Improved Analysis of 1,4-Dioxane in Drinking Water

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1, 4 Dioxane

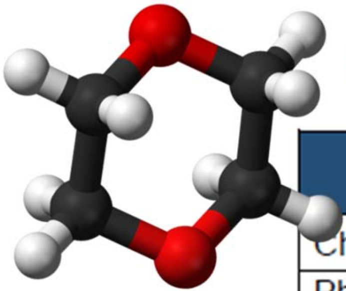

Exhibit 1: Physical and Chemical Properties of 1,4-Dioxane (ATSDR 2012)

Property	1,4-Dioxane
Chemical Abstracts Service (CAS) number	123-91-1
Physical description (physical state at room temperature)	Clear, flammable liquid with a faint, pleasant odor
Molecular weight (g/mol)	88.11
Water solubility	Miscible
Melting point (°C)	11.8
Boiling point (°C) at 760 mm Hg	101.1
Vapor pressure at 25°C (mm Hg)	38.1
Specific gravity	1.033
Octanol-water partition coefficient (log K_{ow})	-0.27
Organic carbon partition coefficient (log K_{oc})	1.23
Henry's law constant at 25 °C (atm-m^3/mol)	4.80×10^{-6}

Abbreviations: g/mol – grams per mole; °C – degrees Celsius; mm Hg – millimeters of mercury; atm-m^3/mol – atmosphere-cubic meters per mole

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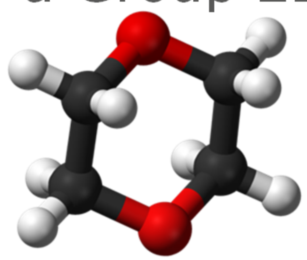
1,4 Dioxane Health Effects

- The US Agency for Toxic Substances and Disease Registry (ATSDR) states that 1,4-dioxane at high levels may cause liver and kidney damage
- The Department of Health and Human Services (DHHS) has stated that 1,4-dioxane is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals
- The US EPA has also classified 1,4-dioxane as "likely to be carcinogenic to humans" by all routes of exposure
- The World Health Organization International Agency for Research on Cancer classifies 1,4-dioxane as a Group 2B compound (possibly carcinogenic to humans)



The ATSDR 2017 Substance Priority List

2017 Rank	Substance Name	Total Points	CAS RN
1	ARSENIC	1674	7440-38-2
2	LEAD	1531	7439-92-1
3	MERCURY	1458	7439-97-6
4	VINYL CHLORIDE	1358	75-01-4
5	POLYCHLORINATED BIPHENYLS	1345	1336-36-3
6	BENZENE	1329	71-43-2
208	1,3-DICHLOROBENZENE	628	541-73-1
209	PENTACHLORODIBENZO-P-DIOXIN	626	36088-22-9
210	N-NITROSODIPHENYLAMINE	625	86-30-6
211	2,4-DICHLOROPHENOL	619	120-83-2
212	2,3-DIMETHYLNAPHTHALENE	619	581-40-8
213	2,3,7,8-TETRACHLORODIBENZOFURAN	619	51207-31-9
214	1,4-DIOXANE	617	123-91-1
215	FLUORINE	613	7782-41-4
216	NITRITE	610	14797-65-0
217	CESIUM-137	610	10045-97-3

As of 2016, 1,4-dioxane had been identified at more than 34 sites on the EPA National Priorities List (NPL); it may be present (but samples were not analyzed for it) at many other sites (EPA 2016b).

ATSDR Agency for Toxic Substances and Disease Registry

https://www.atsdr.cdc.gov/spl/index.html

Where Does 1,4-Dioxane Come From?

- Sources of 1,4-dioxane include widespread use as a stabilizer in certain chlorinated solvents, and is often found in conjunction with chlorinated solvents
- It is a by-product present in many goods, including paint strippers, dyes, greases, antifreeze and aircraft deicing fluids, and in some consumer products (deodorants, shampoos and cosmetics)
- The EU Scientific Committee on Consumer Safety, working on the advice of the International Cooperation on Cosmetics Regulation (ICCR) recommended the limit for 1,4-dioxane in finished cosmetic products be less than 10 ppm

Sources of Exposure

- Traces of 1,4-dioxane may be present in some food supplements, food-containing residues from packaging adhesives or on food crops treated with pesticides that contain 1,4-dioxane
- Air
- Recreational waters
- Drinking water

