

Analysis of 1,4-Dioxane in Consumer Products using Static Headspace and Gas Chromatography with a Triple Quadrupole Mass Spectrometer

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KEYWORDS

Consumer products, 1,4-dioxane, GC-MS/MS, Headspace, CIS Inlet, Multi-injection runs, Liquid addition, Sample preparation.

ABSTRACT

1,4-Dioxane is a chemical contaminant formed in trace amounts as a byproduct during the manufacturing process of detergents, foaming agents, emulsifiers and some solvents, which are widely used ingredients of commercial products such as soaps, detergents, shampoos, cosmetics, and cleaning agents. This has led to detectable levels of 1,4-dioxane in the final products resulting in consumer exposure. 1,4-Dioxane has been identified as a potential human carcinogen. A 2016 report by the Department of Health and Human Services lists 1,4-dioxane as reasonably anticipated to be a human carcinogen. (1) The presence of 1,4-dioxane in cosmetic products is already regulated in several countries around the world. State by state regulation of acceptable concentrations in cosmetics is anticipated, but no limits have been established in the U.S., thus far.

This work shows development of a method for determination of 1,4-dioxane in consumer products using static headspace with GC-MS/MS detection.

INTRODUCTION

The GERSTEL MultiPurpose Sampler (MPS) roboticpro with tool exchange in combination with the GERSTEL Cooled Injection System (CIS 4) provides a fully automated method for sample dilution, addition of internal standard, and static headspace analysis of 1,4-dioxane in consumer products. An Agilent 8890 gas chromatograph with 7010B Triple Quadrupole MS were used for separation and detection of 1,4-dioxane.

Static headspace with GC/QQQ provides adequate limits of detection (LODs) in the low ppb to ppm range for 1,4-dioxane in consumer products. Concentration techniques such as SPME or SPME arrow can provide lower LODs, but they require additional hardware and instrument modifications and generally provide lower sample throughput. This leads to added cost and a less robust analysis than static headspace analysis.

This study presents a method for determination of 1,4-dioxane in consumer products using a simple dilution followed by addition of 1,4-dioxane-d8 as internal standard for quantitation. Additionally, the results of sample stacking in the CIS 4 through multiple injections per GC/MS run are presented, demonstrating an easy way to reach lower LODs for 1,4-dioxane, if needed.

EXPERIMENTAL

Instrumentation:

GERSTEL MPS robotic^{PRO} sampler with static headspace and USM tools, GERSTEL Cooled Injection System (CIS 4), PTV type GC inlet (all controlled by GERSTEL Maestro software), and Agilent 8890 GC/7010B TripleQuad MS with high-efficiency EI source (HES).

Analysis Conditions:

CIS:	Split Flow: 70 mL/min 10 °C (0.25 min); 12 °C/sec, 280 °C (5 min) Tenax-TA [®] liner
Column:	30 m Rxi-5 MS (Restek #13423) di = 0.25 mm, df = 0.25 µm
Pneumatics:	He; Pi = 7.1 psi Constant flow = 1.0 mL/min
Oven:	40 °C (4.0 min), 20 °C/min, 280 °C (4.0 min)
MS Parameters:	
Dwell	50 ms
Collision Energy	5 V
Gain Factor	1
MRM Transitions:	
1,4-dioxane	88-58.1 amu 88-56.9 amu
1,4-dioxane-d8	96-64.1 amu 96-56.9 amu

Standards preparation:

Standards of 1,4-dioxane (Restek #30287) and 1,4-dioxane-d8 (Restek #30287) at 2000 µg/mL were used to prepare standards and spiking solutions. Working standards were prepared in methanol.

Samples were weighed (approximately 0.50 g) into a 20 mL headspace vial and sealed. One mL of water was added followed by 25 µL of a 40 ppm standard of 1,4-dioxane-d8 in methanol.

The samples and standards were equilibrated at 70 °C for ten minutes. Following equilibration, two milliliters of headspace were injected in the CIS 4. The analytes were trapped in the inlet at 10 °C for 0.25 minutes on a CIS 4 liner filled with Tenax- TA[®]. The inlet was heated rapidly to 280 °C to transfer the analytes to the column.

