Methodology Advances in the Sensitive Identification and Quantitation of 1,4-Dioxane in Consumer Products by SPME-EI-GC/MS/MS

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Introduction

1,4-Dioxane is an industrial chemical contaminant that is of concern even at trace levels in consumer products.

The allowable concentrations in the United States are expected to vary from state to state, typically at part per billion to low part per million levels.

There have been several methods developed to analyze for 1,4-dioxane, but none of these methods are adequate to detect 1,4-dioxane in consumer products with complex mixtures and solutions.

1,4-Dioxane is a by-product formed during the synthesis of ethoxylated ingredients used in finished consumer products (cosmetic, personal care, and cleaning products).

It is not used as an ingredient in these products but may be present as a trace contaminant by forming inadvertently during ethoxylation.

1,4-Dioxane can form when two consecutive ethylene oxide units are cleaved from a chain of ethylene oxides and form a ring of 1,4-dioxane.

It can also form when the ethylene oxide ring opens to form ethylene glycol, and then two ethylene glycols dimerize to form 1,4-dioxane. These ingredients include certain detergents, foaming agents, emulsifiers, and solvents identifiable by the prefix, suffix, word, or syllables: PEG, polyethylene, polyethylene glycol, polyoxyethylene, -eth- (e.g., laureth sulfate), or -oxynol-.

Figure 1. Agilent 8890B/7000D GC/TQ PAL3 autosampler

Experimental

System Configuration

A method for the high-sensitivity detection of 1,4-Dioxane was developed on the Agilent 8890B/7000D GC/TQ in Electron Ionization (EI) mode. The sample extraction was performed using a PAL3 autosampler with solid phase microextraction (SPME) tool. The GC was configured with a 30 m DB-8270D column and a 1 m deactivated fused silica column using a purged ultimate union. Backflush was utilized to minimize contamination of the system.
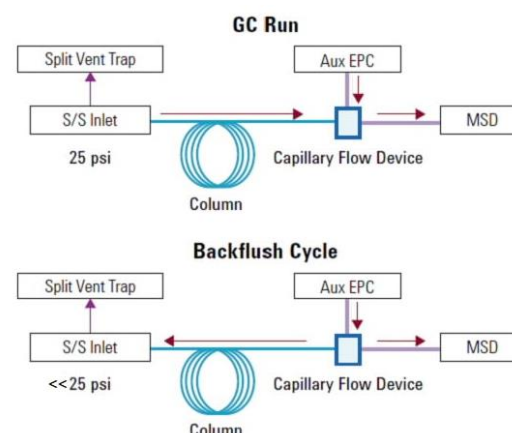

Figure 2. Backflush Setup

The advantage of using a tandem quadrupole mass spectrometer is that a selective precursor to product ion transition is generated, minimizing interferences.
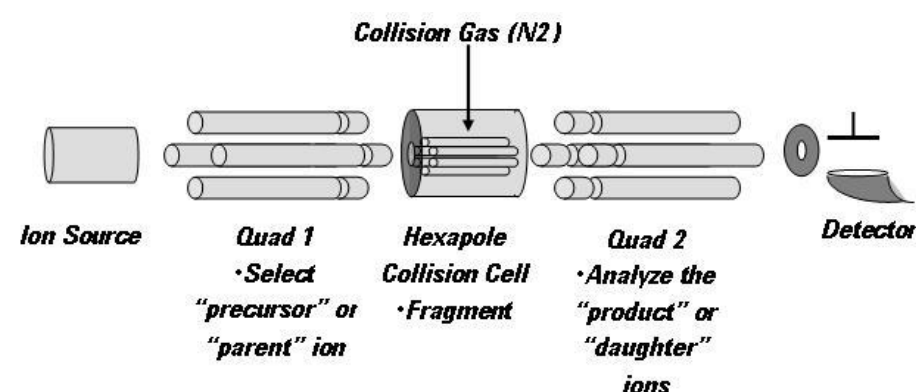

Figure 3. 7000 TQ MRM

Method parameters

The 8890 GC inlet operated in the splitless mode at 280°C. Column flow was 1.0 mL/min,
Column oven: initial 40°C for 4 minutes, ramped 10°C/min to 100°C, then 50°C/min to 160°C, hold for 0.8 minutes.
The analysis time was less than 15 minutes.