UCMR-3 Evaluation of DW Occurrence

- The US EPA Candidate contaminant list (CCL) is developed to be a source of compounds of emerging concern for further investigation
- US Drinking Water regulations specify that 30 analytes be evaluated for regulation every five years
- The Unregulated Contaminant Monitoring Rule (UCMR) is used to asses the occurrence in large and small drinking water supplies of candidate analytes that arise from the CCL.
- The third UCMR collected data from 2013-2015

Contaminant	CAS Registry Number[1]	Minimum Reporting Level	Sampling Points[2]	Analytical Methods
1,4-dioxane	123-91-1	0.07 µg/L	EPTDS	EPA 522

UCMR-3

ELSEVIER

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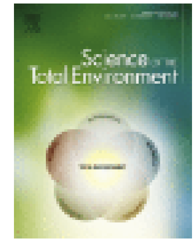

1,4-Dioxane drinking water occurrence data from the third unregulated contaminant monitoring rule

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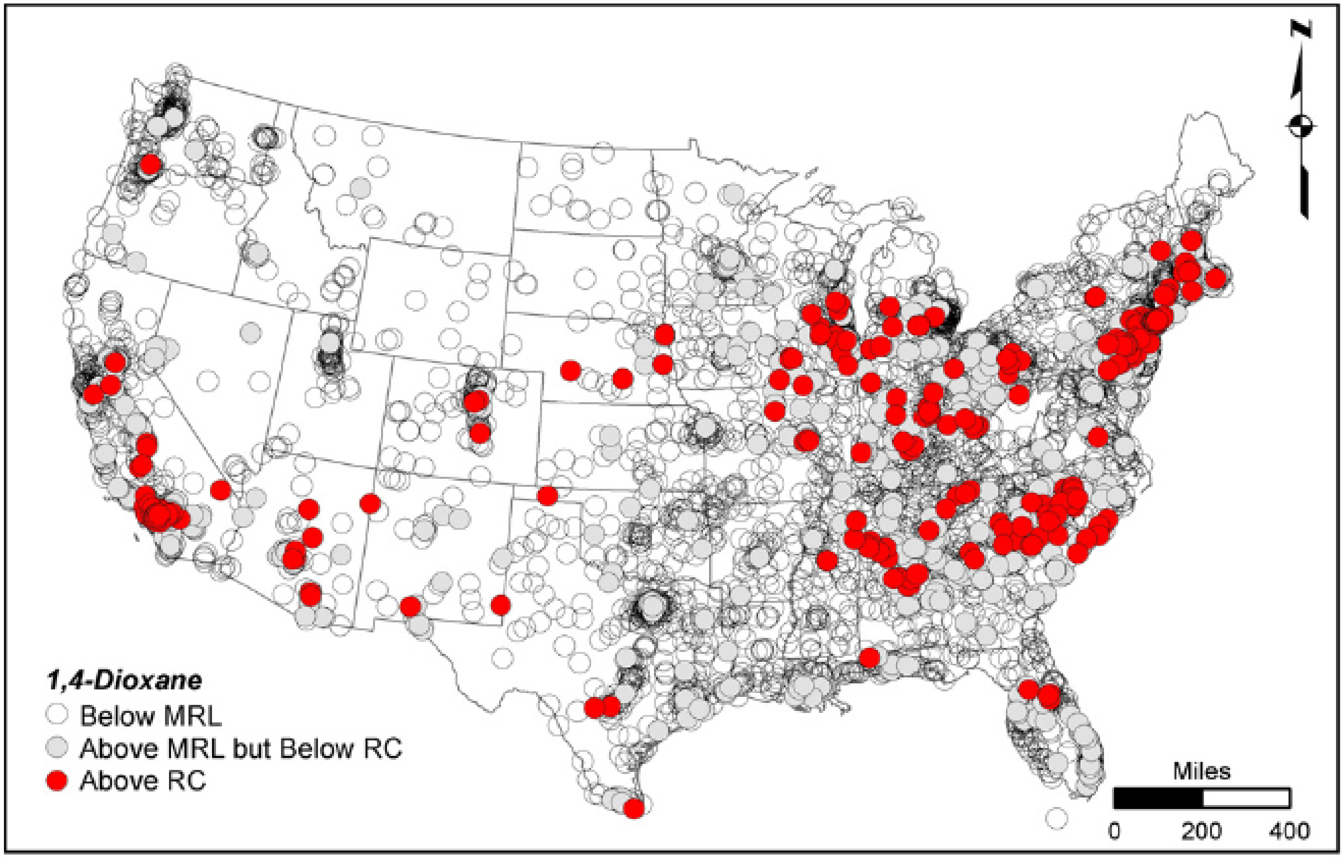
Occurrence Measured Through UCMR-3



Overall, detections were noted in PWSs located in 50 of the 63 states, districts, territories, and tribal areas that conducted UCMR3 monitoring.