RESULTS & DISCUSSION

One milliliter of water was added to some of the more viscous samples in order to reduce the viscosity. Equilibration time and temperature were optimized resulting in values of 10 minutes and 70 °C, respectively, which were entered into the method.

Calibration curves were prepared in the range of 0.025-10 $\mu\text{g/mL}$ of 1,4-dioxane in water and 0.050-20 $\mu\text{g/mL}$ in a hand soap. The hand soap did not contain any detectable level of 1,4-dioxane. The calibration curves are shown in Figure 1. Both curves were found to be linear over the range with a correlation coefficient of 0.9959 for the standards in water and 0.9988 for the standards in soap. Triplicate analysis was performed for 1,4-dioxane in water at a level of 1.25 $\mu\text{g/mL}$ and for the hand soap at a level of 2.50 $\mu\text{g/mL}$. The results showed good precision for each with values of 1.6% and 4.3% RSD, respectively.

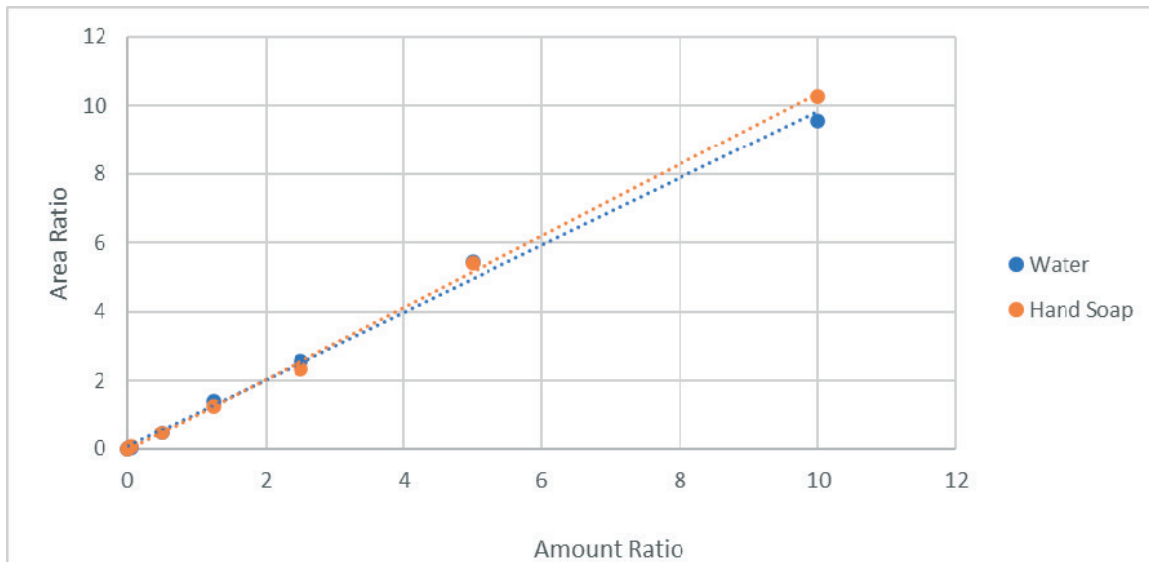


Figure 1: Calibration Curves for 1,4-Dioxane in Water and Hand Soap

Figure 2 shows the chromatograms for 1,4-dioxane (green; 88-56.9) and 1,4-dioxane-d8 (gray; 96-64.1) at a level of 1.25 $\mu\text{g/mL}$ in water.

