °C/min to 230 °C (5 mins)  
 Source: 300 °C  
 Quad: 200 °C  
 Transfer line: 200 °C  
 Simultaneous Full Scan and SIM

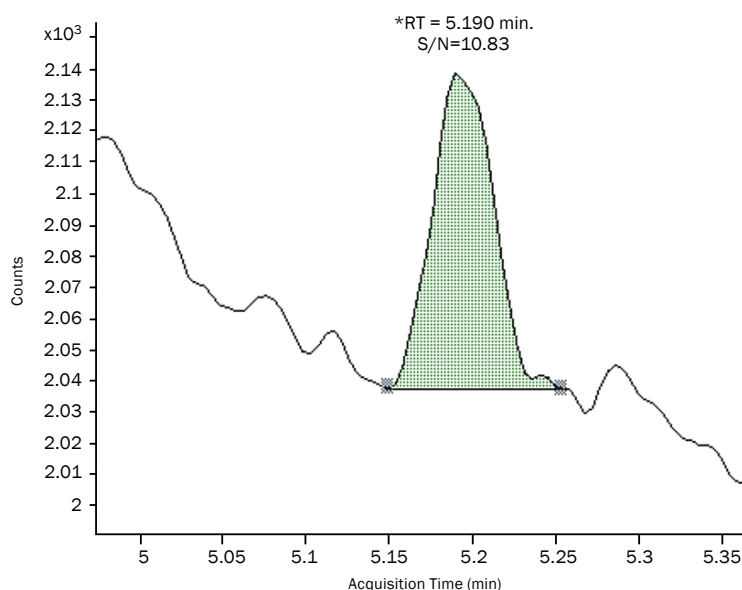
**Results****Analytical performance and method detection limits**

**Figure 2:** Example chromatogram of the 13 target species assessed in this study. Four internal standards were used to monitor the instrument performance and detector response over time as required by Method TO-15A.

The method detection limit (MDL) for this study was calculated by comparing seven replicates of method blanks with seven canisters that were filled with a standard to 10 ppt in accordance with US EPA guidance. The MDL calculated was 10 ppt with an average signal-to-noise (S/N) of 10. This is more than three times higher than required by US EPA Method 327, suggesting smaller sample sizes could be used if desired. Results for the compounds measured at NATTS sites are shown in Figure 2 and Table 1, and the peak shape for ethylene oxide can be seen in Figure 3.

Compound	Linearity (RF RSD)	%RSD 1 ppb (n = 10)	MDL (ppt)
Propene	2.02%	0.59%	1
Chloromethane	19.54%	0.62%	2
Butadiene	8.16%	0.38%	1
Vinyl Chloride	5.14%	0.44%	1
Ethylene oxide	9.49%	1.19%	10
Ethanol	9.04%	2.78%	33
Acrolein	2.36%	0.66%	12
Chloroform	13.00%	0.52%	1
Benzene	25.72%	0.40%	2
Trichloroethene	9.79%	0.40%	1
Tetrachloroethene	4.94%	0.49%	1
Naphthalene	13.04%	0.48%	4

**Table 1:** Linearity, repeatability and method detection limits for twelve air toxics including ethylene oxide and vinyl chloride.

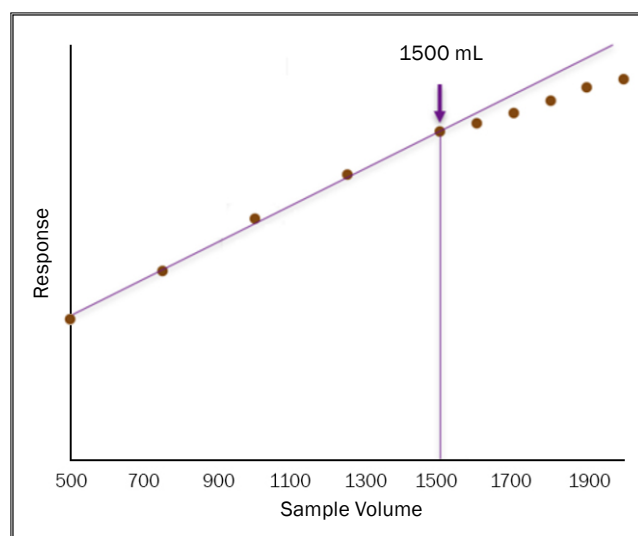


**Figure 3:** Ethylene oxide peak shape and S/N at 10 ppt. The S/N was 10.83, well above the required 3:1 required by Method 327

## Sensitivity

The easiest way to increase sensitivity is to increase the sample size. When using a pre-concentrator system, the maximum volume to sample from a canister is the volume at which the compounds begin to elute from the other end of the focusing trap – the breakthrough volume. The backflush design of Markes' focusing trap enables multiple sorbents to be used. This increases the volume and volatility ranges that can be sampled in a single experiment on a single unit. For ethylene oxide the breakthrough volume was 1500 mL on the trap developed for US EPA Method TO-15A.

Figure 4 shows the breakthrough volume for ethylene oxide. Increasing volumes of sample are taken in a sequence until the curve becomes non-linear indicating the sample is eluting from the end of the focusing trap and breakthrough has been reached.



**Figure 4:** Breakthrough testing for ethylene oxide.

A breakthrough volume of 1.5 L allows scope for method development. For this study a volume of 500 mL of sample was chosen, in line with previous work on low concentration air toxic compounds, detailed in Application Note 169.

