A More Sustainable Analysis of Ethylene Oxide and 1,4-Dioxane in Surfactants with Hydrogen Carrier Gas

Using an Agilent 5977B GC/MSD with an Agilent HydroInert Source

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Abstract

Ethylene oxide (EO) and 1,4-dioxane are critical industrial chemicals often found as residuals in surfactant production. Due to their stringent regulatory requirements, precise analytical methods are essential for detecting these compounds at low concentrations. This study introduces a gas chromatography/mass spectrometry (GC/MS) method using a headspace (HS) sampler and an Agilent HydroInert source with hydrogen carrier gas. This approach addresses the global helium shortage while maintaining high sensitivity and linearity. The method effectively quantifies EO and 1,4-dioxane at regulatory-required levels, ensuring compliance in surfactant manufacturing. Validation results demonstrate that hydrogen carrier gas provides comparable performance to helium, with acceptable linearity, precision, accuracy, and limits of quantification.

Introduction

EO and 1,4-dioxane are key industrial chemicals, frequently found in the production of surfactants. During alkoxylation processes, residual raw materials or byproducts, such as EO and 1,4-dioxane, may remain in the final surfactant product (Figure 1). Although manufacturers have made significant strides in reducing these byproducts, increasing regulatory scrutiny on EO and 1,4-dioxane underscores the need for precise analytical methods to detect these compounds at low concentrations.[1–4] Thus, there is an urgent need to develop methods that can accurately quantify these compounds at levels as low as 0.1 ppm in consumer products.

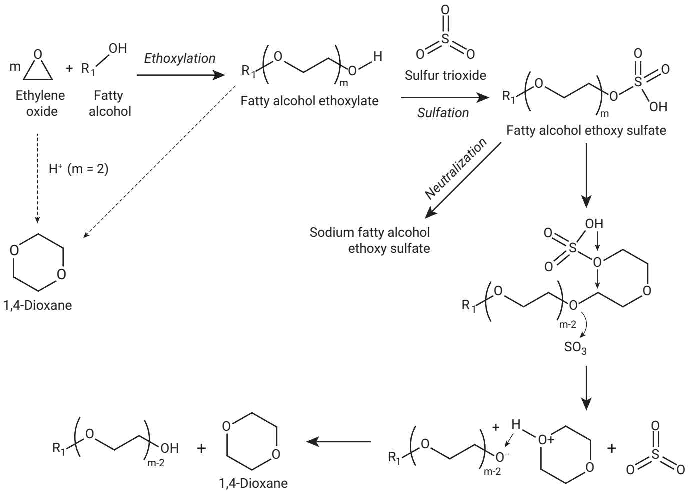


Figure 1. Pathways to 1,4-dioxane formation and residual ethylene oxide during the synthesis of fatty alcohol ethoxylate and sulfate.[5]

This study presents a method for the detection of EO and 1,4-dioxane using GC/MS with an HS sampler and a HydroInert source for hydrogen carrier gas. The use of hydrogen instead of helium not only addresses the global helium shortage but also ensures excellent sensitivity and linearity, while maintaining the integrity of the analytical process. The HydroInert source further eliminates chemical reactions often associated with hydrogen in mass spectrometry, offering a sustainable and reliable solution. The method developed in this study successfully quantifies both EO and 1,4-dioxane at the low concentrations required by current regulations, offering an accurate, reliable approach for compliance in surfactant manufacturing.

Experimental

This work was carried out using an Agilent 7890 GC with helium carrier gas and an Agilent 8890 GC with hydrogen carrier gas. Both GC systems were configured with an Agilent 5977B GC/MSD and PAL3 autosampler for headspace sampling. For the analysis using hydrogen carrier gas, the GC/MSD was fitted with a HydroInert source. The HydroInert source produces spectra in hydrogen that closely match those from helium-based libraries, such as NIST. This ensures spectral fidelity, allowing the same quantification and qualifier ions used in helium methods to be applied in SIM and MRM modes with hydrogen. Method parameters are shown in Table 1.

Table 1. GC and MS method parameters.

