PROMOCHROM TECHNOLOGIES

Application Note
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EPA Method 522

ANALYSIS OF 1,4-DIOXANE IN DRINKING WATER USING AUTOMATED SOLID PHASE EXTRACTION AND GC/MS

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ABSTRACT

1,4-dioxane is a widespread contaminant with possible carcinogenic effects on humans. The Erie County Water Authority (ECWA) utilized PromoChrom's fully automated 8-Channel solid phase extraction (SPE) system to achieve accreditation following EPA Method 522 for the extraction of 1,4 dioxane in drinking water. This application note presents the procedures and the results of their work.

INTRODUCTION

1,4-dioxane was widely used as a stabilizer for chlorinated solvents and a by-product in the manufacturing of paint strippers, dyes, greases, antifreeze, polyethylene terephthalate (PET) and detergents (USEPA 2017). The US EPA has deemed 1,4-dioxane a probable human carcinogen. It is highly soluble and resistant to biodegradation in water and soil, allowing it to migrate rapidly in ground water.

This Application Note demonstrates the fully automated extraction of 1,4-Dioxane in 500 mL of aqueous sample following EPA Method 522 Option 1. It includes background, precision (IDP), accuracy (IDA) and determination of detection limits (MDL). The results were generated by ECWA using a PromoChrom SPE-03 8-channel system and have been approved by their accrediting body.

MATERIALS

- PromoChrom SPE-03 system with MOD-005
- Restek 6 mL, 2 g coconut charcoal SPE cartridge
- Reagents and standards following EPA Method 522
- GC-MS

METHOD SUMMARY

The workflow is based on EPA Method 522. Reagent water fortified with the dechlorinating and anti-microbial agents, surrogate (1,4-dioxane-d_8) and analyte (1,4-dioxane) were extracted using the following method programmed on the SPE-03.

Solvent 1 = DCM, **Solvent 2** = MeOH, **Solvent 3** = H_2O, **W1** = Aqueous waste, **W2** = Organic waste

Table 1 - EPA Method 522 Steps Programmed on SPE-03

Action	Inlet 1	Flow	Volume	***Description***
Elute W2	Solvent 1	5 mL/min	8 mL	*Condition with 8 mL DCM**
Air-Purge W2	Air	5 mL/min	5 mL	*Push solvent through cartridges completely*
Elute W2	Solvent 2	5 mL/min	8 mL	*Condition with 8 mL MeOH**
Air-Purge W2	Air	5 mL/min	5 mL	*Push solvent through cartridges completely*
Elute W2	Solvent 2	5 mL/min	3 mL	*Condition with 3 mL MeOH, not letting it dry*
Elute W1	Solvent 3	10 mL/min	25 mL	*Wash with 5 x 5 mL strokes of H_2O*
Add Samp W1	Sample	10 mL/min	510 mL	*Load all 500 mL of sample*
Blow N2	Time based		10 min	*Dry cartridges for 10 mins at 2.5 L/min, 30psi*
Collect 1	Solvent 1	3 mL/min	4 mL	*Collect with DCM as elution solvent into fraction 1*
Wait	Time based		1 min	*Let cartridge soak for 1 min*
Collect 1	Solvent 1	3 mL/min	3 mL	*Collect with another 3 mL of DCM*
Collect 1	Solvent 1	3 mL/min	3 mL	*Collect with another 3 mL of DCM*
Air-Purge 1	Air	10 mL/min	10 mL	*Ensure remaining DCM in lines and cartridges are delivered into fractions*

*ECWA uses 8 mL of DCM and MeOH to preserve the same steps used during manual extraction of EPA Method 521

Up to 8 x 500 mL samples can be extracted simultaneously in 132 minutes using the method above. With the new SPE-03 pump, the extraction time can be further reduced to under 110 minutes. After the fractions are collected, the top layer of water is pipetted off before topping the fractions up to 10 mL using DCM. Alternatively, labs have also used drying cartridges. Internal standard (THF-d_8) is then added followed by anhydrous sodium sulfate to remove water. 1 µL is injected into GC-MS.

