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Environmental

Helium-conserving method for trace-level analysis of 1,4-dioxane in drinking water with purge and trap and GC-MS

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Keywords

1.4-dioxane, volatile organic compounds (VOCs), drinking water, U.S. EPA, purge and trap (P&T), GC-MS, Helium Saver technology

Goal

Demonstration of an analytical method for the quantification of 1,4-dioxane in drinking water down to 0.2 ppb using purge and trap coupled to GC-MS with helium saving technology. Method linearity, method detection limit (MDL), precision, and mid-point calibration check were assessed to evaluate method performance.

Introduction

1,4-Dioxane is a solvent used in numerous commercial laboratory applications, detergents used by cleaning services or laundromats, and in the industrial processing of other chemicals such as adhesives and sealants. It is also a byproduct produced in some manufacturing processes, leading to its presence in surface water when these products are washed into the wastewater system. Communities that source their drinking water from smaller or slow-flowing streams are at risk of contamination from 1,4-dioxane due to industrial discharges or from large populations washing 1,4-dioxane-containing consumer products down the drain. These activities, individually or combined, pose a significant risk of exposure to 1,4-dioxane through drinking water.[1] Exposure to substantial amounts of 1,4-dioxane can cause damage to internal organs such as the liver and kidneys.

1,4-Dioxane presents an unreasonable risk of injury to human health, including the potential to cause cancer and harm the liver and nasal tissue. The U.S. EPA is in the risk management process and addressing the risk presented by 1,4-dioxane. It will release a proposed rule in the future under the Toxic Substances Control Act (TSCA), section 6, to help protect people from the identified risks of even low amounts of 1,4-dioxane contamination. 1,4-Dioxane is restricted via various regulations including the EPA's Safe Drinking Water Act (SDWA) and the TSCA. Often, drinking water is pretreated with advanced oxidation processes to remove 1,4-dioxane before consumption. However, it is still important to test drinking water for the compound to reduce the chance of public exposure.

For drinking water analysis in the United States, 1,4-dioxane is typically analyzed by solid phase extraction (SPE) and a gas chromatograph-mass spectrometer (GC-MS) using U.S. EPA Method 522. This application is a demonstration of the ability of purge and trap (P&T) to reach a low-level detection limit needed for 1,4-dioxane analysis more efficiently, using less solvent and fewer consumables, and conserving helium. As 1,4-dioxane is a volatile organic compound, or VOC, it is well suited to analysis involving P&T concentration and GC-MS to analyze at trace levels. The following evaluation describes the use of the Teledyne LABS Tekmar Lumin P&T concentrator combined with the AQUATek LVA autosampler with analysis performed by the Thermo Scientific™ TRACE™ 1610 Gas Chromatograph (GC) and the Thermo Scientific™ ISQ™ 7610 Mass Spectrometer (MS) System equipped with Thermo Scientific™ Nevervent™ technology with a Thermo Scientific™ HeSaver-H_2Safer™ SSL Injector and Thermo Scientific™ ExtractaBrite™ Ion Source and the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) for analysis of 1,4-dioxane. U.S. EPA Method 5030 in conjunction with U.S. EPA Method 8260 was followed for the analysis and evaluated for linearity, method detection limit (MDL), precision, and reproducibility.

Experimental

Sample preparation

Two working calibration standards were prepared in methanol at the concentrations of 10 parts per million (ppm) and 50 ppm from a standard of 1,4-dioxane (Restek No. 30287).

An eight-point linear calibration curve was prepared from 0.2 to 50 ppb for 1,4-dioxane with a regression value (r^2) ≥0.995. The relative response factor (RRF) was calculated for 1,4-dioxane using the internal standard: 1,4-dioxane-d8. The internal standard was prepared in methanol from a standard of 1,4-dioxane-d8 (Restek No. 30614) at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Purge and trap conditions

Table 1. Tekmar Lumin P&T and AQUATek LVA water method conditions.

Standby	Variable	Desorb	Variable
Valve oven temp.	140°C	Desorb preheat temp.	245°C
Transfer line temp.	140°C	Desorb temp.	250°C
Sample mount temp.	90°C	Desorb time	1.00 min
Standby flow	10 mL/min	Drain flow	300 mL/min
Purge ready temp.	40°C	GC start signal	Begin Desorb
MCS purge temp.	20°C	**Bake**	**Variable**
Purge	**Variable**	Bake time	2.00 min
Purge temp.	20°C	Bake temp.	270°C
Purge time	8.00 min	MCS bake temp.	200°C
Purge flow	100 mL/min	Bake flow	200 mL/min
Dry purge temp.	20°C	**AQUATek LVA**	**Variable**
Dry purge time	1.00 min	Sample loop time	0.35 min
Dry purge flow	100 mL/min	Sample transfer time	0.35 min
Sample heater enable	On	Rinse loop time	0.30 min
Sample temp.	60°C	Sweep needle time	0.30 min
Pre-purge time	0.00 min	Presweep time	0.25 min
Pre-purge flow	0 mL/min	Water temp.	90°C
Preheat time	0.00 min	Bake rinse cycles	1
Trap	Vocarb 3000 K	Bake rinse drain time	0.35 min
Chiller tray	On, 10°C		
Purge gas	Nitrogen		