	Helium Carrier Gas	Hydrogen Carrier Gas
Headspace Parameters	80 °C for 15 min	80 °C for 15 min
GC Split	10:1	10:1
GC Column	Agilent J&W DB-624, 60 m × 0.25 mm × 1.40 µm (p/n 122-1364)	Agilent J&W DB-624, 60 m × 0.25 mm × 1.40 µm (p/n 122-1364)
GC Velocity	29 cm/s	46 cm/s
GC Oven Ramp	Hold 50 °C for 2 min, ramp to 240 °C at 14.5 °C/min	Hold 40 °C for 4 min, ramp to 240 °C at 25 °C/min
MS Transfer Line	280 °C	280 °C
MS Source Temperature	300 °C	300 °C
MS Target Group Ions 1	*m/z* 29, 43	*m/z* 29, 43
MS Target Group Ions 2	*m/z* 57, 64, 88, 96	*m/z* 57, 64, 88, 96

Internal standards (ISTD) were used for quantitation. These standards account for dilution or sample handling errors and correct for standard and sample matrix differences between samples within an analysis set.

Surfactant samples were prepared by adding 2 g of sample and 2 g of 1 ppm 1,4-dioxane-d8 ISTD to headspace vials.

Calibration standards were prepared according to Table 2. Appropriate aliquots of water and 2 g of 1 ppm 1,4-dioxane-d8 ISTD were added to headspace vials. Once complete, Standard 1 was prepared and aliquots of Standard 1 were added to each headspace vial already containing the water and ISTD. Preparing in this order ensured there was no loss of EO.

Standard 1 was prepared by adding 7.4 g of Milli-Q water in a 20 mL scintillation vial and then transferring 1.2 g of the 50 ppm standard containing EO and 1,4-dioxane (ordered as a solution in PEG). The standard was then quickly capped, shook well, and labeled as 7 ppm stock.

Table 2. Calibration standards preparation.

Standard	Concentration (ppm)	Water (g)	Standard 1 (g)
2	0.016	1.999	0.004
3	0.03	1.99	0.01
4	0.06	1.98	0.017
5	0.5	1.85	0.15
6	1.5	1.6	0.4
7	2.5	1.3	0.7
8	4.0	0.9	1.1
9	5.0	0.5	1.5

Results and discussion

A method for the analysis of ethylene oxide and 1,4-dioxane in surfactants was developed using hydrogen carrier gas. This method was benchmarked against method performance using helium carrier gas. Both methods were compared using the method validation criteria shown in Table 3.

Table 3. Criteria for method validation.

Statistic	Method Validation Requirement
1. Slope	Linear ($p < 0.05$)
2. Intercept	Not significant ($p > 0.05$)
3. Pearson Correlation	$R^2 > 0.99$
4. Residuals Normality	Normal distribution ($p > 0.05$)
5. Homoscedasticity	Homoscedastic ($p > 0.05$)
6. Outliers	Outliers not detected ($p > 0.05$)
7. Lowest Limit of Quantitation (LOQ)	S/N > 10
9. Precision at LOQ	< 11% RSD
9. Accuracy at LOQ	80 to 110% recovery
10. Precision at Three Spike Levels	< 11% RSD
11. Accuracy at Three Spike Levels	80 to 110% recovery

Method validation requirements for linearity are listed in rows 1 to 6 in Table 3. Figures 2 to 4 demonstrate acceptable performance for both helium and hydrogen carrier gases. A strong linear correlation is observed with $R^2 > 0.99$ for both compounds using both carrier gases. The data also shows a normal distribution and homoscedasticity across all calibration curves.

