

# Analysis of 1,4-dioxane in Water by Purge and Trap and Triple Quadrupole GC/MS

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## Abstract

1,4-dioxane is a likely human carcinogen and has been found in groundwater at multiple sites throughout the United States. The physical and chemical properties and behavior of 1,4-dioxane create challenges for characterization and treatment. While it is relatively short-lived in the atmosphere (1 to 3-day half-life), 1,4-dioxane is highly mobile and may leach readily from soil to groundwater, where it has a long lifetime as it does not readily biodegrade in the environment.

This study uses a Teledyne Tekmar Atomx XYZ purge and trap system coupled to an Agilent 7010B Mass Spectrometer (MS) system in dynamic multiple reaction monitoring (dMRM) mode. Agilent MassHunter software created a working linear calibration curve and method detection limits (MDLs) for 1,4-dioxane.

The Agilent 7010B triple quadrupole GC/MS is the most sensitive version of the Agilent compact benchtop triple quadrupole (MS/MS) systems, providing attogram-level detection limits in electron ionization (EI) mode. The breakthrough in sensitivity allows for the optimization of sample preparation, reduces maintenance cycles by injecting less, and achieves new detection limits.

The Atomx XYZ is Teledyne Tekmar's most advanced purge and trap system and is based on the time-tested Atomx instrument platform. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure that the system is both reliable and robust.

Current methodology for the analysis of 1,4-dioxane in water is limited by poor purging efficiency, which causes elevated detection limits. However, due to the low µg/L guidelines established across the country (Table 1), modifications to existing sample preparation procedures and more sensitive instrumentation is required to achieve faster turnaround times and lower levels of detection for 1,4-dioxane.

## Introduction

1,4-dioxane is found in many locations due to its widespread use as a stabilizer in certain chlorinated solvents, paint strippers, greases, and waxes. Additionally, it is a byproduct present in many goods, including paint strippers, dyes, greases, antifreeze, aircraft deicing fluids, and in some consumer products. 1,4-Dioxane is also used as a purifying agent in the manufacture of pharmaceuticals and is a byproduct in the manufacture of polyethylene terephthalate (PET).

Because of the widespread prevalence of 1,4-dioxane as a contaminant in ground and drinking water and its potentially harmful effects therein, 1,4-dioxane is included on the fourth drinking water contaminant candidate list and is included in the Third Unregulated Contaminant Monitoring Rule (EPA 2009; EPA 2016a). EPA risk assessments indicate that the drinking water concentration representing a  $1 \times 10^{-6}$  cancer risk level for 1,4-dioxane is 0.35 µg/L (EPA IRIS 2013). While no federal maximum contaminant level (MCL) for drinking water has been established (EPA 2012), various states have established drinking water and ground water guidelines (Table 1).

**Table 1.** Drinking water and ground water guidelines established.

State	Guideline (µg/L)	Source
Alaska	77	AL DEC 2016
California	1.0	Cal/EPA 2011
Colorado	0.35	CDPHE 2017
Connecticut	3.0	CTDPH 2013
Delaware	6.0	DE DNR 1999
Florida	3.2	FDEP 2005
Indiana	7.8	IDEM 2015
Maine	4.0	MEDEP 2016
Massachusetts	0.3	MADEP 2004
Mississippi	6.09	MS DEQ 2002
New Hampshire	0.25	NH DES 2011
New Jersey	0.4	NJDEP 2015
North Carolina	3.0	NCDENR 2015
Pennsylvania	6.4	PADEP 2011
Texas	9.1	TCEQ 2016
Vermont	3.0	VTDEP 2016
Washington	0.438	WA ECY 2015
West Virginia	6.1	WV DEP 2009

1,4-Dioxane is a clear volatile liquid used primarily as a solvent and is subject to federal and state regulations and reporting requirements. 1,4-Dioxane has been reportable as a Toxics Release Inventory (TRI) chemical under Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) since 1987. It is designated as a Hazardous Air Pollutant (HAP) under the Clean Air Act (CAA), and is a hazardous substance under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). It was listed on the Safe Drinking Water (SDWA) Candidate Contaminant List (CCL) and identified in the third Unregulated Contaminant Monitoring Rule (UCMR3).

