

Application Data Sheet

No. 130

GC-MS

Gas Chromatograph Mass Spectrometer

Determination of 1,4-Dioxane in Shampoo Using the OPTIC-4 Multimode Inlet

Difficult matrix introduction (DMI), one of the injection modes provided by the OPTIC-4 multimode inlet, is effective at simplifying the pretreatment process. In this method, the micro vial into which the sample has been placed is put into a liner. The liner is then heated by the inlet so that the target components are introduced into the column. By adjusting the inlet temperature, it is possible to leave the nonvolatile components in the micro vial, enabling GC/MS measurements with simple pretreatment.

A method for easily quantifying the amount of 1,4-dioxane in shampoo using DMI was investigated. 1,4-dioxane can be produced in extremely small quantities as a byproduct of the process of manufacturing surfactants, the main component in shampoos and detergent for tableware. It is suspected of causing cancer in humans. The headspace method is often used for this substance. In this case, however, a simple method of quantitative determination utilizing DMI was investigated. In addition, the possibility of consecutive automatic analysis with the AOC-6000, in anticipation of cases in which there are a number of samples, was also investigated.

Experiment

1.00 g samples of a commercially available shampoo were measured out and poured into three vials, respectively, followed by 1.00 g of ultrapure water. A 1,4-dioxane solution was then added to two of the vials to reach a 1,4-dioxane concentration of 2.00 µg/mL and 50.00 µg/mL, respectively. In addition, a 1,4-dioxane-*d*8 solution was added to all three vials to reach a 1,4-dioxane-*d*8 concentration of 10.00 µg/mL. After this, they were well agitated. 3.0 µL of each sample obtained were injected into a separate micro vial. Each micro vial was placed in a liner, which was then passed through the O-ring for sealing the inlet. After both ends were capped, the liner was placed into the rack for the AOC-6000. A consecutive automatic analysis was then performed with a GC/MS.

Table 1: Analytical Conditions

Instrument		MS	
Injection Port:	OPTIC-4	Interface Temperature:	250 °C
Liner:	L100011, DMI liner with taper	Ion Source Temperature:	200 °C
GC-MS:	GCMS-QP2020	Data Acquisition Time:	1 to 5 min
Autosampler:	AOC-6000 (LINEX-2 and CDC Station included)	Measurement Mode:	SIM
Column:	SH-Rxi-5SiIMS (0.25 mm × 30 m, df = 0.25 µm)	1,4-dioxane	<i>m/z</i> 88, 58, 43
		1,4-dioxane- <i>d</i> 8	<i>m/z</i> 96, 64, 46
Injector		Event Time:	0.2 sec
Vent Time:	1 min	Detector Voltage:	Relative to the Tuning Result 0 kV
Method Type:	Split		
Equilibration Time:	5 sec		
End Time:	16 minute		
Injector Temperature:			
	35 °C (10 sec) → (50 °C/sec) → 120 °C (1 min) → 35 °C		
Carrier Gas:	Helium		
Carrier Control Mode:	Flow control		
Start Column Flow:	1.2 mL/min		
End Column Flow:	1.2 mL/min		
Initial Split Flow:	250 mL/min		
Split Flow:	24 mL/min		
Septum Purge Flow:	10 mL/min		
Cryotrap:	-100 °C (100 sec) → (50 °C/sec) → 220 °C		
GC			
Column Oven Temperature:			
	40 °C (8 min) → (30 °C/min) → 220 °C (1 min)		

Results

Figs. 1 and 2 show the SIM chromatograms obtained from the analysis of the shampoo containing 1,4-dioxane at a concentration of 2.00 µg/mL and 50.00 µg/mL, respectively. Table 2 shows the results of calculating the concentrations from the peak area ratio between 1,4-dioxane with *m/z* 88 and 1,4-dioxane-*d*8 with *m/z* 96.

When the recovery rates for the 1,4-dioxane added to the shampoo were calculated, favorable results of 102.0 % for the 2.00 µg/mL addition and 100.6 % for the 50.00 µg/mL addition were obtained. After the analyses were finished, a dull white solid was found to have adhered to the walls of the micro vials.

From the results above, it is evident that measurements can be performed with high sensitivity up to several µg/mL, and that favorable quantitative determination can be performed by adding the isotope 1,4-dioxane-*d*8.

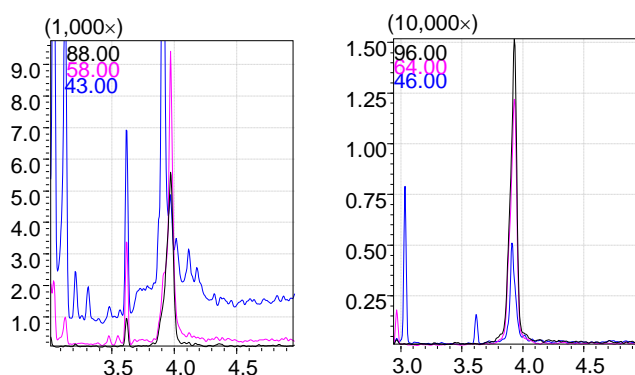


Fig. 1: SIM Chromatograms of 1,4-Dioxane (Left) and 1,4-Dioxane-*d*8 (Right) in Shampoo Spiked with 2.00 µg/mL 1,4-Dioxane

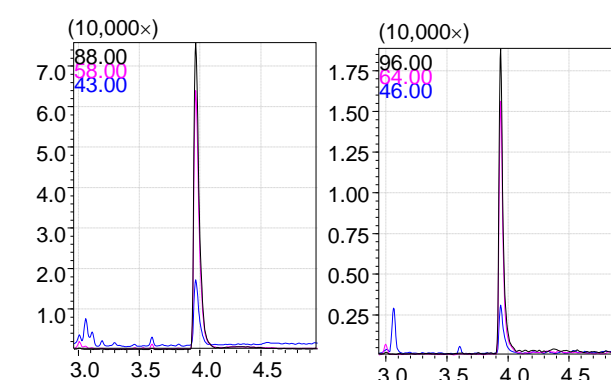


Fig. 2: SIM Chromatograms of 1,4-Dioxane (Left) and 1,4-Dioxane-*d*8 (Right) in Shampoo Spiked with 50.00 µg/mL 1,4-Dioxane

Table 2: Quantitative Results

Sample	Concentration (µg/mL)	Blank corrected Concentration (µg/mL)	Recovery Rate (%)
Shampoo	1.57		
Shampoo Spiked at 2.00 µg/mL	3.61	2.04	102.0
Shampoo Spiked at 50.00 µg/mL	51.88	50.31	100.6

Conclusions

A method for easily quantifying the amount of 1,4-dioxane in shampoo using the OPTIC-4 in DMI mode was investigated. An easy pretreatment method was adopted in which 1.00 g of the shampoo was diluted with 1.00 g of ultrapure water, and then spiked with 1,4-dioxane-*d*8, followed by injection of 3 µL into a micro vial. By setting the inlet temperature to 120 °C, the high boiling point substances, which may cause column degradation, contained in the samples were left behind in the micro vials.

In addition, favorable quantitative values were obtained by adding the isotope 1,4-dioxane-*d*8, without analyzing a standard sample for creating a calibration curve. This method allowed simpler and easier quantitative determination in comparison to the headspace method, which requires the creation of a multi-point calibration curve for quantitative determination.

By using temperature differences, the DMI mode can thermally extract only target components selectively while leaving behind high boiling point components, which may cause degradation of columns. Thus, it is effective for simplifying pretreatment.

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