David T. Adamson, Elizabeth A. Piña, Abigail E. Cartwright, Sharon R. Rauch, R. Hunter Anderson, Thomas Mohr, John A. Connor, 1,4-Dioxane drinking water occurrence data from the third unregulated contaminant monitoring rule, Science of the Total Environment 596–597 (2017) 236–245.

US EPA Health Advisories

Drinking Water Standards and Health Advisories

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Chemicals	CASRN Number	Standards			Status HA Document	Health Advisories						Cancer Descriptor
						10-kg Child						
		Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	RfD (mg/kg/day)	DWEL (mg/L)	Life-time (mg/L)	mg/L at 10^{-4} Cancer Risk	
Diisopropylmethylphosphonate	1445-75-6	-	-	-	F '89	8	8	0.08	3	0.6	-	D
Dimethrin	70-38-2	-	-	-	F '88	10	10	0.3	10	2	-	D
Dimethyl methylphosphonate	756-79-6	-	-	-	F '92	2	2	0.2	7	0.1	0.7	C
Dimethyl phthalate	131-11-3	-	-	-	-	-	-	-	-	-	-	D
Dinitrobenzene (1,3-)	99-65-0	-	-	-	F '91	0.04	0.04	0.0001	0.005	0.001	-	D
Dinitrotoluene (2,4-)	121-14-2	-	-	-	F '08	1	1	0.002	0.1	-	0.005	L
Dinitrotoluene (2,6-)	606-20-2	-	-	-	F '08	0.4	0.04	0.001	0.04	-	0.005	L
Dinitrotoluene (2,6 & 2,4)[1]		-	-	-	F '92	-	-	-	-	-	0.005	B2
Dinoseb	88-85-7	F	0.007	0.007	F '88	0.3	0.3	0.001	0.035	0.007	-	D
Dioxane p-	123-91-1	-	-	-	F '87	4	0.4	0.03	1	0.2	0.035	L
Diphenamid	957-51-7	-	-	-	F '88	0.3	0.3	0.03	1	0.2	-	D

The results of UCMR-3 have not resulted in a regulated maximum contaminant level of 1, 4 dioxane, but EPA risk assessments indicate that the drinking water concentration representing a 1 x 10^{-6} cancer risk level is 0.35 µg/L

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State Guidelines

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

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Methods of Analysis

- A number of existing EPA methods have been evaluated for use for different matrices
- US EPA Method 522 for drinking water has been shown to provide reliable results and low detection limits

- This talk will describe the implementation of Method 522 in a commercial laboratory incorporating automation to improve method performance

Solid Phase Extraction with Automation

- Cartridges need controlled flow for best performance
- Automation provides less technician interaction
  - Less potential evaporation of volatile analyte
  - Less chance of introducing contamination
- Method automatically reproducibly implemented, good for multitasking workforce

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Extraction Method

Step	Operation	Solvent	Solvent Volume (mL)	Vent Purge Time (s)	Vacuum Pump Rate (s)	Saturation Time (s)	Soak Time (s)	Drain Time (s)	Done Loading Sample Delay (s)	Dry Time (s)	N2 Blanket
1	Condition	Methylene chloride	5	30	3	4	10	60			
2	Condition	Methylene chloride	5	30	3	4	10	60			
3	Condition	Methanol	5	30	3	3	10	60			
4	Condition	Methanol	5	30	3	3	10	6			
5	Condition	Water	5	15	3	3	10	4			
6	Condition	Water	5	15	3	3	10	4			
7	Condition	Water	5	15	3	3	10	4			
8	Load Sample				3				45		
9	Air Dry Disk Timer				6					600	OFF
10	Elute Sample Container	Methylene chloride	3	15	3	3	120	60			OFF
11	Elute Sample Container	Methylene chloride	3	15	3	3	120	60			OFF
12	Elute Sample Container	Methylene chloride	3	15	3	3	120	90			OFF