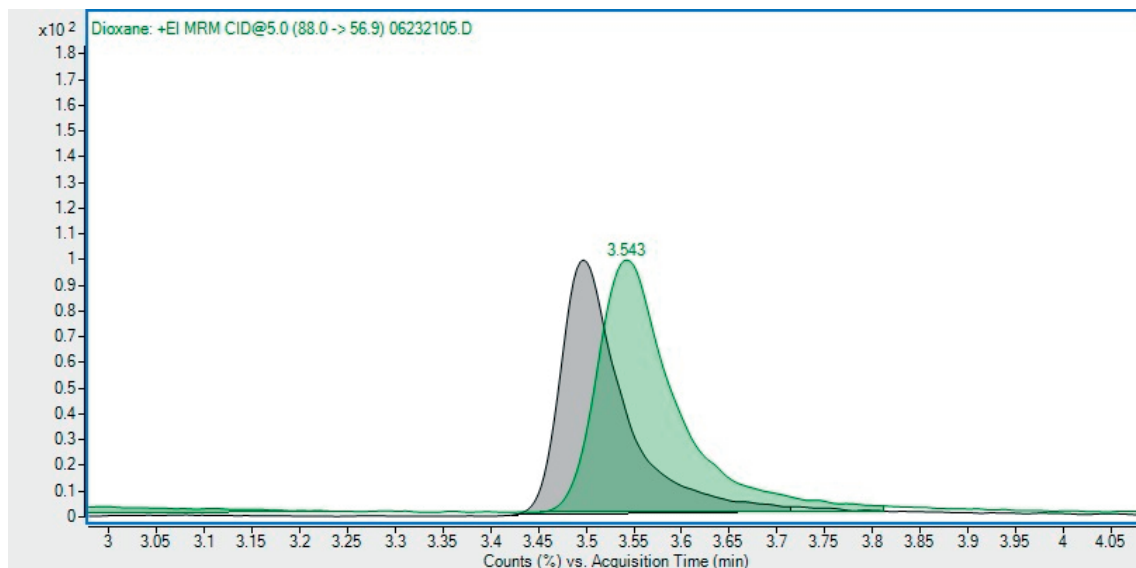


Figure 2: Example Chromatograms for 1,4-Dioxane and 1,4-Dioxane-d8

The method was applied to a variety of consumer products. The results are shown in Table 1.

Product	[1,4-Dioxane] $\mu\text{g/mL}$
Hand Soap	Not detected
Dish Soap 1	Not detected
Dish Soap 2	2.21
Dishwasher Soap	Not detected
Body Wash	0.012
Shampoo 1	0.062
Shampoo 2	1.42
Conditioner	Not detected
All Purpose Cleaner 1	0.057
All Purpose Cleaner 2	Not detected
Window Cleaner	Not detected
Laundry Detergent 1	3.76
Laundry Detergent 2	15.0
Fabric Softener	Not detected
Toilet Bowl Cleaner	0.11

Table 1: Analysis Results for Consumer Products

Detectable levels of 1,4-dioxane were found in 8 of the 15 products tested. The highest level, 15.0 $\mu\text{g/mL}$, was seen in Laundry Detergent 2. The lowest detected level was 0.012 $\mu\text{g/mL}$ in Body Wash 1. The detection limits for each matrix would have to be determined individually due to the differences in surfactant concentration and other ingredients, which could affect the partitioning between the sample and headspace. The addition of water and use of a deuterated internal standard account for the differences in matrix composition. The detection limit could be estimated from the signal to noise for the internal standard.

In order to determine the precision, several of the samples were run in triplicate. The results are shown in Table 2.

Sample	N	Average	RSD
Dish Soap 2	5	2.20	2.7%
Laundry Detergent 1	3	3.69	1.7%
Shampoo 2	3	1.46	2.7%
Laundry Detergent 2	3	14.6	1.8%

Table 2: Precision Data for 1,4-Dioxane Analysis

The results show excellent precision for these samples with RSDs ranging from 1.7-2.7%.