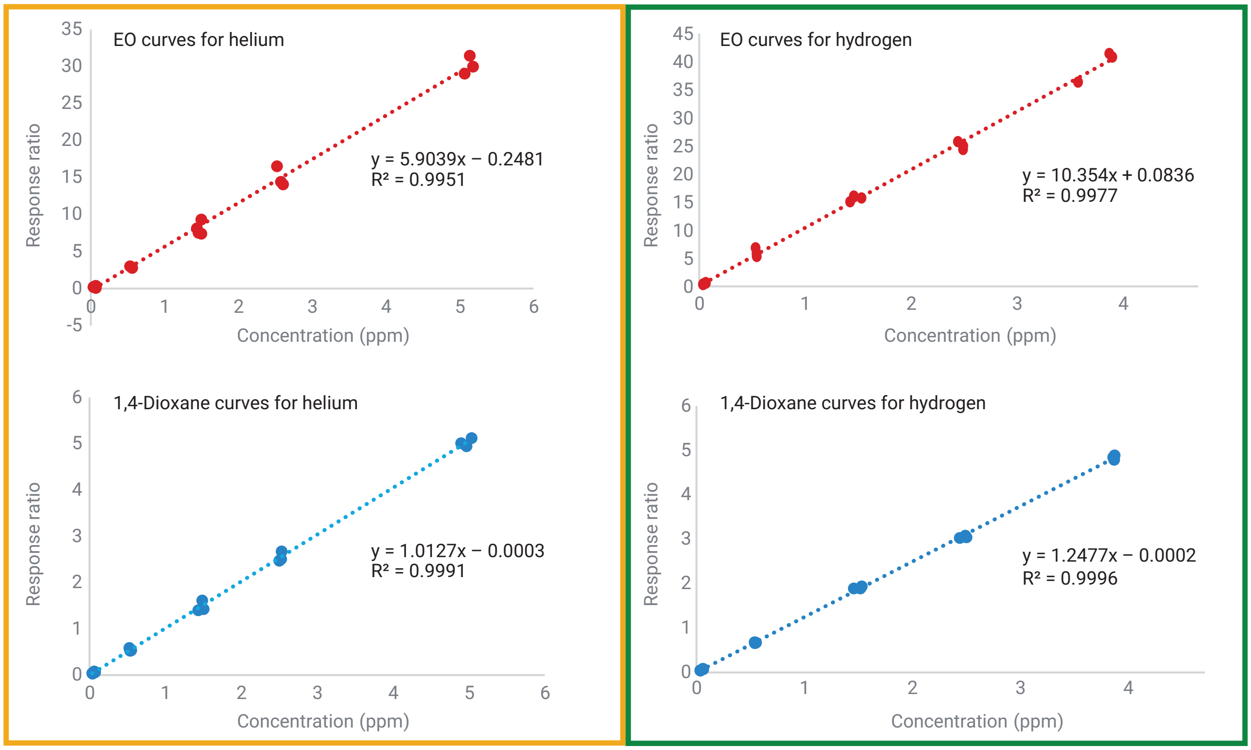


Figure 2. Calibration linearity for ethylene oxide and 1,4-dioxane using both helium and hydrogen carrier gases.

