APPLICATIONS

# Optimized Analysis of 1,4-Dioxane in Tap Water by GC/MS Using a Zebron™ ZB-624 GC Column

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*Tim was raised in Texas where it was completely too hot, then moved to Pennsylvania and Ohio where it was entirely too cold. He finally settled on California where the weather is just right.*

*Growing concern over the negative health effects associated with dioxane have led to increased global regulation and testing of this compound. This work presents an optimized method for testing of 1,4-dioxane in drinking water by EPA Method 522 using a Zebron ZB-624 GC column.*

## Introduction

EPA Method 522 is used to determine 1,4-dioxane (dioxane) levels in drinking water. Dioxane is a highly water-soluble solvent which has a multitude of industrial uses. Therefore, there is a high likelihood that dioxane can migrate into groundwater systems. In fact, dioxane has been detected in groundwater supplies in numerous locations throughout the United States. Regulatory agencies are especially concerned because dioxane does not readily bind to soils and is resistant to naturally occurring biodegradation processes.

Because of its serious environmental implications, a rapid and robust analytical testing method for dioxane is necessary. EPA Method 522 requires a 624 type column for analysis by GC/MS following SPE extraction of either a 100 mL or 500 mL water sample. Presented here is an optimized EPA 522 GC/MS protocol on a Zebron ZB-624 GC column. The method's effectiveness is demonstrated on a 100 mL tap water sample.

## Materials and Methods

Tap water samples were collected and prepared using the EPA 522 extraction procedure as shown in **Table 1**, and demonstration of method efficiency was performed using a secondary option for preparation as shown in **Table 2**. Following sample preparation, samples were analyzed by GC/MS as shown in **Table 3**.

**Table 1.**
Sample preparation protocol following EPA 522 extraction (Option 1).

| Option 1 | |
|---|---|
| **Step** | **Protocol** |
| 1 | Open the tap and allow the system to flush until the water temperature has stabilized. Collect samples from the flowing system into a vessel containing sodium sulfite (chlorine reducer (50 mg/L)). |
| 2 | Add sodium bisulfate (1 g/L) and verify that the pH is < 4. |
| 3 | Fortify samples with 1,4-dioxane (analyte) and 1,4-dioxane-d8 (surrogate standard) at the appropriate concentration levels. (Samples are now ready for solid phase extraction (SPE)). |

**Table 2.**
Sample preparation protocol using SPE extraction and a vacuum manifold.

| Option 2 | |
|---|---|
| **Step** | **Protocol** |
| 1 | Condition Supelco® Supelclean™ ENVI-Carb™ Plus cartridges (54812-U) with 1 mL of dichloromethane (DCM), 2 mL of methanol, 2 mL of methanol and 3 mL of water. |
| 2 | Using a reservoir, load 100 mL tap water sample and elute at approximately 10 mL/min. |
| 3 | Dry cartridge using high vacuum for 10 minutes. |
| 4 | Fill each cartridge with DCM and soak for 1 minute. |
| 5 | Continue to add DCM and elute dropwise until 1.5 mL of eluent has been collected. |
| 6 | Bring sample volume to 2 mL with DCM and add THF-d8 internal standard at the appropriate concentration. |
| 7 | Remove residual water by passing samples through Strata® Silica anhydrous sodium sulfate cartridges (Part No.: 8B-S124-JCH). (Samples are now ready for GC/MS analysis.) |