If lower detection limits are needed for static headspace analysis, the Maestro software includes a feature called Multiple Headspace Static Enrichment (MHSE) that allows multiple injections to be stacked up in the CIS 4 from a single sample. The injections can be cryofocused, or as in this study, trapped on a packed bed liner using Tenax-TA®. Figure 3 shows an overlay for a single 2 mL injection and three 2 mL injections for the Shampoo 2 sample. The Red and Green traces show the peaks for 1,4-dioxane-d8 for one and three injections, respectively. The Purple and Yellow traces show the peaks for 1,4-dioxane for one and three injections, respectively. The ratios for the peak areas for 1,4-dioxane and 1,4-dioxane-d8 are 3.1 and 3.2, respectively, showing efficient trapping and a corresponding increase in signal for the analyte and internal standard.

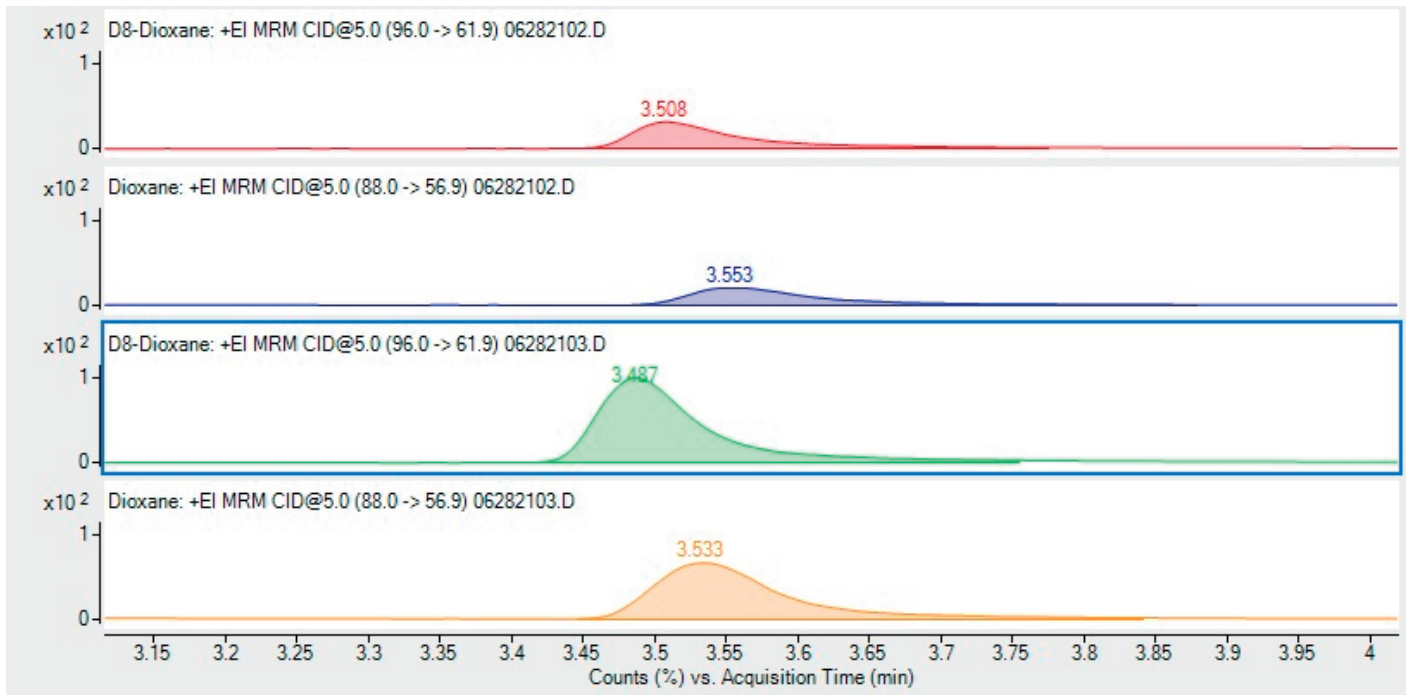


Figure 3: Stacked View of Chromatograms for Single and Triple Injections

The Maestro software also enables full automation of the method including addition of the diluent and internal standard using a Preplet, which is part of the method. This allows the analyst to simply weigh out the sample, seal it and place it on the autosampler. Figure 4 shows the Preplet used for this method. Two simple ADD steps are included with the method. The Maestro Scheduler for this method is shown in Figure 5. The green blocks show the two ADD steps, the yellow block is the incubation of the sample in the agitator, the red block is the static headspace injection, the purple block is the syringe flushing after injection and the beige blocks are the GC run and cool down times. Maestro automatically calculates the maximum overlap for sample preparation and analysis ensuring the highest throughput.

