

# Ethylene oxide measurement – techniques for sample collection and overcoming the challenges of this analysis

Hannah Calder,<sup>1</sup> Ryan Francis,<sup>1</sup> Tarun Anumol,<sup>2</sup> Simone Novaes-Card<sup>2</sup>

1. Markes International Ltd, 1000B Central Park, Western Avenue, Bridgend, CF31 3RT, UK. 2. Agilent Technologies, 2850 Centerville Rd, Wilmington, DE, 19808, United State

## 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. This incredibly low-level toxicity led to it being incorporated into the list of compounds measured at US EPA National Air Toxics Trends Stations (NATTS) sites in 2019. Monitoring at NATTS sites was a first step but did not address the risks to the public and workers from releases of ethylene oxide at industrial sites.

However, there are many analytical challenges to overcome such as:

- Sampling bias from formation of ethylene oxide in canisters of all types
- Sensitivity due to the molecules small size
- Chromatographic interferences

In response to the analytical challenges and limited monitoring the US EPA published draft method 327 in 2023. Method 327 provides analysts with a standard method for 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.

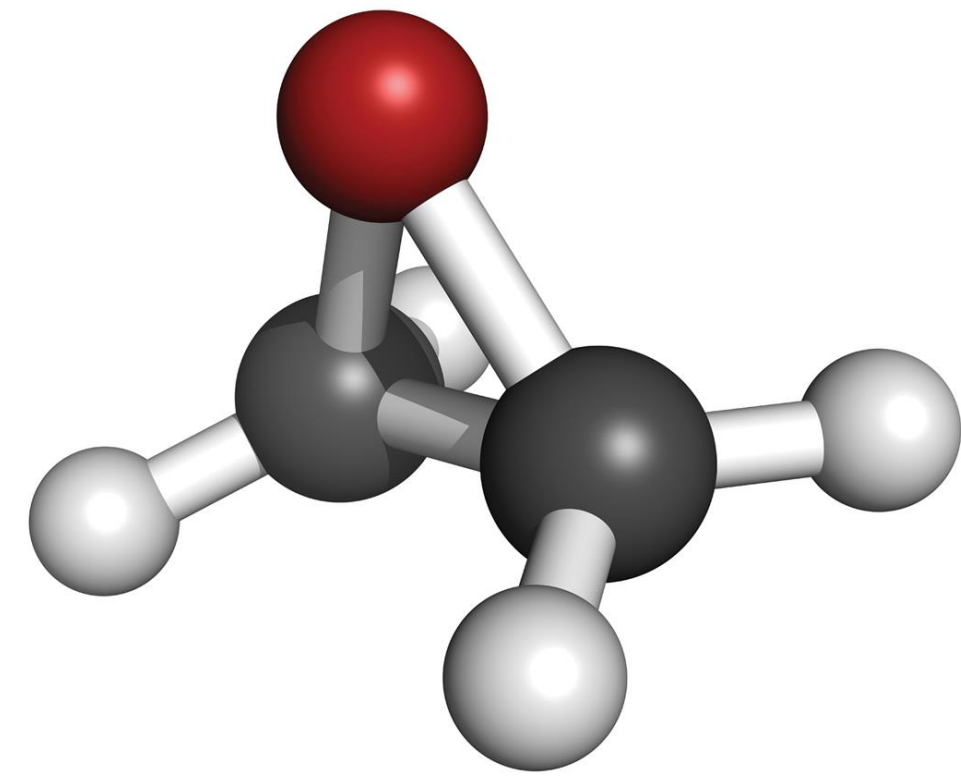


Figure 1: Ball and stick representation of the ethylene oxide molecule

In this poster data is discussed which has been generated in line with the draft method using the Markes International UNITY-Kori-CIA Advantage-xr. Utilising the Dry-Focus-3 mechanism for advanced water management and wide range backflushed trap for enhanced compound retention and method flexibility. Development of a cryogen free chromatographic program for the GC, which still managed interferences, was of importance to reduce analytical costs. Oven programs utilising cryogen had been published as the only option prior to this work.