**Table 3.**
GC/MS conditions for analysis of tap water samples.

| | |
|---|---|
| **Column:** | Zebron ZB-624 |
| **Dimensions:** | 30 meter x 0.25 mm x 1.4 µm |
| **Part No.:** | 7HG-G005-27 |
| **Guard Column:** | 5 m Z-Guard™ (7AG-G000-00-GZ0) |
| **Injection:** | Splitless @ 200 °C (hold 0.5 min), 2.0 µL |
| **Recommended Liner:** | Zebron PLUS Single Taper Z-Liner™, 4 mm ID |
| **Liner Part No.:** | AG2-0A13-05 (for Agilent® systems) |
| **Carrier Gas:** | Helium @ 1.5 mL/min (constant flow) |
| **Oven Program:** | 30 °C for 1 min to 90 °C @ 20 °C/min to 250 @ 50 °C/min |
| **Detector:** | MSD @ 250 °C |
| **Sample:** | **Peak** **Analyte** **SIM Ions** **Window (min)**<br>1 THF-d8 46*, 78 ,80 4.00 – 4.75<br>2 1,4-dioxane-d8 96*, 62, 64 4.75 – 7.8<br>3 1,4-dioxane 88*, 58 4.75 – 7.8 |

## Results and Discussion

As shown in **Figures 1** and **2**, the Zebron™ ZB-624 GC column provided excellent peak shape and resolution for the EPA Method 522 analytes. The GC/MS method was modified from the original EPA 522 GC parameters to reduce analysis time. Specifically, the carrier gas flow ate was increased to 1.5 mL/min and the oven ramps were increased from 7 °C/min to 20 °C/min and 20 °C/min to 50 °C/min. These method modifications result in a faster analysis time of less than 8 minutes without sacrificing method performance. The neat seven-point calibration curve generated ranged from 5 to 2000 ng/mL and showed good linearity for 1,4-dioxane ($R^2$ = 0.9994) and 1,4-dioxane-d8 ($R^2$ = 0.9995).

To demonstrate method efficiency, a tap water sample fortified with analyte and surrogate standards at low (3 µg/L) and high (25 µg/L) levels was processed. In this instance, extraction protocol Option 2 (shown in **Table 2**), which requires a 100 mL sample extracted with a 400 mg activated carbon SPE cartridge, was chosen. The sample extracts were quantified by comparison to a standard calibration curve (**Figures 3** and **4**). The results, listed in **Table 4**, show high recovery values that fall with in the 70 – 130 % range specified by the EPA method.