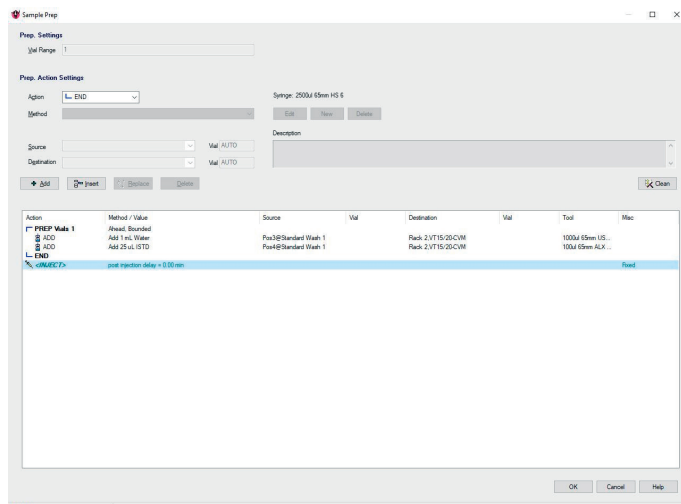


Figure 4: Preplet for Sample Preparation

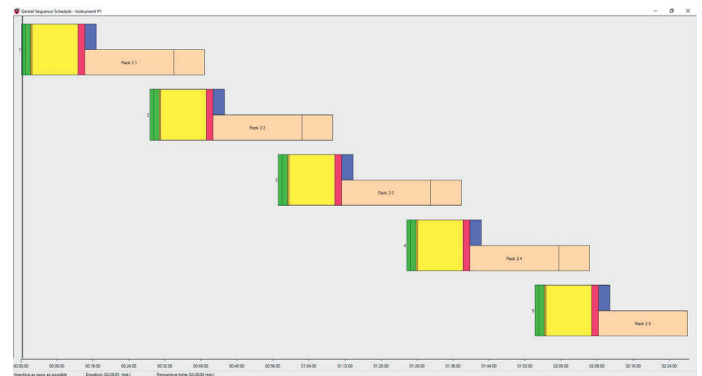


Figure 5: Maestro Scheduler for Sample Preparation and Analysis

In addition to calculating the amount of 1,4-Dioxane in a consumer product, the GC/QQQ can also be used to gather full MS data in the first quadrupole in order to monitor fragrance and other VOCs in the product. Figure 6 shows the total ion chromatogram for the Shampoo 1 sample. The compounds identified in the chromatogram include fragrance compounds alpha-pinene (woody, pine), ethyl 2-methylpentanoate (fruity, green melon), beta-myrcene (woody, citrus), hexyl acetate (green, fruity), limonene (citrus, orange) and 3-carene (citrus herbal). Siloxanes and silanes present in the chromatogram include hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and (4-hexylbenzene-1,3-diyl) bistrimethyl silane. These compounds are added to the shampoo to repair damaged hair. Decanol isomers are also present in the chromatogram and function as emollients, viscosifiers and sheen agents in personal care products.