There have been several methods developed to test for 1,4-dioxane, primarily for soil and water. None of these methods meet the requirements to accurately detect low levels of 1,4-dioxane in water at ppt levels without extensive sample cleanup, requiring the need for the development of a testing method using purge and trap and GC/TQ technologies.

Drinking water analysis of Volatile Organic Compounds (VOCs) is performed using purge and trap concentration, following standard US EPA methods. This application modifies the purge and trap and gas chromatograph/mass spectrometer (GC/MS) parameters to create a robust method to detect 1,4-dioxane at the part-per-trillion level (ppt), despite its poor purge efficiency.

The quantitation of the target analyte 1,4-dioxane is performed by adding 1,4-dioxane- $d_8$  as an internal standard to all samples, controls, and calibrators. The deuterated analog of 1,4-dioxane behaves identically to 1,4-dioxane, both physically and chemically, allowing reproducible and accurate quantitation of 1,4-dioxane. This method has a linear quantitation range from 0.1 µg/L to 10 µg/L (ppb). A sample size of 10 mL (purge volume) is used to achieve low detection limits.

## Experimental

### Acquisition method

All analyses were performed on the Atomx XYZ system and the 7010B Mass Spectrometer. MS/MS was used to enhance sensitivity and selectivity. MassHunter software was used for all calculations.

As this is a triple quadrupole method, tuning is performed as per manufacturers recommendation using autotune. After initial full autotune, a passing Check Tune must be performed before the start of a batch and/or every 24 hours. If the check tune does not pass, corrective action must be performed, followed by a full autotune.

GC method parameters are shown in Table 2. Atomx XYZ method details are shown in Table 3. MS parameters are listed in Tables 4 and 5.

### Materials

- Volumetric flasks, Class A, 1 mL, 10 mL, and 50 mL with ground glass stoppers
- Analytical balance
- Gas-Tight syringes, various volumes as appropriate
- 40 mL glass VOA vials
- Caps/bonded septa
- 1 mL mininert V-vials with lids
- Agilent 121-1324UI: DB-624 UI column, 20 m × 0.18 mm, 1.0 µm
- Agilent 60 µL (straight, UI) (part number 5190-4047)
- Ultrahigh purity helium
- Ultrahigh purity nitrogen
- Methanol, purge and trap grade
- DI Water

**Table 2.** Agilent 7010B triple quadrupole GC method parameters used for the analysis of 1,4-dioxane.

GC Inlet Parameters	
Temperature	200
Pressure	14.1 psi
Septum Purge Flow	3 mL/min
Inlet Mode	Split
Split Ratio	200:1
Liner	60 µL (straight) UI (p/n 5190-4047)
GC Oven Parameters	
Column	Agilent DB-624 UI, 20 m × 0.18 mm, 1.0 µm (p/n 121-1324UI)
Column flow	0.7 mL
Run Time	18 min
Initial Temperature	35 °C
Initial Hold Time	4 min
Column Ramp	15 °C/min
Ramp Final Temperature	240 °C
Hold Time	0.333 min

**Table 3.** Atomx XYZ method parameters used for the analysis of 1,4-dioxane.

Atomx XYZ Method		Atomx XYZ Method	
Purge Settings		Desorb Settings	
Sample Equilibrate Time	0 min	Water Needle Rinse Volume	12 mL
Presweep Time	0.25 min	Sweep Needle Time	0.25 min
Prime Sample Fill Volume	3 mL	Desorb Preheat Temperature	245 °C
Sample Volume	10 mL	Desorb Time	2.0 min
Sweep Sample Time	0.25 min	Drain Flow	100 mL/min
Sweep Sample Flow	100 mL/min	Desorb Temperature	250 °C
Spurge Vessel Heater	Yes	GC Start Signal	Begin Desorb
Spurge Vessel Temperature	80 °C	Bake Settings	
Prepurge Flow	0 mL/min	Number of Water Bake Rinses	5
Prepurge Time	0 min	Water Bake Rinse Volume	12 mL
Purge Time	11.0 min	Bake Rinse Sweep Time	0.4 min
Purge Flow	40 mL/min	Bake Rinse Sweep Flow	100 mL/min
Purge Temperature	20 °C	Bake Rinse Drain Time	0.6 min
MSC Purge Temperature	30 °C	Bake Time	6 min
Dry Purge Time	2 min	Bake Flow	200 mL/min
Dry Purge Flow	100 mL/min	Bake Temperature	260 °C
Dry Purge Temperature	20 °C	MSC Bake Temperature	180 °C