**Figure 1.**
Extracted ion chromatogram for 1000 ng/mL calibration curve, THF-d8 (internal standard) at 500 ng/mL.

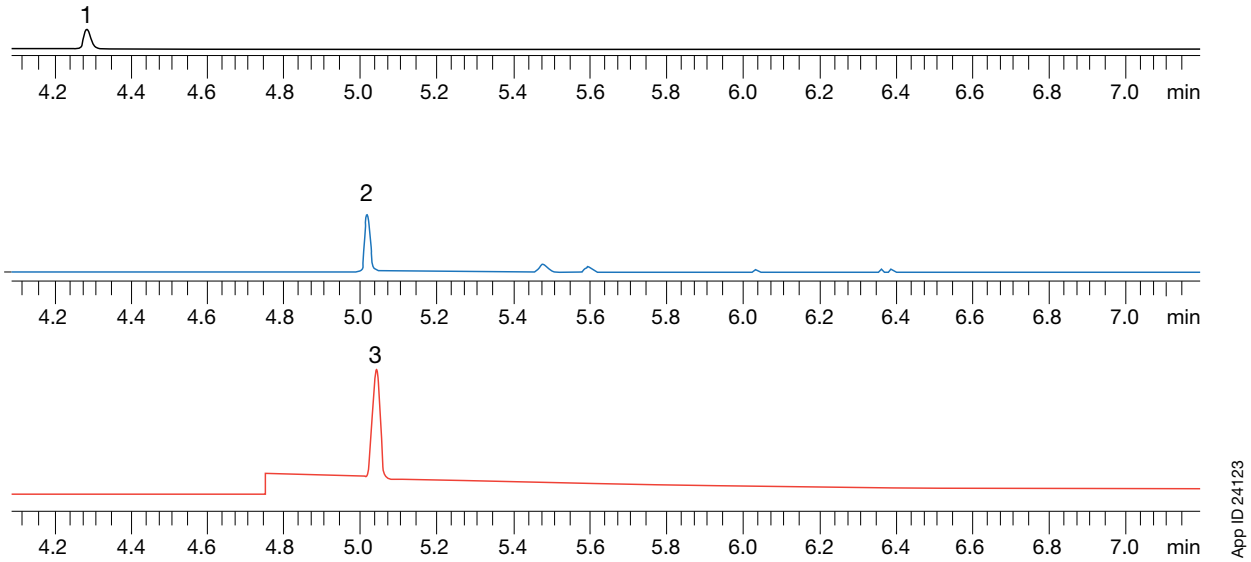



**Figure 2.**
Extracted ion chromatogram for tap water extract, 25 ng/mL.

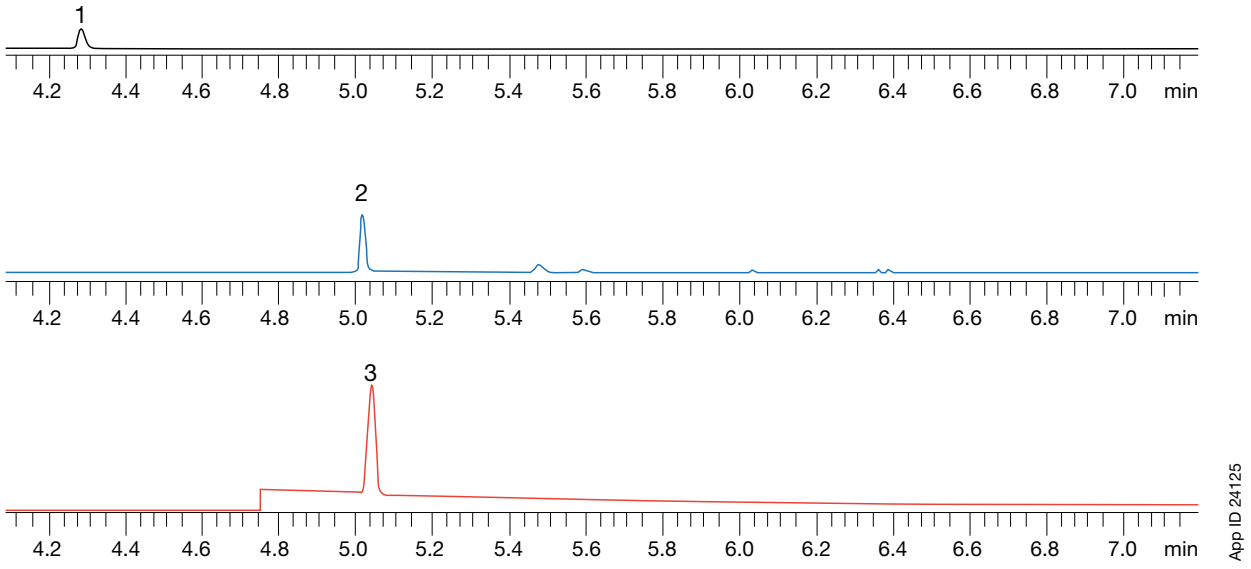


**Figure 3.**
1,4-dioxane (analyte) calibration curve, 5 to 2000 ng/mL.

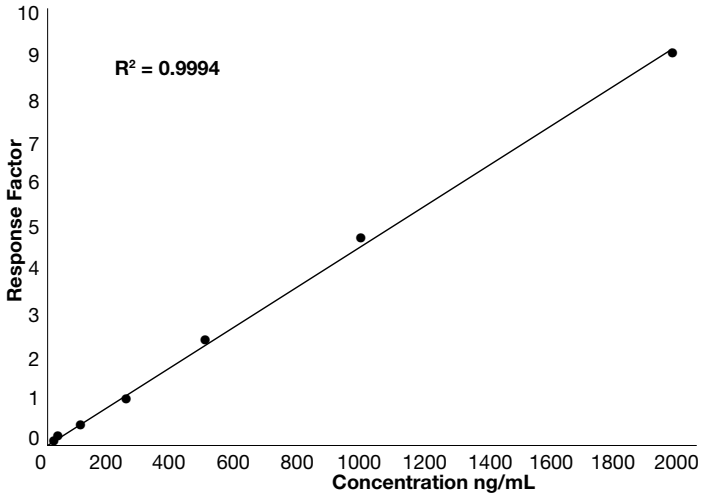



**Figure 4.**
1,4-dioxane-d8 (surrogate standard) calibration curve, 5 to 2000 ng/mL.

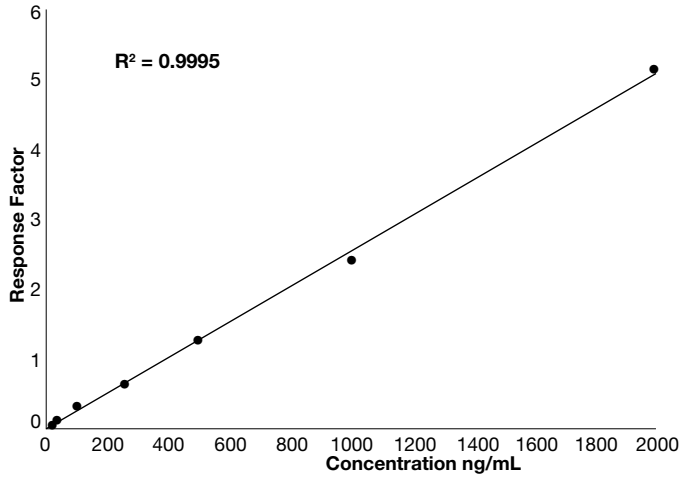



**Table 4.**
100 mL tap water LFSM mean recovery values.

| Compound | µg/L | Mean Recovery (%) (n=3) | RSD (%) (n=3) |
|---|---|---|---|
| 1,4-dioxane | 3 | 96 | 4.2 |
| 1,4-dioxane-d8 | 3 | 109 | 5.9 |
| 1,4-dioxane | 25 | 103 | 7.8 |
| 1,4-dioxane-d8 | 25 | 105 | 8.8 |

## Conclusion

The Zebron™ ZB-624 GC column provided excellent peak shape and resolution for the EPA Method 522 GCMS analysis. The GC/MS method was modified from the original EPA 522 GC parameters, resulting in a faster analysis time and excellent linearity.

The extraction data collected shows that the modified GC method is effective for the analysis of real-world samples and will benefit a laboratory wishing to improve sample throughput without sacrificing method performance.