## 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 interferences investigated were acetaldehyde, methanol and trans-2-butene. These were added to the standards from two additional gas standards. All gas standards were at a concentration of 1ppm.

Canisters: 6L SilcoCans from Restek with air as balance gas  
 Pre-concentrator: Markes UNITY-CIA Advantage-xr  
 Water removal: Markes Kori-xr  
 Focusing trap: Markes U-TO15-KXR  
 GC: Agilent 8890B  
 Column: DB-624MS  
 MS: Agilent 5977B



Figure 2: The UNITY-Kori-CIA Advantage-xr system used for method 327 connected to the Agilent 8890-5977

## Results and discussion

### Sampling bias

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

The UNITY-Kori-CIA Advantage-xr instrument 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.

### Sensitivity

The easiest way to increase sensitivity is the increase your sample size. When using a pre-concentrator system, the maximum volume you can sample from a canister is the volume at which compounds begin to elute from the other end of the focusing trap – the breakthrough volume. Due to the backflush design of the Markes focusing trap multiple sorbents can be accommodated which increases the volume and volatility ranges that can be sampled. For ethylene oxide the breakthrough volume was 1500 mL on the trap developed for TO-15a.

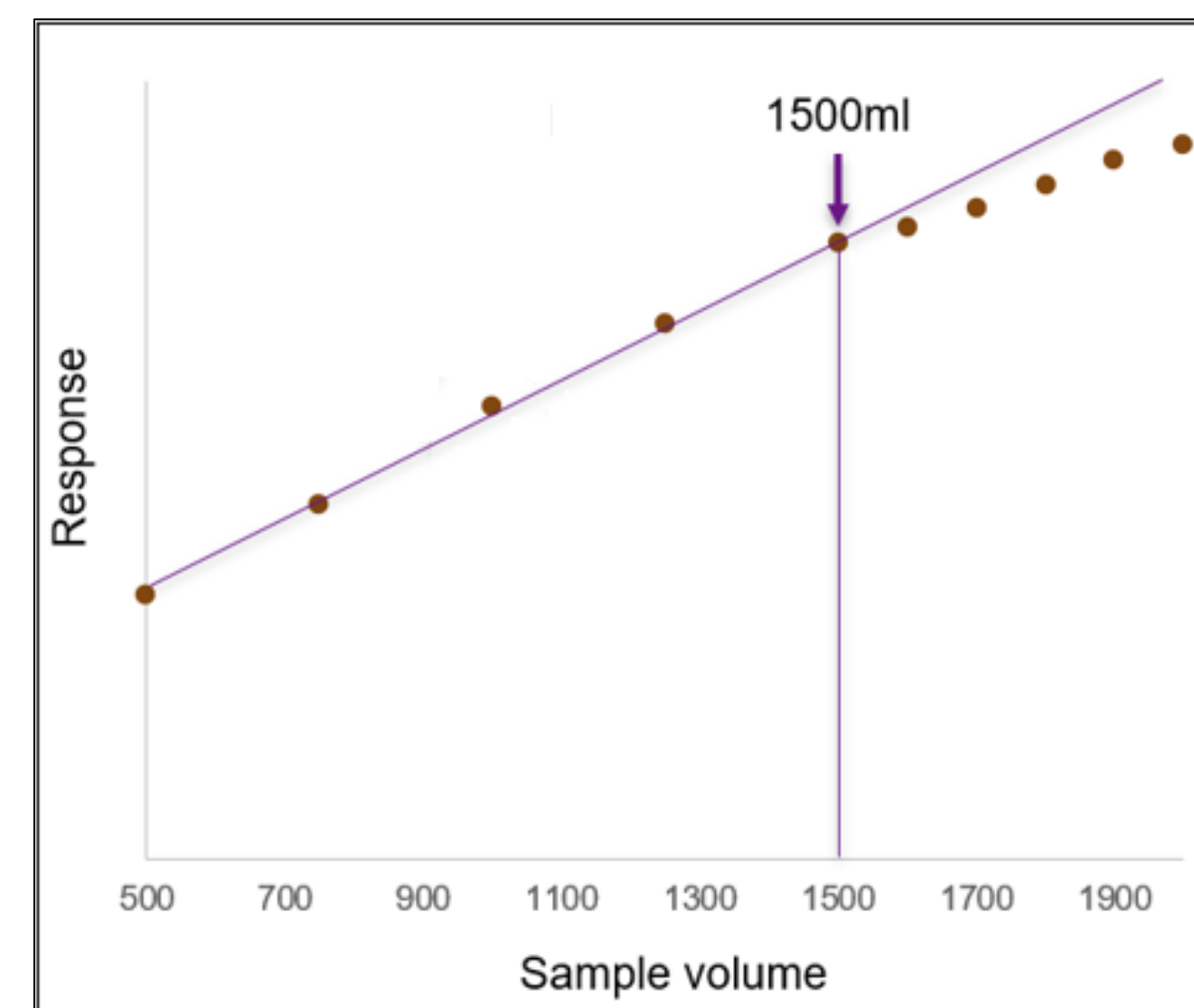


Figure 3: Breakthrough volume shown for ethylene oxide. Increasing volumes of sample are taken in a sequence until the curve becomes no linear indicating the sample is eluting from the end of the focusing trap.