**Table 4.** Agilent 7010B triple quadrupole MS method parameters used for the analysis of 1,4-dioxane.

MS Parameters	
Tune File	atunes.eihs.tune.xml
MS Transfer Line Temperature	250 °C
Helium Quench Flow	2.25 mL/min
N <sub>2</sub> Collision Gas	1.5 mL/min
Source Temperature	250 °C
Gain Factor	20

**Table 5.** Agilent 7010B triple quadrupole MS compound-specific dMRM parameters for the analysis of 1,4-dioxane.

MS dMRM Parameters		Transition	Retention Time (RT)	Left RT Delta	Right RT Delta	Collision Energy
Target	1,4-dioxane	88 → 58.1 88 → 56.9	7.64 min	0.6 min	0.6 min	5 eV 5 eV
Internal Standard	1,4-dioxane-d <sub>8</sub>	96 → 64.1 96 → 61.9	7.58 min	0.6 min	0.6 min	5 eV 5 eV
Wide/Wide quadrupole resolution windows						

### Calibrator and ISTD preparation

Two stock solutions of 1,4-dioxane at 20 mg/L and 1,4-dioxane-d<sub>8</sub> at 4 mg/L were prepared in methanol. The 20 mg/L 1,4-dioxane solution may be transferred to a mininert vial and placed in a freezer for future use. The 4 mg/L 1,4-dioxane-d<sub>8</sub> solution was transferred to a vessel on the Atomx unit and added to every calibration level and sample automatically (10 µL).

Class A volumetric flasks and gas-tight syringes were used to make the calibrator solutions of 1,4-dioxane.

A series of calibration standards to encompass the desired calibration range were prepared (0.1 µg/L, 0.2 µg/L, 0.4 µg/L, 1 µg/L, 2 µg/L, 5 µg/L, and 10 µg/L). Calibration levels were created by adding specific volumes of the 20 mg/L solution to 50 mL volumetric flasks (partially filled with DI water) with a gas-tight syringe and then filling the flask to the line with DI water. Once prepared and thoroughly mixed, the calibration solutions were transferred into 40 mL VOA vials, ensuring zero-headspace when capped.

The linear calibration range for this analysis as validated was 0.1 to 10 µg/L.

Quality control checks require the average response factor for the calibration curve to have a relative standard deviation (RSD) of less than 20%. Each calibration point must have an accuracy of ±30% from the true value. When verifying the limit of quantitation, the accuracy must be within ±50% of the true value. The limit of quantitation must have a peak-to-peak signal-to-noise (height) value of greater than 3:1 to be classified as a peak.

### Sample preparation

Aqueous samples were collected in 40 mL VOA vials with zero headspace, and analyzed as-is within seven days of the sampling date. If the concentration of 1,4-dioxane in the water sample is suspected to be high, or over the calibration range, the Atomx dilution feature may be used with a dilution of up to 1:100.

### Quality control

Each batch of 20 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 at least one sample in the batch.

Quality control for this method was monitored throughout data collection. Method blanks yielded nondetectable levels to ensure that there was no carryover.

The initial calibration (ICAL) was verified with the use of a certified reference material from a second source (ICV) and fell within 30% of the true value.

A continuing calibration verification (CCV) was prepared in the same manner as the calibration midpoint at 1 µg/L, was analyzed at the beginning of each analytical batch, and fell within 20% of the true value.