The PAL3 used a C-WR/PDMS/10 fiber, incubation for 2.5 minutes at 50 °C, desorption for 2 minutes.

The 7000D TQ transfer line was operated at 260°C, He quench flow 2.25, N_2 collision flow 1.5, source at 270 °C.

dMRM parameters

1,4-Dioxane (88>58.1 and 88>56.9, CE 5 eV)

1,4-Dioxane-d_8 (96>64.1 and 96>61.9, CE 5 eV)

Experimental

Sample preparation

An analytical balance is used to weigh the consumer product sample, typical weight is between 100 to 200 mg. The weight is noted for calculations.

Dilution factors were applied to compensate for sample weight variation.

A series of calibration standards to encompass the desired calibration range were prepared.

Calibration levels are created by pipetting 50 μL of the appropriate 1,4-dioxane solution and 50 μL of the 20 mg/L 1,4-dioxane-d8 internal standard into a 20 mL headspace vial with magnetic cap. When calculating the concentration levels of the calibration solutions, a 100% transfer of material is assumed for total amount. Thus, for the low calibration level, 50 μL of 0.2 mg/L 1,4-dioxane is 10 ng on fiber.

The initial calibration was verified with the use of a certified reference material that was diluted and analyzed at 10, 1, and 0.1 ppb. In each case, the percent difference was less than 10%.

Calibration

A nine-point calibration curve was used for quantification in the range of 0.1 to 400 ppb. The R^2 value was greater than 0.999 using a linear calibration, ignoring the origin, and using a 1/x weighting in this calibration. Calibration data is shown in Figure 4.

1,4-dioxane - 9 Levels, 9 Levels Used, 9 Points, 9 Points Used, 12 QCs

$y = 1.161987 * x - 0.005503$
$R^2 = 0.99947950$
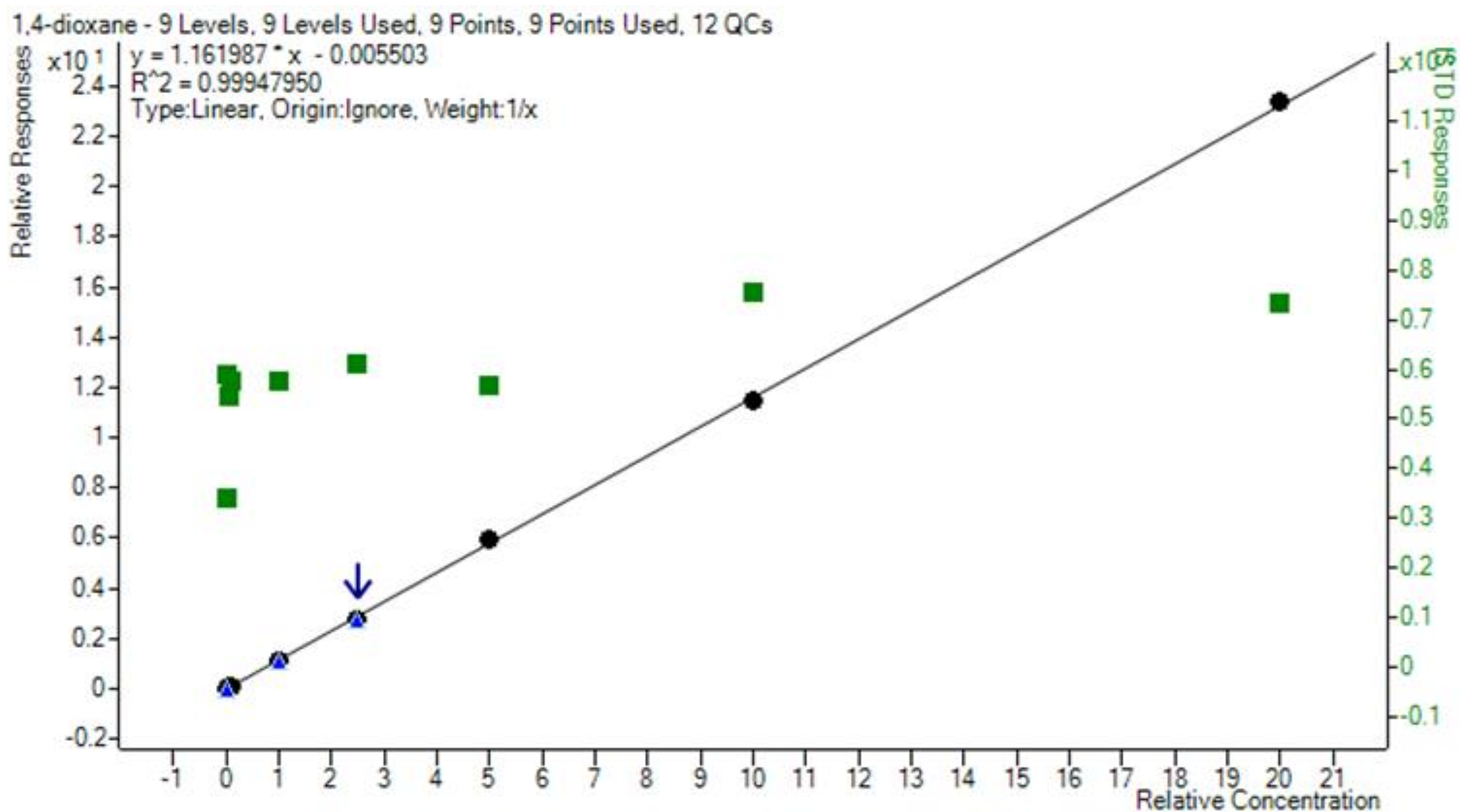Type:Linear, Origin:Ignore, Weight:1/x