Seven 0.5 ppb standards were prepared to calculate the MDL. Also, seven 10 ppb standards were prepared for the accuracy and precision calculations of the mid-point calibration check. All calibration, MDL, and mid-point calibration check standards were analyzed with the Tekmar Lumin P&T and AQUATek LVA conditions in Table 1. GC-MS conditions are shown in Table 2.

GC-MS parameters

In order to perform the chromatographic separation, a Thermo Scientific™ TraceGOLD™ TG-VMS Column, 30 m × 0.25 mm, 1.4 µm film (Cat. No. 26080-3320) was used. To reduce helium consumption, the HeSaver-H_2Safer option for the SSL injector was utilized. The injector reduces carrier gas consumption by decoupling the GC column gas from the gas used to pressurize the inlet and maintain split and septum purge flows. The critical separations were maintained with a run time of 8 minutes.

Table 2. GC-MS conditions.

TRACE 1610 GC conditions	
Column	TraceGOLD TG-VMS, 30 m x 0.25 mm, 1.4 µm film Helium carrier gas, 2 mL/min column flow
Oven temp. profile	45°C, 2 min 30°C/min to 225°C Run time, 8.0 min
SSL inlet	200°C, 20:1 split Purge flow 5.0 mL/min 0.40 min helium delay
ISQ 7610 MS conditions	
Temp.	Transfer line, 230°C Ion source, 280°C
Scan	1,4-dioxane-d8 ions, *m/z* 96, *m/z* 64 1,4-dioxane ions, *m/z* 88, *m/z* 58 Minimum baseline peak, 1.8 s Desired scans per peak, 20

For this analysis, the ISQ 7610 MS operated in Selected Ion Monitoring (SIM) mode for increased selectivity, as required for this application. Extended method parameters for the ISQ 7610 MS are shown in Table 2.

Instrument control and data processing

Chromeleon software controls the Tekmar P&T systems, allowing a single software for method setup, processing, and reporting. Details of the full method can be found and downloaded from the Thermo Scientific™ AppsLab Library.[3]

Results and discussion

Linearity and sensitivity

The Tekmar Lumin P&T has an innovative Moisture Control System (MCS) that improves water vapor removal, thereby reducing peak interference and increasing GC column lifespan. Figure 1 displays consistent peak shape of a 0.5 ppb 1,4-dioxane standard with minimal water interference.

A calibration range of 0.2–50 ppb was evaluated. The calibration curve was used to calculate the linear correlation coefficient (r^2) of the calibration curve, aiming for an r^2 ≥0.995 to meet EPA criteria. The XLXR detection system of the ISQ 7610 MS, with its extended linear dynamic range and lifespan, enabled extended calibration curves and reduced replacement needs. An MDL of 0.12 ppb was obtained from seven injections of the 0.5 ppb standard. This data is shown in Table 3.