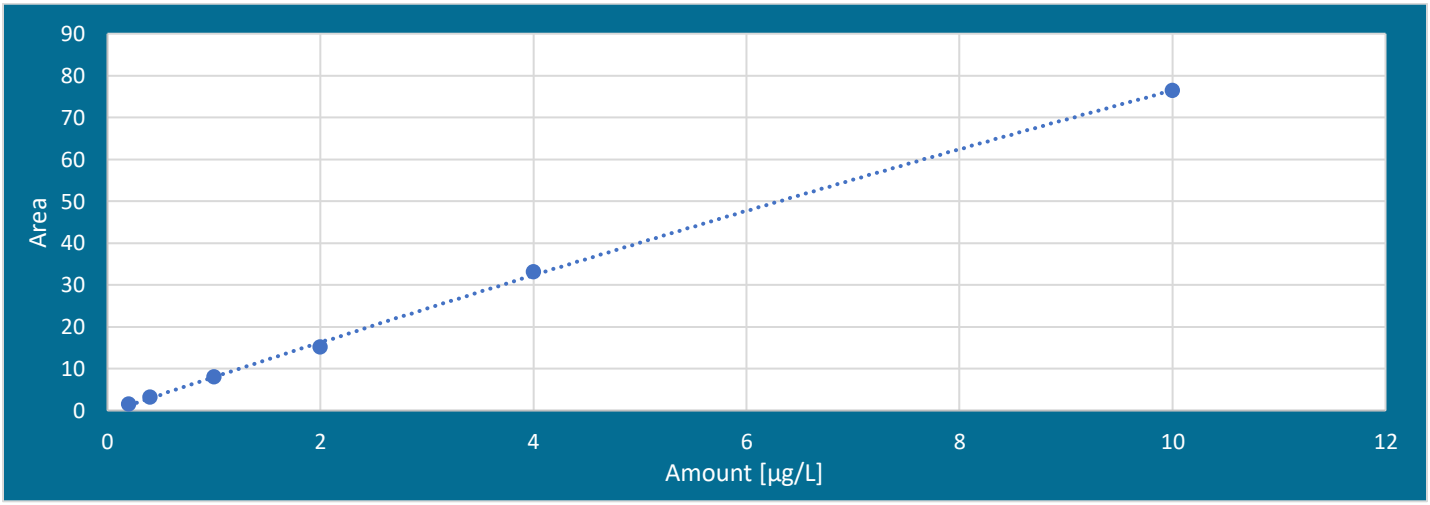
GC-MS CONDITIONS

Parameter	Value
GC-MS	GC with Single-Quad MS
GC Column	Thermo TG-VMS, 20 m x 0.18 mm ID with 1 µm film
Injection	200 °C splitless injection 4 mm single taper with glass wool 0.5 min split delay Constant column flow at 1.2 mL/min
Temperature Program	Initial temperature at 30 °C for 3 min Ramp at 5 °C /min to 90 °C Ramp at 20 °C /min to final temperature of 200 °C Total run time of 20.5 min
MS	Full scan with mass range from 24-100 amu Acquisition start at 4.4 min Source temperature at 200 °C Transfer line temperature at 200 °C

Method requirements were met with a shorter and thinner film GC column which is also used for a different analysis. Running MS in full scan gives a complete spectrum for better confirmation and is also able to achieve the required sensitivity.

ECWA uses a 6-point calibration curve from 0.20 ppb to 10 ppb, $R^2 = 0.9995$

Figure 1 - Calibration Curve for 1,4-Dioxane on GC-MS



RESULTS

Accuracy and Repeatability

The Initial Demonstration of Precision (IDP) and Initial Demonstration of Accuracy (IDA) results were determined from a batch of 4 LFBs spiked in the middle of the calibration range at 5 µg/L. The method requires %RSD to be < 20% and the average recovery to be within ±20% of the actual concentration.

Table 2 - IDC Recoveries at 5.0 µg/L

	IDC-1	IDC-2	IDC-3	IDC-4	Average	%RSD
Recovery	114%	111%	106%	85%	104%	12.6%

Minimum Reporting Limit

ECWA chose 1.0 µg/L to be their Minimum Reporting Limit (MRL), which is the same as the New York State Maximum Contaminant Level (MCL) for 1,4-Dioxane. The method requires that the Upper PIR Limit must be ≤ 150% recovery and Lower PIR Limit must be ≥ 50% recovery. Below are the results of a batch of 7 LFBs spiked at the MRL.

Table 3 - MRL recoveries at 1.0 µg/L

	MRL-1	MRL-2	MRL-3	MRL-4	MRL-5	MRL-6	MRL-7	Upper PIR	Lower PIR
Recovery	111%	114%	105%	106%	112%	113%	106%	125%	95%

Detection Limit and Background

The State of New York requires the extraction and analysis of 7 low level spiked samples and 7 MDL Blanks for Method Detection Limit (MDL) calculation, performed over at least 3 days. ECWA determined their MDL to be 0.042 µg/L based on the results of seven 0.15 µg/L replicates completed from 01/11/2021 to 01/13/2021.

Table 4 - MDL recoveries at 0.15 µg/L

	MRL-1	MRL-2	MRL-3	MRL-4	MRL-5	MRL-6	MRL-7	Average	RSD
Recovery	104%	100%	101%	117%	114%	91%	103%	104%	8.7%
Date	1/11	1/11	1/12	1/12	1/13	1/13	1/13		

7 blanks were also extracted over the same span of three days. EPA Method 522 requires blank levels to be < 1/3 of the MRL, which is < 0.33 µg/L in this case. The instrument did not detect any traces of 1,4-Dioxane.

Table 5 - Reagent Blank Results

	RB-1	RB-2	RB-3	RB-4	RB-5	RB-6	RB-7
Concentration	0	0	0	0	0	0	0
Surrogate Recovery	97%	78%	97%	110%	80%	82%	81%
Date	1/11	1/11	1/12	1/12	1/13	1/13	1/13

CONCLUSIONS

The SPE-03 system successfully met all method requirements in terms of accuracy, repeatability and background. Once the samples, SPE cartridges and fraction collection tubes are attached to the SPE-03, it takes only 110 mins of unattended operation to complete a batch of 8 samples.

In addition to EPA Method 522, Erie County Water Authority uses the same system to extract PFAS following EPA Methods 533 and 537.1. The SPE-03 is capable of performing a wide range of challenging SPE procedures that require automatic bottle rinsing (eg. PFAS, PPCPs, nitrosamines, pesticides, PAHs and PCBs) while demonstrating clean background.

References

USEPA 2017 https://www.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf

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