## Results and discussion

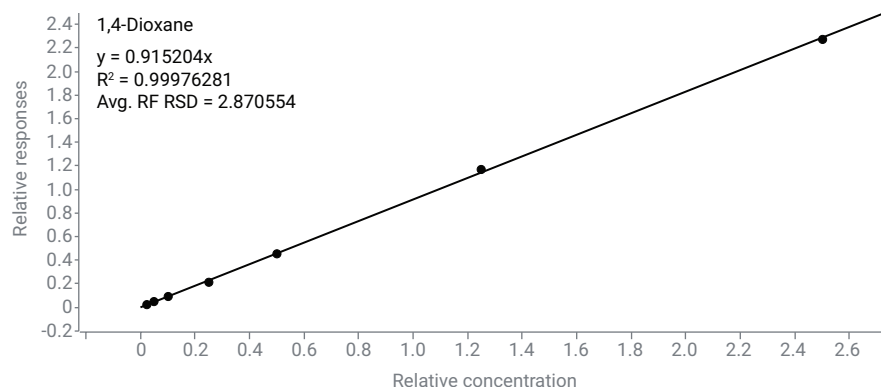
### Agilent 7010B GC/MS system equipped with an Atomx XYZ purge and trap system

Calibration data: Average of Response Factors, Ignore Origin, Weighting None

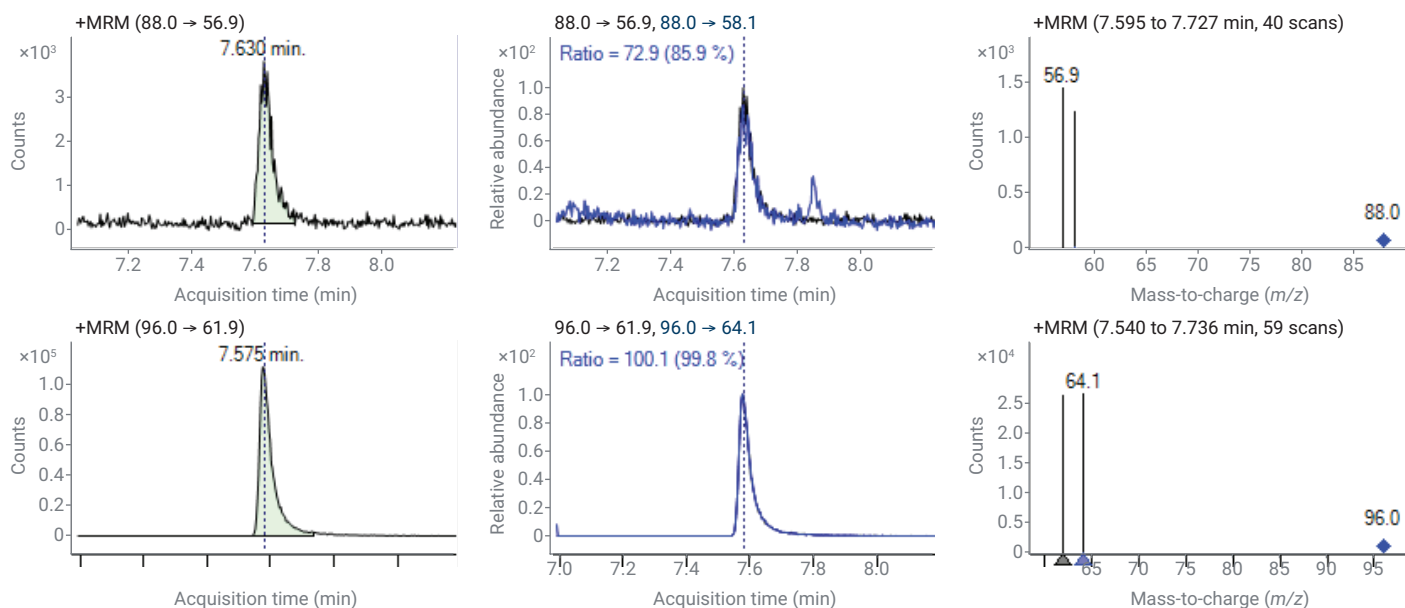
Seven levels used  $R^2 = 0.9997$ , Avg. RF RSD = 2.87% (Figure 1)

- Two continuing calibration checks: Accuracy 101% and 98%
- Multiple blanks were run throughout the batch
- Two LCS QCs: accuracy 98% and 99.6%

The MDL for 1,4-dioxane was calculated based on EPA methodology (EPA 821R16-006). The MDL was determined by spiking a sample (predetermined to contain nondetectable levels of 1,4-dioxane) at a concentration of 0.1 µg/L of 1,4-dioxane. Seven replicates of the spiked sample were injected, and an example chromatogram is shown in Figure 2.