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GC/MS Conditions

Parameter	Value
Injection Volume	1 µL
Inlet Temperature	280 °C
Mode	Splitless
Gas Type	Helium
Column Conditions	Zebron™ ZB-5 (Phenomenex), 30 m, 0.25 mm, 0.25 µm
Mode	Consistent Flow
Oven Program	30°C hold for 2 minutes Ramp 5 °C/min to 50°C Ramp 50 °C/min to 200°C Hold for 6 minutes
MS Ions Monitored	Tetrahydrofuran-d_8 – <u>46</u>, 78, 80 1,4-dioxane-d_8 – <u>62</u>, 64, 96 1,4-dioxane – <u>58</u>, 88

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Method Detection Limits

MDL Sample	MDL (µg/L)
1	0.069
2	0.074
3	0.070
4	0.073
5	0.067
6	0.063
7	0.063
8	0.068
SD	0.00409
MDL	0.0123

Minimum Level

HR_{PIR} Sample	HRPIR
1	0.069
2	0.074
3	0.070
4	0.073
5	0.067
6	0.063
7	0.063
Mean	0.068
SD	0.0044
HR_{PIR}	0.0175

	PIR	Criterion	
Upper	85.8	$\leq$150%	Pass
Lower	50.8	$\geq$50%	Pass

Initial Demonstration of Accuracy and Precision

LFB	Measured Concentration (µg/L)
1	39.9
2	40.9
3	52.2
4	46.1
5	48.6
Average	45.5
SD	5.17
RSD	11.3

The criterion for accuracy is that mean recovery is $\pm$ 20% of the true value. The true value is 50 µg/L. The recovery is 91.1%, well within the acceptable window. The precision (%RSD) must be $\leq$ 20% and 11.3 is better than the requirement.

Lab Fortified Blank Results

LFB	Measured Conc (µg/L)	Spike Conc (µg/L)	% Recovery	Surrogate % Recovery
Low LFB	6.05	5	121	73.6
Med LFB	46.1	50	92.3	72.8
High LFB	449	500	89.8	78.0

The surrogate compound, 1, 4 dioxane d-8, was within 70-130% recovery in all cases. The medium and high LFB recoveries were within 70-130 % recovery. The low LFB was within 50-150% recovery of the true value.

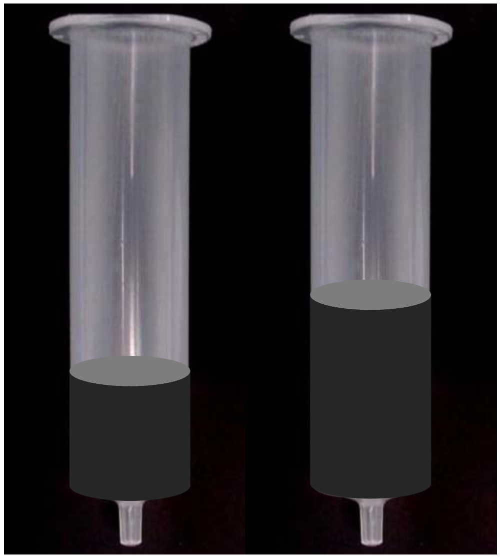
Continuing Calibration Check Results (CCC)

Standard	Measured Value (µg/L)	True Value (µg/L)	% Recovery
Low CCC	5.17	5	103
High CCC	472	500	94.5