Figure 4. Calibration curve for 1,4-dioxane on the Agilent 7000D TQ system from 0.01 to 400 ppb. Internal standard response is shown with green squares.

Robustness

Eight replicates of the spiked sample were injected over several days, an example chromatogram is shown in Figure 5.
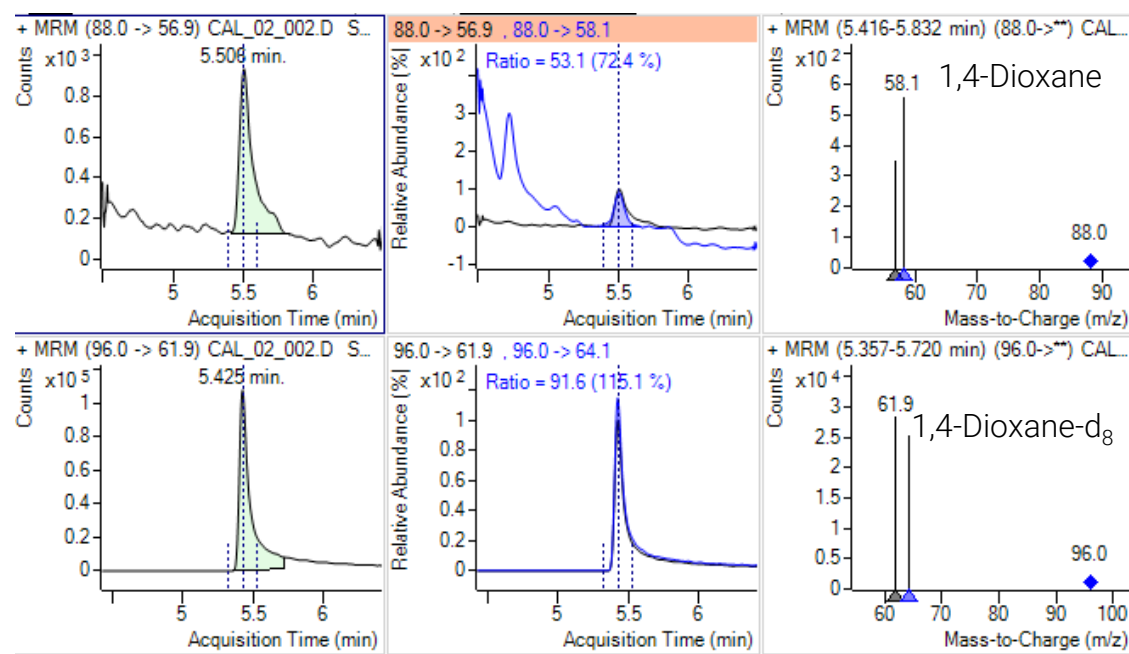