# APPLICATIONS

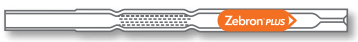
## Ordering Information

### Zebron™ ZB-624 GC Columns

| Length (m) | ID (mm) | df (µm) | Temp. Limits (°C) | Part No. |
|---|---|---|---|---|
| 20 | 0.18 | 1.00 | -20 to 260 | 7FD-G005-22 |
| 30 | 0.25 | 1.40 | -20 to 260 | 7HG-G005-27 |
| 30 | 0.32 | 1.80 | -20 to 260 | 7HM-G005-31 |
| 30 | 0.53 | 3.00 | -20 to 260 | 7HK-G005-36 |
| 60 | 0.25 | 1.40 | -20 to 260 | 7KG-G005-27 |
| 60 | 0.32 | 1.80 | -20 to 260 | 7KM-G005-31 |
| 60 | 0.53 | 3.00 | -20 to 260 | 7KK-G005-36 |
| 75 | 0.53 | 3.00 | -20 to 260 | 7LK-G005-36 |
| 105 | 0.53 | 3.00 | -20 to 260 | 7NK-G005-36 |

***Note:*** If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G005-27-B. Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

### Zebron PLUS GC Inlet Liners

| Description | Dimensions ID x L (mm) | Part No. | Unit. |
|---|---|---|---|
| **For Agilent® or Thermo Scientific® GC Systems** | | | |
| Single Taper Z-Liner™  | 4 x 78.5 | AG2-0A13-05<br>AG2-0A13-25 | 5/pk<br>25/pk |

Find more Zebron GC columns and accessories at
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