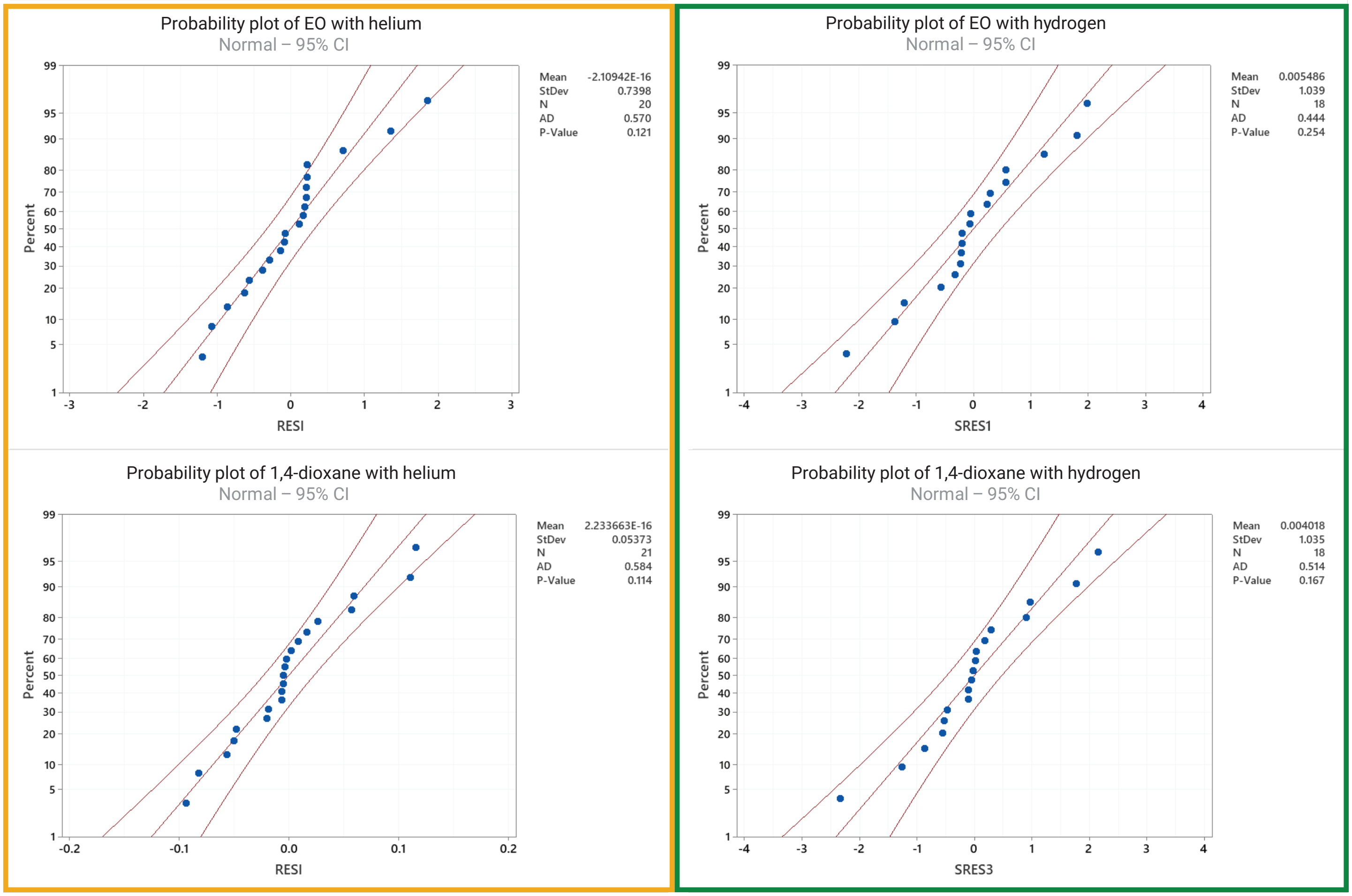
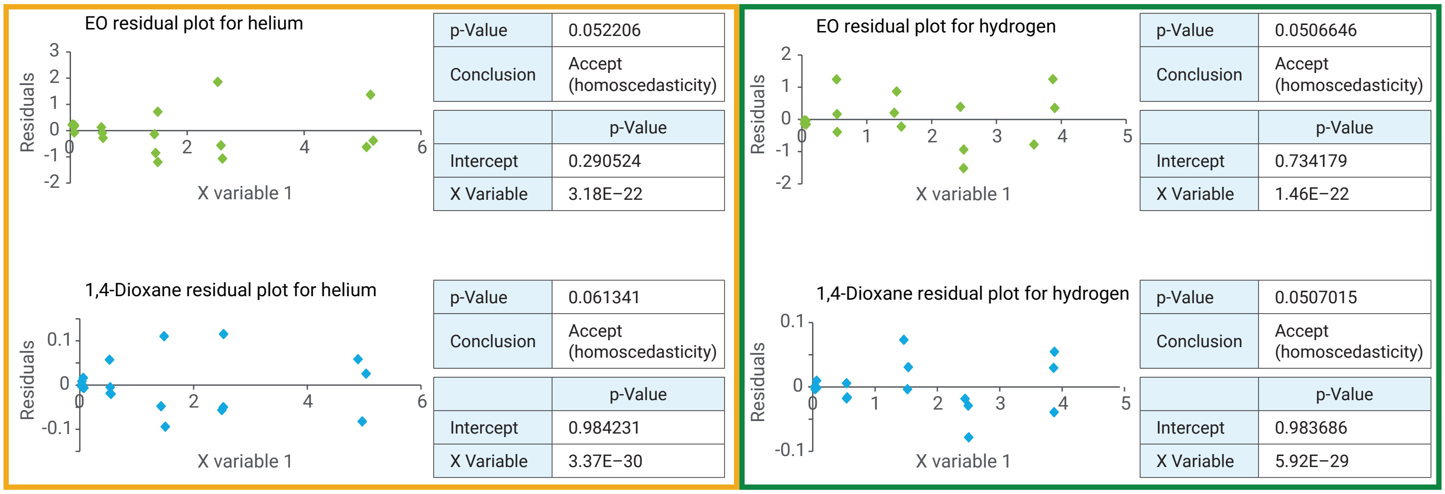


Figure 3. Probability plots for residual data showing normal distribution for ethylene oxide and 1,4-dioxane using both helium and hydrogen carrier gases.