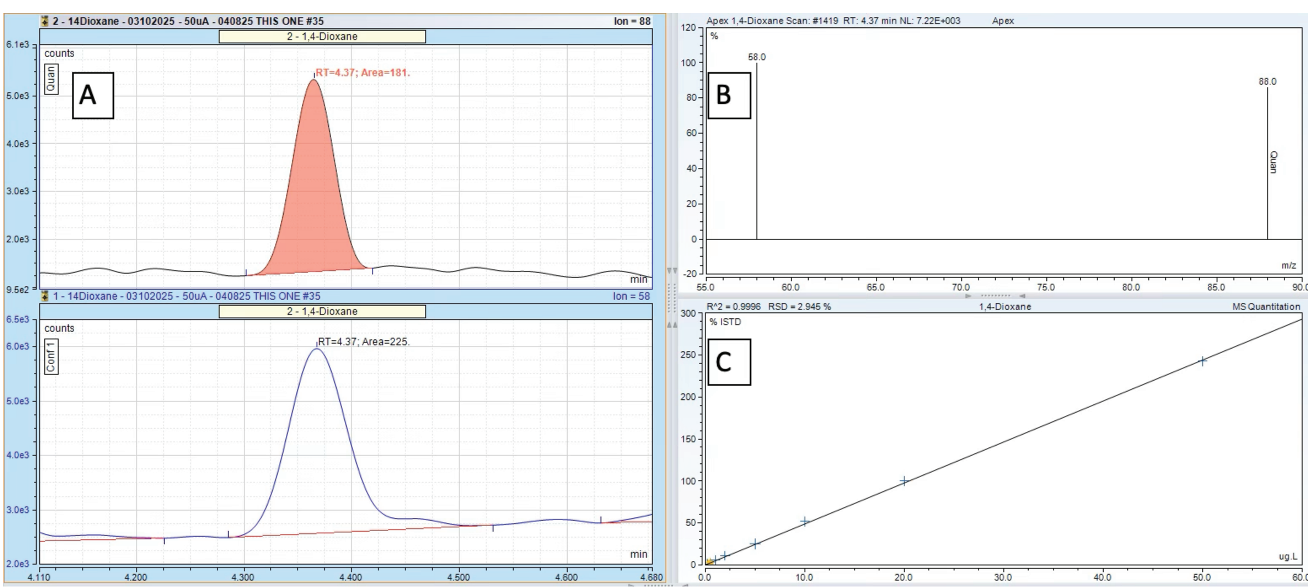

Figure 1. Chromeleon CDS results browser showing extracted ion chromatograms for 1,4-dioxane in the 0.5 ppb water standard, quantitation ion (*m/z* = 88) and one confirming ion (*m/z* = 58) (A); a measured spectrum of 1,4-dioxane (B); and a linear calibration over a concentration range of 0.2 ppb to 50 ppb (C).

Table 3. Linearity, method detection limits, and mid-point calibration check.

Compound	Calibration (0.2–50 ppb)			Method detection limits (n=7, 0.5 ppb)			Mid-point calibration check (n=7, 10 ppb)	
	RT	Ion	Linear ($r^2 \geq 0.995$)	MDL (ppb)	Precision (≤20%)	Accuracy (±30%)	Precision (≤20%)	Accuracy (±20%)
1,4-dioxane-d8 (IS)	4.35	96						
1,4-dioxane	4.36	88	0.9996	0.12	6.2	122	5.1	122

Method robustness

For use as a routine testing method, it is important that the analytical method is stable and reproducible. To demonstrate this, 10 ppb standards (n=35) in water were injected at intervals over a 215-sample injection sequence. The samples were acquired with no user intervention at all on the P&T, GC, or MS system, and their concentrations were plotted to demonstrate the stability of the results. Figure 2 shows the reproducibility of 1,4-dioxane over 215 injections with excellent percentage RSD.

Reduced helium consumption and cost savings

The HeSaver-H_2Safer technology significantly extends helium cylinder lifetimes and offers substantial gas savings during idle periods and sample injection/analysis. Users can estimate its impact on helium consumption, cost, and cylinder lifetime using the Thermo Scientific™ Gas Saver Calculator tool.[4] By using this technology for 1,4-dioxane analysis, the helium cylinder lifespan can nearly quadruple compared to a standard SSL injector, making it a prime choice for helium conservation. Figure 3 shows the helium saver calculator.

