GCMS-QP^{TM}2020 NX HS-20 NX (Loop Model)

Application News

1,4-Dioxane Analysis on Surface Water and Tap Water by Static Headspace and GCMS

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User Benefits

- Simple sample preparation procedure, direct sample analysis
- Sample recovery within 80 % to 120 %

Introduction

1,4-dioxane can be produced as a byproduct from certain manufacturing processes and remain in the final products, such as soaps, and detergents and other consumer and commercial products [1]. It may be possible for 1,4-dioxane to be released into the environment from these products when they are used and washed down the drain[1]. Exposure to a contaminated environment may result in the population being exposed to 1,4-dioxane. This can be dangerous as it has the potential to cause adverse health effects, such as liver toxicity and cancer.[1]. Therefore, 1,4-dioxane in environment, such as water, needs to be controlled and monitored to protect the public health.

In this application news, a method using static headspace coupled with GCMS has been optimized to quantify 1,4-dioxane in surface water and tap water, with reference to Application Data Sheet No. 108 [2]. The instrument detection limit has been determined to be 0.1 µg/L, with a signal-to-noise ratio (S/N) greater than 3. The limit of quantitation has been set at 1 µg/L, with S/N result greater than 30 and an area % RSD (n=5) of 4.2 %. The percentage recovery for 1,4-dioxane ranged from 100 % to 120 %.

Experimental

Analysis condition

GCMS-QP2020 NX with HS-20 NX (Shimadzu Corporation, Japan) were used in this work (Figure 1). GCMS-QP2020 NX is equipped with a patented ion source technology for ultra trace analysis. The HS-20 NX (Loop Model) headspace autosampler is designed with a short transfer line to minimize analyte loss, thereby resulting in high sensitivity detection for this application.

The analytical conditions used in this study are summarized in Table 1.

Standard and sample preparations

Sodium chloride and 1,4-dioxane were purchased from Merck. Mili-Q grade water was used as a diluent in this application. Sodium chloride would be added for "salting out" effect which increases the sensitivity of 1,4-dioxane during headspace analysis.

For the preparation of calibration standard solutions, 1,4-dioxane was diluted with Mili-Q water to final concentrations of 1, 2, 5, 10, 20, 50 and 100 µg/L.

Figure 1: GCMS-QP^{TM}2020 NX and HS-20 NX Headspace Autosampler

Table 1: Static headspace and GCMS analytical conditions for analysis of 1,4-dioxane in water.

Headspace Autosampler Parameter (HS-20 NX, Loop Model)	
Oven Temp.	70 °C
Sample Line Temp.	150 °C
Transfer Line Temp.	150 °C
Shaking Level	5
Multi Injection Count	1
Pressurizing Gas	Nitrogen
Pressurizing Gas Pressure	57 kPa
Equilibrating Time	30.0 min
Pressurizing Time	1.0 min
Pressure Equilib. Time	0.1 min
Load Time	0.5 min
Load Equilib. Time	0.1 min
Injection time	1.0 min
Needle Flush Time	1.0 min
GC Cycle Time	27.0 min
Sample Loop Volume	1 mL
GC Parameter	
Carrier Gas	Helium
Injection Mode	Split mode, split ratio 5
Flow Control Mode	Linear Velocity, 62.5 cm/s
Purge Flow	3 mL/min
Column	SH-I-624 Sil MS (30 m x 0.32 mm ID x 1.8 µm df) [P/N: 227-36077-01]
Column Oven Temperature Program	40 °C (hold time: 2 min) → rate: 20 °C/min to 230 °C (hold time: 5 min)
MS Parameter	
Ion Source Temp.	200 °C
Interface Temp.	230 °C
Solvent Cut Time	2 min
Acq. Mode	SIM
SIM Ion for 1,4 Dioxane	88, 58

To create a calibration curve, 2 mL of each calibration standard solution was aliquoted into separate 20-mL headspace vials containing 0.7 g of sodium chloride. The vials were then promptly sealed with a crimp cap and loaded onto the headspace autosampler for analysis.