EO residual plot for helium

p-Value	0.052206
Conclusion	Accept (homoscedasticity)

	p-Value
Intercept	0.290524
X Variable	3.18E–22

EO residual plot for hydrogen

p-Value	0.0506646
Conclusion	Accept (homoscedasticity)

	p-Value
Intercept	0.734179
X Variable	1.46E–22

1,4-Dioxane residual plot for helium

p-Value	0.061341
Conclusion	Accept (homoscedasticity)

	p-Value
Intercept	0.984231
X Variable	3.37E–30

1,4-Dioxane residual plot for hydrogen

p-Value	0.0507015
Conclusion	Accept (homoscedasticity)

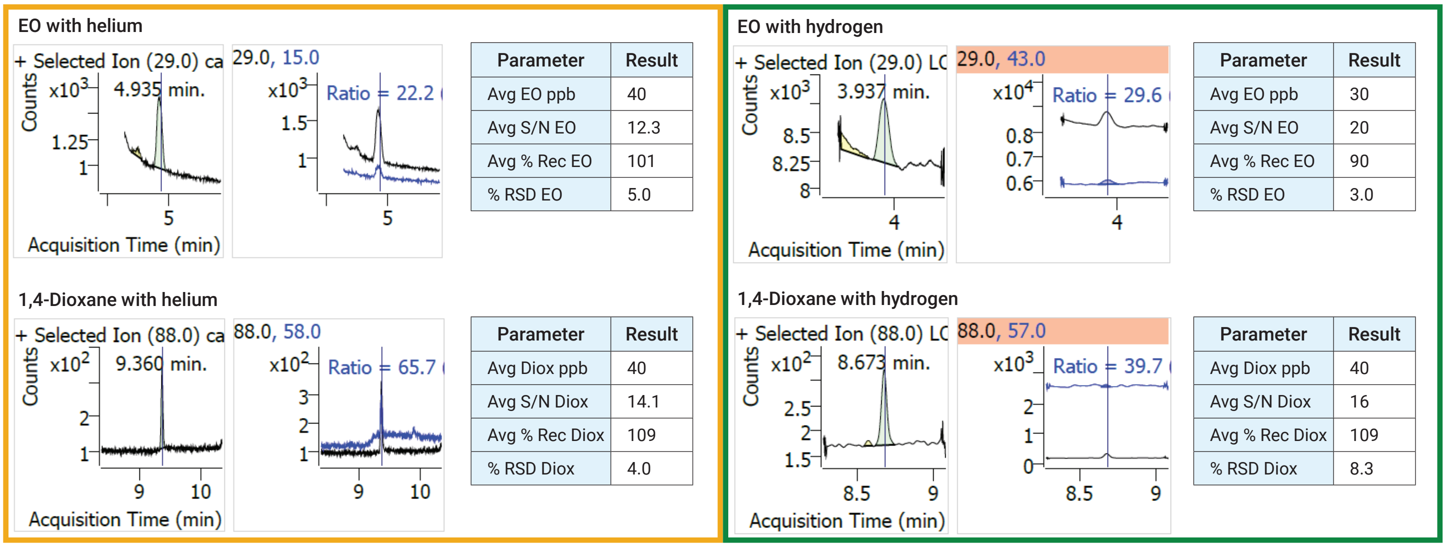
	p-Value
Intercept	0.983686
X Variable	5.92E–29

Figure 4. Homoscedasticity and slope intercept results showing the residual variance is equal across calibration curves.

Method validation requirements for lowest limit of quantitation (LOQ) are listed in rows 7 to 9 of Table 3. Figure 5 shows acceptable method performance for precision and accuracy at LOQ level for both carrier gas methods. LOQs are measured between 30 and 40 ppb for EO and 1,4-dioxane for both methods. Good accuracy and precision are demonstrated at LOQ level with recovery ranging from 90 to 109% and relative standard deviation from 3 to 8.3%.

Method precision and accuracy are further demonstrated at three spiking levels, as seen in Figure 6. Both helium and hydrogen carrier gases offer acceptable performance per the criteria shown in rows 10 and 11 of Table 3. Relative standard deviation ranges from 0.7 to 10.2% and recovery from 87 to 110%.

Comparing method performance based on the stated method validation criteria, both helium and hydrogen offer acceptable performance for measuring EO and 1,4-dioxane in surfactants. Linearity, precision, and accuracy were proven for both methods, as well as the ability to achieve an LOQ of 30 to 40 ppb for EO and 1,4-dioxane.