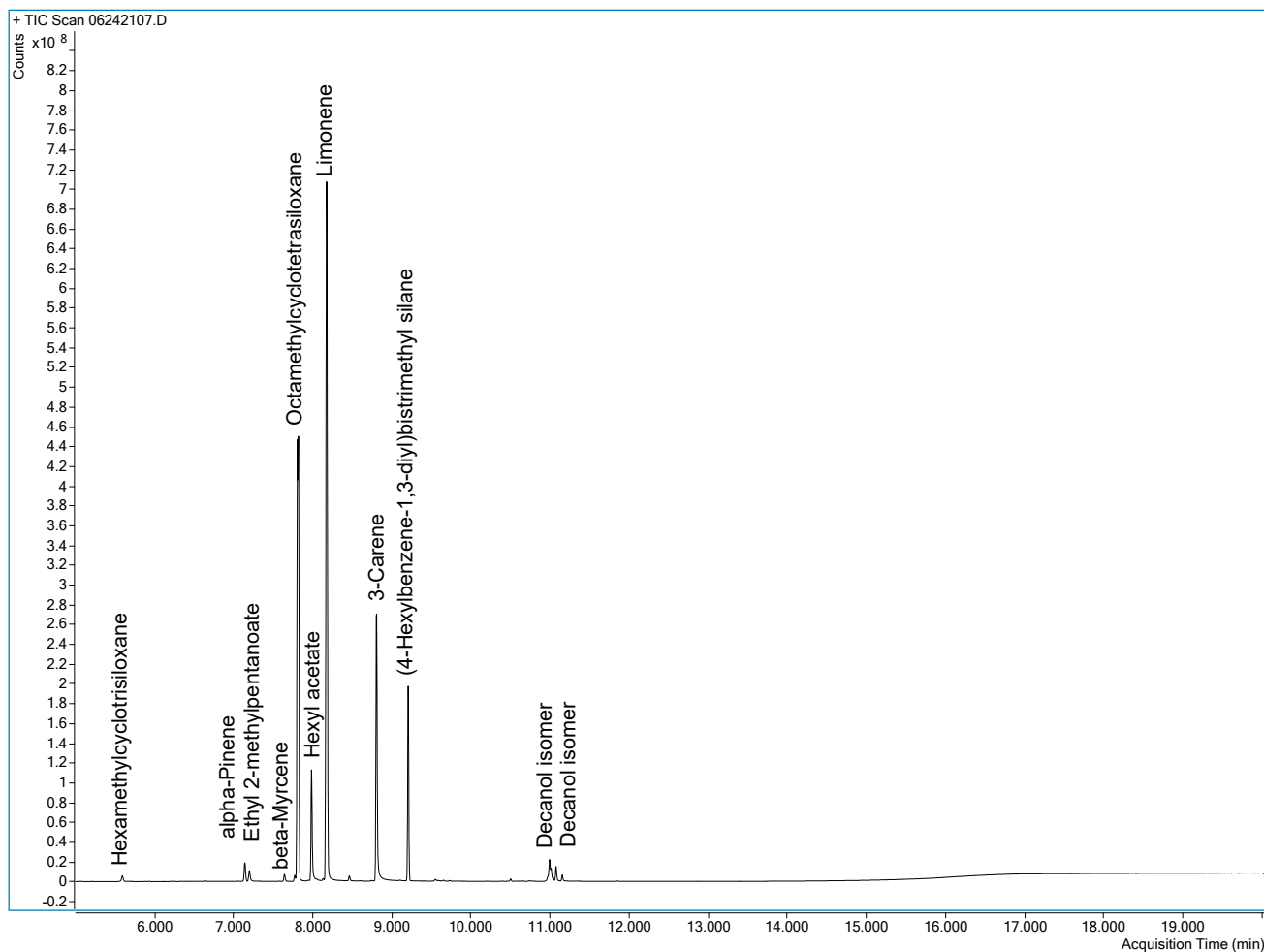


Figure 6: Total Ion Chromatogram for Shampoo 1

CONCLUSIONS

Headspace analysis with GC/QQQ mass spectrometry provides a simple and easy methodology with sufficient sensitivity to determine 1,4-dioxane in consumer products at the required concentration levels. The Maestro software enables the use of simple sample preparation steps to provide full automation of the method including sample dilution and addition of internal standard. If additional mass on column is needed, Multiple Sample Headspace Enrichment mode can be employed by simply checking a box in the software and selecting the number of injections desired. Additional sample information can be gathered by running the GC/QQQ in MRM and full scan mode.

REFERENCES

1. <https://ntp.niehs.nih.gov/whatwestudy/assessments/cancer/roc/index.html>

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