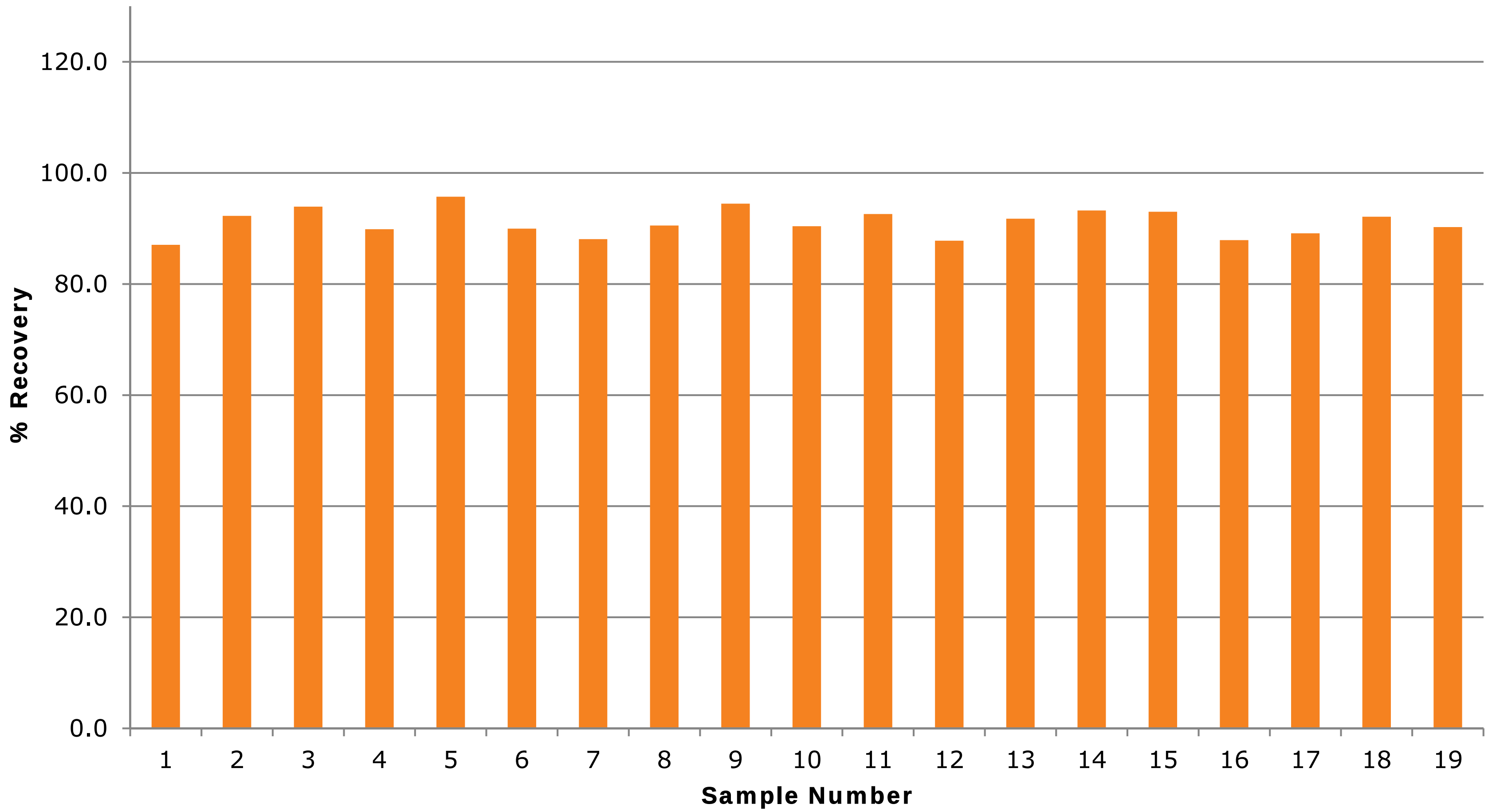
The acceptable recovery for a low CCV is ± 50% of the true value and 103% is well within that window. The high CCC criterion is that the recovery fall within ± 30% of the true value and the 94.5 % recovery observed meets this requirement.

3-gram vs. 2-gram Cartridge

- 3-gram cartridge allowed faster sample processing
- 3-gram cartridge allowed better surrogate recoveries
- Fewer re-runs (less than 1%)



Surrogate Recovery (3-gram cartridge)



Performance Evaluation Sample (PT)

Sample	Measured Value (µg/L)	True Value (µg/L)	% Recovery	Acceptable Range (µg/L)
PT Sample 1	7.82	8.00	97.8	4.8-11.2

Conclusions

- The method developed meets the quality control requirements specified in US EPA Method 522
- Automation provides less technician interaction required
  - Less potential evaporation of a volatile analyte
  - Less chance of introducing contamination
- For laboratories that run many methods, or run this method infrequently, automation enhances reproducibility
- Use of a system that can switch between disks and cartridges increases system usage and efficiency in the laboratory
- This method may be extended to other types of water, including small amounts of particulate in the future

Questions?