Tap water and river water were used as the samples. For sample preparation, 2 mL of each sample was aliquoted into separate 20-mL headspace vials containing 0.7 g of sodium chloride. The vials were then promptly sealed with a crimp cap and loaded onto the headspace autosampler for analysis.

■ Results

Sensitivity, Repeatability and Linearity

Figure 2 displays a 7-point external standard calibration curve (1, 2, 5, 10, 20, 50, and 100 µg/L) of 1,4-dioxane. The R^2 value is 0.999, demonstrating the capability of both the instruments and the method to achieve excellent linearity within the range of 1 µg/L to 100 µg/L. The instrument detection limit (IDL) was determined to be 0.1 µg/L, with a signal-to-noise ratio (S/N) greater than 3 (Figure 3a). The lowest calibration level, 1 µg/L, is displayed in Figure 3b. As shown in Table 2, all the 1 µg/L results have a S/N greater than 10. The area % RSD (n=5) for 1,4-dioxane at a concentration of 1 µg/L was found to be 4.2 % (Table 2).

Table 2: Area count repeatability results (n=5) and signal-to-noise ratios of 1,4 dioxane at 1 µg/L.

Compound		1	2	3	4	5	% RSD
1,4-dioxane	Area count	2793	2543	2814	2679	2627	4.2
	S/N	40	31	34	35	31	

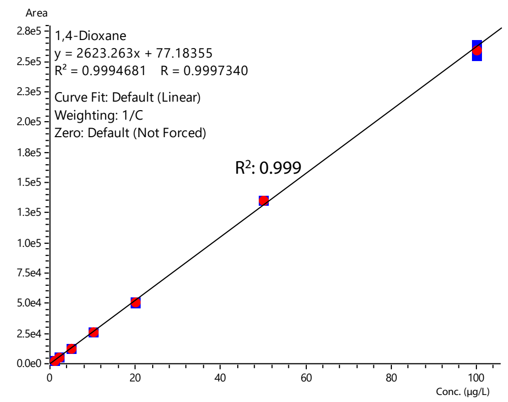

Figure 2: A seven-point calibration curve of 1,4-dioxane.

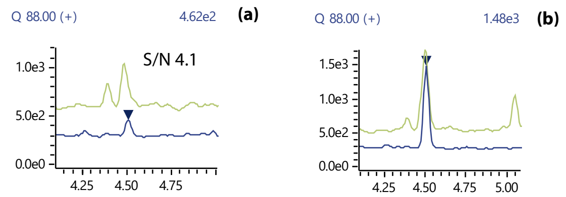

Figure 3: Mass chromatograms of 1,4-dioxane at: (a) 0.1 µg/L; (b)1 µg/L.

Quantitation and Recovery Results

The two different samples, tap water and river water, were tested, and neither of them contained 1,4-dioxane.

A recovery test was conducted on these two samples. Each sample was spiked to achieve final concentrations of 1, 10, and 100 µg/L. In this recovery study, all the results were within the range of 100 % to 120 % (Table 3).

Table 3: 1,4-dioxane recovery results in tap water and river water.

Sample		Conc Result (µg/L)	% Recovery
Tap water	Unspiked	N.D.*	
	1 µg/L spiked	1.150	115
	10 µg/L spiked	10.854	109
	100 µg/L spiked	112.664	113
River water	Unspiked	N.D.*	
	1 µg/L spiked	1.146	115
	10 µg/L spiked	10.769	108
	100 µg/L spiked	109.319	109

*Not Detected

■ Conclusion

A static headspace-GCMS method was optimized for the analysis of 1,4-dioxane in tap water and river water using HS-20 NX (Loop Model) autosampler with GCMS-QP2020 NX. The IDL was determined to be at 0.1 µg/L with an S/N greater than 3. Excellent linearity (R^2 value > 0.999) was achieved for 1,4-dioxane. Recoveries were within the range of 100 % to 120 % for the samples analyzed in this experiment.

■ Acknowledgement

We would like to express our sincere appreciation to Leong En Kai, student from Nanyang Technological University, Chemistry and Biological Chemistry Department, for his valuable contribution to this project during his internship program in Shimadzu (Asia Pacific).

■ References

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04-AD-0303-EN First Edition: Apr 2024

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