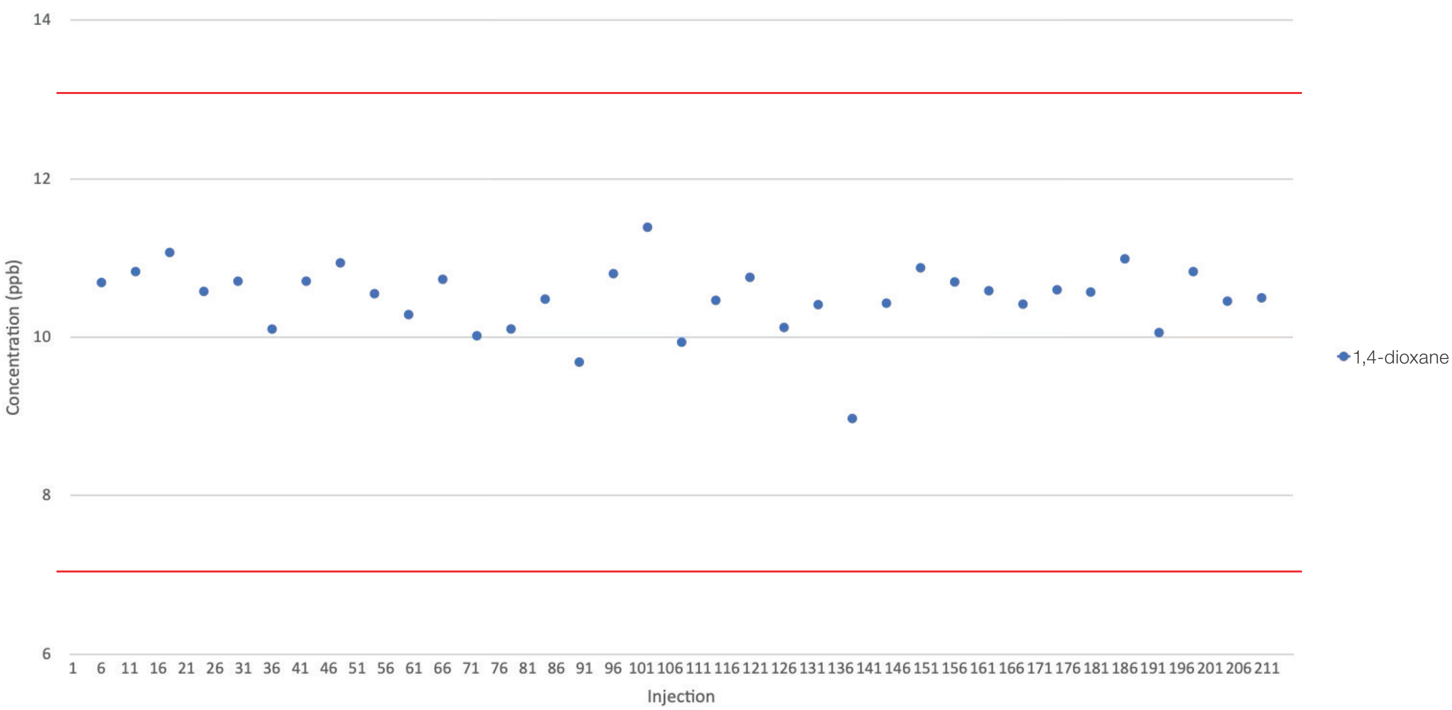

Figure 2. Results of n=35, 10 ppb 1,4-dioxane standard in water samples in a 215-injection sequence. Red lines represent ±30% accuracy.

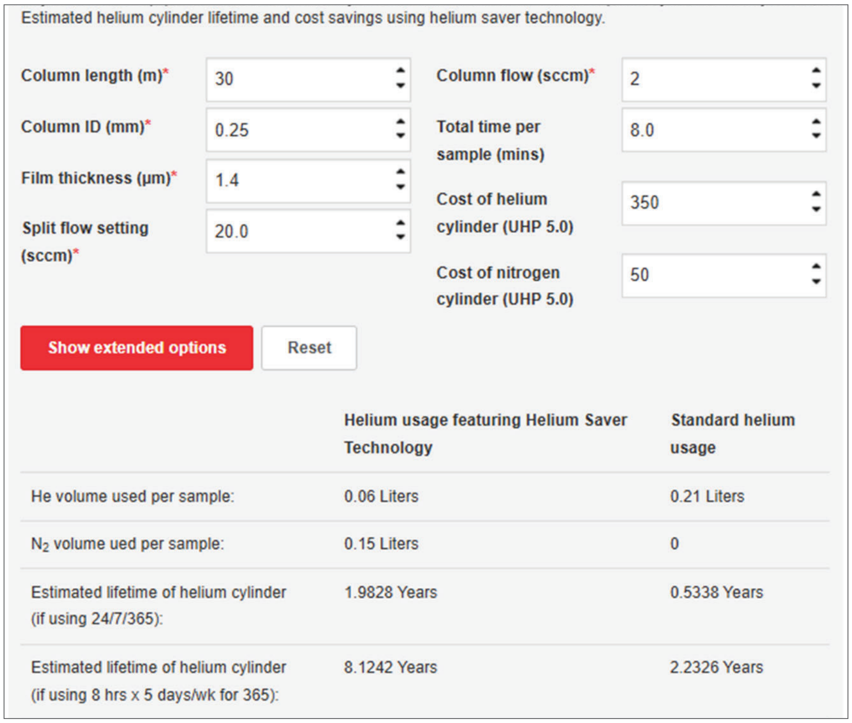

Figure 3. Helium saver calculator showing almost 4× savings of carrier gas.

Conclusion

This study demonstrates the capability of the Teledyne LABS Tekmar Lumin P&T and AQUATek LVA coupled with the TRACE 1610 GC and the ISQ 7610 MS to process low-level 1,4-dioxane in drinking water samples:

- The linearity of the calibration curve from 0.2 to 50 ppb passed method requirements.
- The application proved robust during an extended study with n=35 samples of a 10 ppb 1,4-dioxane standard.
- The study involved a 215-injection sequence with a 4.2% precision and 105% accuracy of the recovery.
- The HeSaver-H_2Safer SSL injector used almost 4× less helium during the analysis without sacrificing system performance.

References

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