MS parameters were optimised to provide the best sensitivity, but the number of interferences mean it is not practical to run with only SIM mode to enhance the sensitivity. SIM/scan mode is advised and has been used in this study.

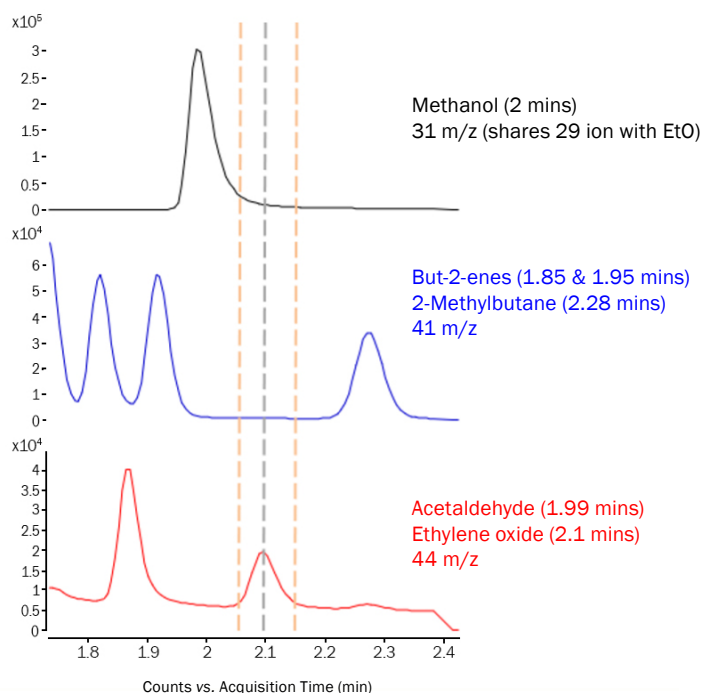
## Sampling bias

Ethylene oxide growth in canisters is beyond the control of the analyst. To ensure the lowest possible detection limits, the canisters chosen for the study were all silicon-ceramic lined and screened post-cleaning and prior to the analysis for any ethylene oxide background.

The UNITY-CIA Advantage-xr with Kori-xr module had no ethylene oxide detected in instrument blanks or autosampler bias checks. When the MDL blanks were performed, there was no ethylene oxide detected in any of the samples.

## Managing interferences

The flexibility of the UNITY-xr system's injection parameters and the connection between the transfer line and the GC column allows users to easily optimise chromatography and switch columns for optimal separation. In this case, various columns and carrier flow parameters were tested to separate ethylene oxide from the most challenging interferences, which were difficult to resolve using SIM due to shared ions. This approach was successful (as shown in Figure 5), enabling a fully cryogen-free approach to the analysis of ethylene oxide.



**Figure 5:** Final chromatographic separation of the ethylene oxide from the three interferents.

Water has the potential to interfere significantly with the analysis of ethylene oxide and should be removed prior to injection into the GC-MS. Bulk water removal was achieved using the Kori-xr water management device with the Dry-Focus-3 mechanism, ensuring any residual water was removed from the trap. During method development a 100% RH standard was used, and the trap was set to a purge temperature of 25°C. The purge time was then increased to assess how long the trap could be purged at this temperature without loss of the ethylene oxide or the most volatile compound chloromethane. The ethylene oxide response was stable between one and three minutes of purging with an RSD of 2.95% over all nine replicates. The most volatile air toxic compound typically measured by this analytical set up is chloromethane which also remained stable up to three minutes of purging.

## Conclusions

The results shown, using the UNITY-CIA *Advantage*-xr coupled with Kori-xr, meet the requirements of US EPA Method 327 in real samples, with a method detection limit of 10 ppt. Sensitivity can be further improved by increasing sample size, with volumes of up to 1.5 L possible before breakthrough of ethylene oxide.

Labs intending to carry out this method will need robust SOPs for managing sampling bias linked to canisters, even if the pre-concentration instrument and the GC-MS show no bias. This study demonstrated the possibility of managing interferents without the need for cryogenic cooling of the oven, which will benefit labs by making the system more productive, easier, and more economical to run.

This work also illustrated how easily a previously developed method could be transferred between two instruments in different labs. The TO-15A method developed in Markes' US lab was easily transferred to the Markes UK lab, with no significant changes required to accommodate ethylene oxide.

## References

1. Ethylene Oxide (EtO): Status Update on Available Measurement and Monitoring Technologies  
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2. US EPA Technical Note: Secondary Calibration Source Use for Ethylene Oxide Analysis in the National Air Toxics Trends Stations Network. 22/8/2019  
[https://www.epa.gov/sites/default/files/2021-04/documents/eto\\_stability\\_memo\\_082219.pdf](https://www.epa.gov/sites/default/files/2021-04/documents/eto_stability_memo_082219.pdf)
3. US EPA Method 327 - Fugitive and Area Source Measurement of Selected Volatile Organic Hazardous Air Pollutants Using Specially Prepared Canisters  
<https://www.epa.gov/system/files/documents/2024-07/method-327.pdf>

## Trademarks

UNITY-xr™, UNITY-CIA *Advantage*-xr™, Kori-xr™ and Dry-Focus 3™ are trademarks of Markes International.

*Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.*