**Figure 1.** Calibration curve for 1,4-dioxane analysis on the Agilent 7010B GC/MS system with the Atomx XYZ purge and trap system.



**Figure 2.** Example chromatography from one of the (0.1 µg/L) sample injections used for method detection limit (MDL) calculation of 1,4-dioxane on the Agilent 7010B GC/MS system with the Atomx XYZ purge and trap system.

The MDL was determined to be 0.0198 µg/L with a response RSD of 7.8%, as detailed in Table 6. A stability study was performed, as shown in Table 7.

### Best practices

Best practices for the analysis of 1,4-dioxane in water by purge and trap with triple quadrupole GC/MS are listed in Table 8.

**Table 6.** Method detection limit was determined using 0.1 µg/L samples. Calculations were done automatically from Agilent MassHunter software with an average signal-to-noise ratio of 9.36.

Name	Retention Time (min)	Transition (m/z)	Concentration Average (µg/L)	Concentration RSD (%)	Method Detection Limit (µg/L)	Limit of Quantitation (µg/L)	S/N	Resp. RSD (%)
1,4-Dioxane	7.633	88.0 → 56.9	0.1288	4.9	0.0198	0.0629	9.36	7.8

**Table 7.** Stability study of continuing calibration and quality control samples using a 1.0 µg/L standard (calculations done automatically using Agilent MassHunter software).

Sample		1,4-Dioxane Results			
Type	Level	Retention Time (min)	Response	Calculated Concentration (µg/L)	Accuracy (%)
CC	4	7.64	129123	0.95	95.32
CC	4	7.64	123273	0.92	92.49
CC	4	7.63	81382	1.05	104.92
QC	4	7.64	124063	0.92	92.04
QC	4	7.64	122084	0.93	93.49

**Table 8.** Best practices for the analysis of 1,4-dioxane.

Instrument Measure	Frequency	Requirement	Correction
Check Tune	Before every batch/every 24 hours	Pass	Corrective action/perform full Autotune
Initial Calibration Verification (ICV)	Immediately after calibration	ICV ±30% true value	Reanalyze ICV, rerun calibration/corrective action
Continuing Calibration Verification (CCV)	Before each batch	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 sec to midpoint ICAL or first CCV	Inspect and perform instrument maintenance
Matrix Blank (MB)	With every batch of 20 or fewer samples	Analyte <LOQ	Reprepare/Reanalyze/corrective action
Laboratory Control Spike and Duplicate (LCS, LCSD)	With every batch of 20 or fewer samples	RPD of LCS/LCSD <20%	Reanalyze/corrective action
Matrix Spike and Duplicate (MS, MSD)	With every batch of 20 or fewer samples	Spike Recovery ±30% RPD of MS/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.			
Recalibrate when the CCV no longer passes within 20% of true value or maintenance has been performed.			

## Conclusion

This method presents a sensitive, robust, and selective method to determine 1,4-dioxane in water using EPA 8260D purge and trap methodology. 1,4-Dioxane is notoriously difficult to analyze due to its solubility in water. Using elevated purge temperature along with MS/MS offers a reasonable analysis time along with the ability to detect very low concentrations of 1,4-dioxane without sacrificing laboratory throughput. This simple, yet reliable method demonstrates excellent sensitivity with low detection limits of 0.02 µg/L (20 ppt) being easily quantified and distinguishable from baseline. Furthermore, MDL and accuracy and precision for seven 0.1 µg/L standards showed no interference from excessive water. The benefits of using the Agilent triple quadrupole MS/MS capabilities and the Teledyne Tekmar Atomx XYZ purge and trap cannot be underestimated in lowering detection limits, reducing sample matrix interference, and improving signal-to-noise (S/N) ratio. The method described herein provides high selectivity and sensitivity with a more confidence-driven solution for the analysis of 1,4-dioxane in water.

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9. Modified SW-846 8270 SIM
10. Modified SW-846 8270 SIM with isotope dilution

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