Figure 5. Example chromatography from one of the spiked sample injections (0.1 ppb) used for method detection limit calculation of 1,4-dioxane on the Agilent 8890 GC system.

Method Detection Limit

The MDL for 1,4-dioxane was calculated based on EPA methodology (EPA 821-R-16-006). The MDL was determined by spiking a sample (predetermined to contain nondetectable levels of 1,4-dioxane) at a concentration of 0.1 ppb. 8 replicate measurements were performed. The MDL was determined to be 0.011 ppb, as detailed in Table 1.

Name	RT (min)	Transition (m/z)	Concentration RSD (%)	MDL (ppb)	LOQ (ppb)
1,4-Dioxane	5.49	88.0 → 56.9	3.7	0.011	0.037

Table 1. Method detection limit was determined using 0.1 ppb samples. Calculations were done automatically from Agilent MassHunter software. The average signal-to-noise was 88.6 .

Quality Control

Each batch of 10 samples includes a method blank (MB), a laboratory control sample (LCS), a laboratory control sample duplicate (LCSD), a matrix spike (MS), and a matrix spike duplicate (MSD). A sample duplicate is included for each sample prepared in the same manner as the sample.

Quality control for this method was evaluated throughout data collection. Method blanks yielded nondetectable levels to ensure that there was no carry over. 12 quality control samples were analyzed, and the accuracy ranged from 90 to 110%.

Instrument Measure	Frequency	Requirement	Correction
Initial Calibration Verification (ICV)	Immediately after calibration	ICV ± 30% true value	Reanalyze ICV, rerun calibration, corrective action
Continuing Calibration Verification (CCV)	Before batch and after every 10 analytical runs excluding blanks	CCV ± 20% true value	Reanalyze CCV, rerun calibration, corrective action
Internal Standard (ISTD)	Added to every sample, QC, calibration, and instrument check		
Retention Time (RT)	Evaluate in every sample	ISTD RT ± 0.33 min Analyte RT < 10 s To midpoint ICAL or first CCV	Inspect and perform instrument maintenance
Matrix Blank (MB)	With every batch of 10 or fewer samples	Analyte < LOQ	Replace fiber and recalibrate
Laboratory Control Spike and Duplicate (LCS, LCSD)	With every batch of 10 or fewer samples	Reproducibility of LCS and LCSD < 20%	Reanalyze, corrective action
Matrix Spike and Duplicate (MS, MSD)	With every batch of 10 or fewer samples	Spike recovery ± 30% Reproducibility of MS and MSD < 20%	Reanalyze, corrective action
Replace reference materials when responses do not pass criteria are low compared to past calibrations or reach their expiration date			
Replace the SPME fiber if the peak shape is degraded, or other problems are suspected			
Recalibrate when the CCV no longer passes within 20% of true value or maintenance has been performed			

Table 2. Best practices for the analysis of 1,4-dioxane.

Conclusions

This method presents a sensitive, robust, and selective method to determine 1,4-dioxane in consumer products including cosmetic, personal care, and cleaning products. The benefits of using the Agilent triple quadrupole GC/MS capabilities and SPME cannot be underestimated in providing very simple sample preparation, reducing sample matrix interference and improving signal-to-noise. This method provides high selectivity and sensitivity with a more confidence driven solution for the analysis of 1,4-dioxane.

References

Tugulea, A. Principles of SPME. Chromedia Analytical Sciences 2020

Tahara, M.; Obama, T.; Ikarashi, Y. Development of Analytical Method for Determination of 1,4-Dioxane in Cleaning Products. International Journal of Cosmetic Science 2013, 35(6), 575–580

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