EO with helium

Parameter	Result
Avg EO ppb	40
Avg S/N EO	12.3
Avg % Rec EO	101
% RSD EO	5.0

1,4-Dioxane with helium

Parameter	Result
Avg Diox ppb	40
Avg S/N Diox	14.1
Avg % Rec Diox	109
% RSD Diox	4.0

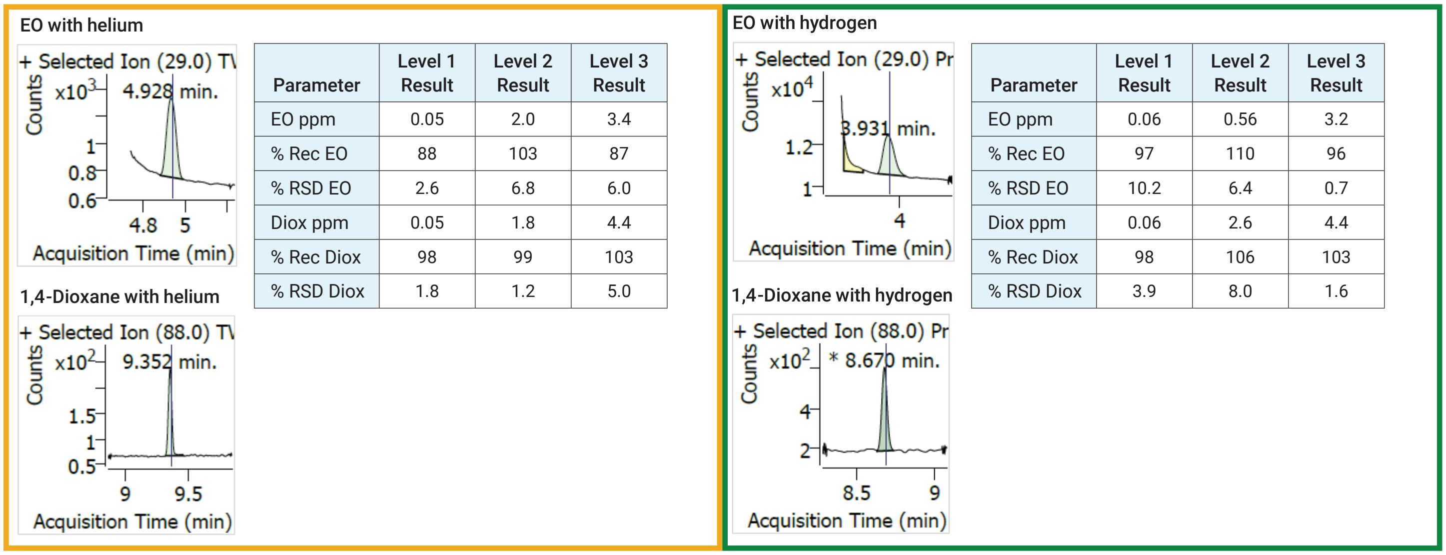
EO with hydrogen

Parameter	Result
Avg EO ppb	30
Avg S/N EO	20
Avg % Rec EO	90
% RSD EO	3.0

1,4-Dioxane with hydrogen

Parameter	Result
Avg Diox ppb	40
Avg S/N Diox	16
Avg % Rec Diox	109
% RSD Diox	8.3

Figure 5. Limits of quantification tested for ethylene oxide and 1,4-dioxane using both helium and hydrogen carrier gases.



EO with helium / 1,4-Dioxane with helium

Parameter	Level 1 Result	Level 2 Result	Level 3 Result
EO ppm	0.05	2.0	3.4
% Rec EO	88	103	87
% RSD EO	2.6	6.8	6.0
Diox ppm	0.05	1.8	4.4
% Rec Diox	98	99	103
% RSD Diox	1.8	1.2	5.0

EO with hydrogen / 1,4-Dioxane with hydrogen

Parameter	Level 1 Result	Level 2 Result	Level 3 Result
EO ppm	0.06	0.56	3.2
% Rec EO	97	110	96
% RSD EO	10.2	6.4	0.7
Diox ppm	0.06	2.6	4.4
% Rec Diox	98	106	103
% RSD Diox	3.9	8.0	1.6

Figure 6. Precision and accuracy measurements in spiked samples for ethylene oxide and 1,4-dioxane using both helium and hydrogen carrier gases.

Conclusion

This work establishes a first of its kind method using hydrogen carrier gas to reliably measure ethylene oxide and 1,4-dioxane in surfactants. Mass spectrometry detection was optimized for use with hydrogen by installing an Agilent HydroInert source. The HydroInert source helps to avoid sensitivity loss and spectral anomalies that are common with hydrogen carrier gas applications, resulting in suitable linearity, precision, accuracy, and LOQs for this analysis.

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