This can be easily set up in Markes MIC software due the “unlockable parameters” which enables method parameters like sample volume to be edited in the sequence table. This eliminates the need to generate multiple methods during method development significantly saving analyst time.

It is not always practical to take large volumes of sample and there are trade-offs such as increased quantities of water and CO<sub>2</sub> which then require management. For this study, a volume of 500 mL of sample was chosen for the rest of the method development in line with what had been used in previous work on low concentration air toxic compounds.

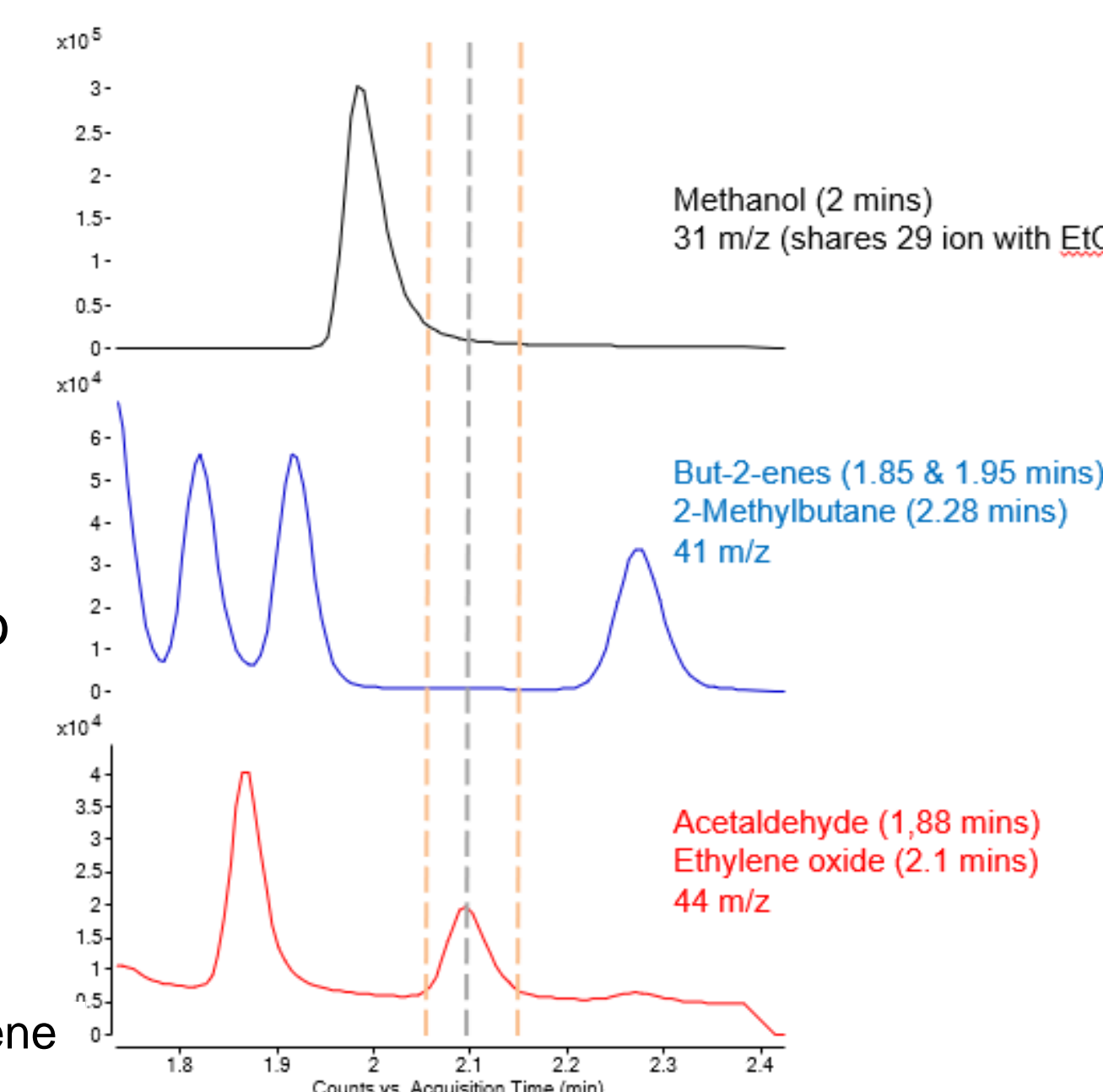
MS parameters were also optimised with the aim of giving the best sensitivity. However, due to the number of interferences it is not practical to run with only SIM mode to enhance the sensitivity. SIM/scan mode is advised and has been used here.

### Managing interferences

Flexibility in the injection parameters of the UNITY-xr system and how the transfer line connects to the GC column, means that it is simple for a user to really optimise the chromatography and change columns to ensure the optimum separation. In this case different columns and carrier flow parameters were trialled to separate the ethylene oxide from the interferences that were most difficult to resolve using SIM due to shared ions.

This was successful (as shown in Figure 4) enabling a fully cryogen free approach to the analysis of ethylene oxide.

Figure 4: Final chromatographic separation of the ethylene oxide from the three interferences.



### Managing interferences (cont.)

Water has the potential to interfere significantly with the analysis and should be removed prior to injection into the GC-MS.

Markes uses the Dry-Focus-3 mechanism which utilises the Kori-xr water management device for the removal of the bulk of the water and an elevated trap purge to drive any residual water from the trap prior to injection. 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.

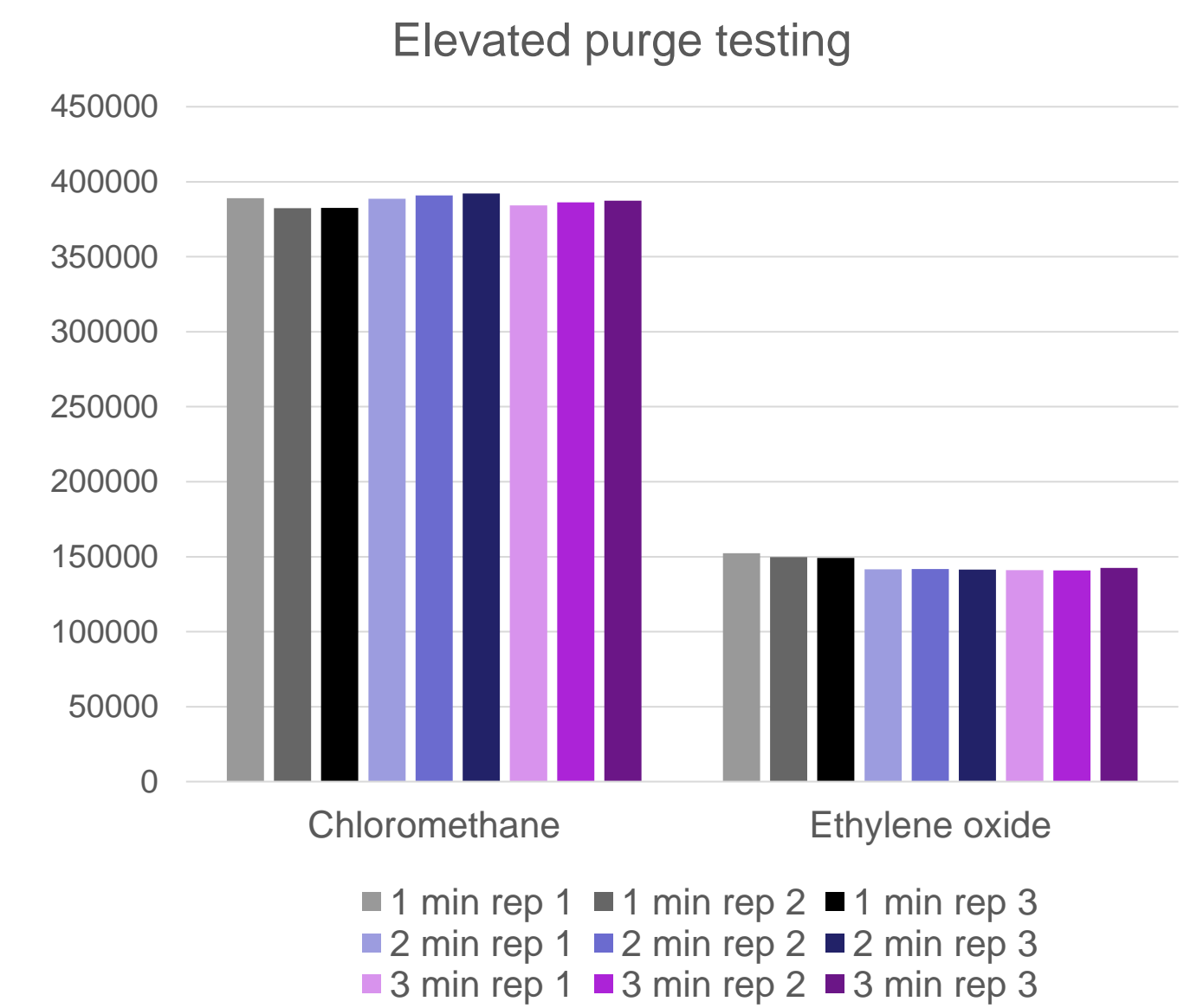


Figure 5: Ethylene oxide was stable from 1 minute to 3 minutes of purging with an RSD of 2.95% over all 9 replicates. Chloromethane also remained stable up to 3 minutes of purging.

### Method detection limits

The method detection limit (MDL) for this study was calculated by comparing n = 7 method blanks with n = 7 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 S/N of 10.

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
Acetaldehyde	19.35%	1.71%	43
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

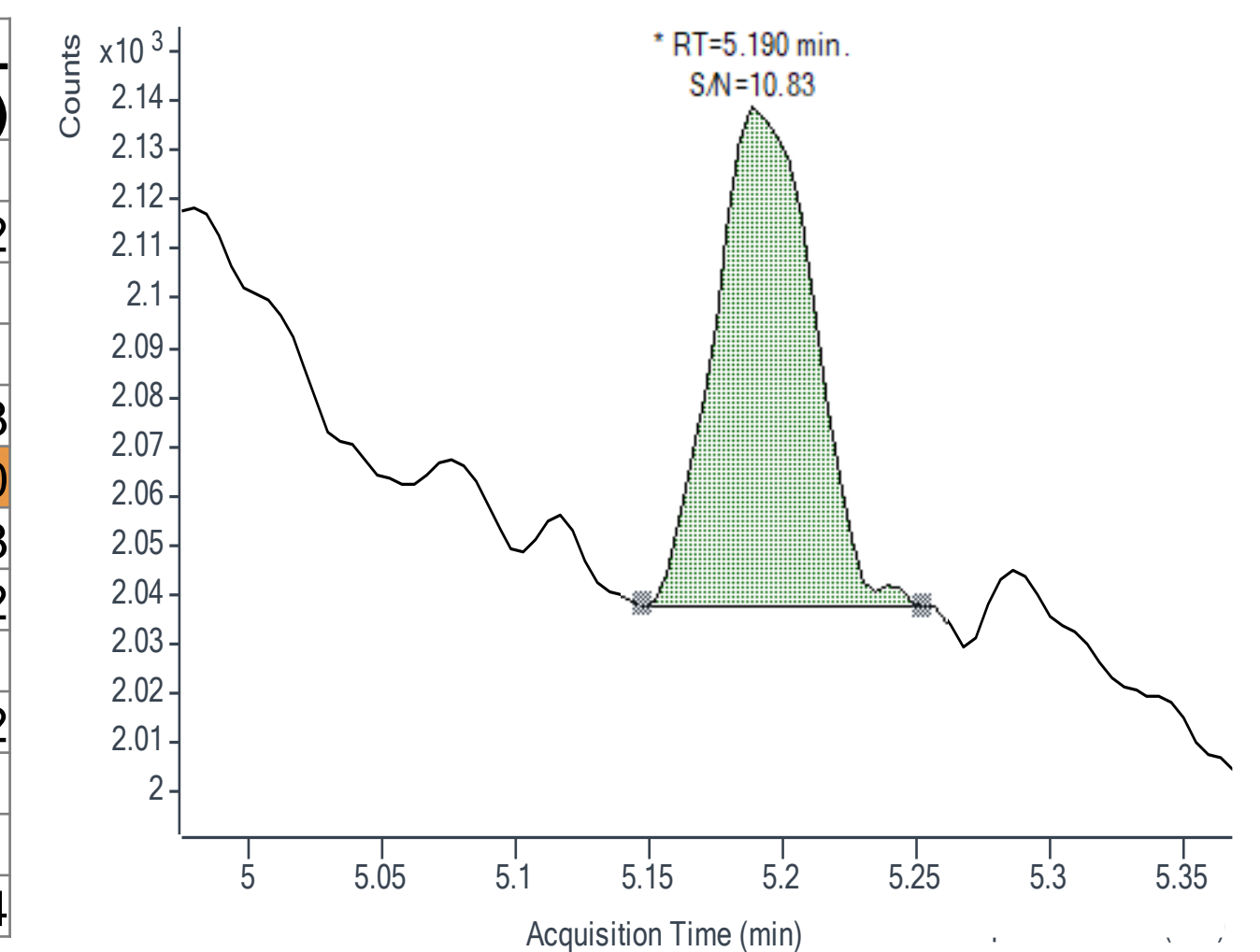


Table 1: Results table showing the linearity, reproducibility and method detection limit calculated from a 10 ppt level standard.

Figure 6: Ethylene oxide peak shape and signal to noise (S/N) at 10 ppt. The S/N was 10.83, well above the required 3:1 required by method 327.

## Conclusions

The results shown meet the requirements of draft method 327 and have the ability to reach the 11 ppt 100-in-1-million cancer risk level in real samples with a method detection limit of 10 ppt. Sensitivity can also be further improved by increasing sample size with volumes of up to 1.5L possible before breakthrough of ethylene oxide.

Labs intending to carry out this method will need robust SOPs for managing sampling bias linked to canisters but the pre-concentration instrument itself does not show any bias. This work has shown that it is possible to manage interferences without the need for cryogenic cooling of the oven. This will benefit labs through ease of use and by making the system both more productive and cheaper to run.

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

## Acknowledgements

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