Application Note: 52185

Maximizing Speed and Separations for Lowering Drinking Water Detection Limits with GC/MS

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Key Words

- ISQ Single Quadrupole GC-MS
- Purge and Trap
- Single Ion Monitoring (SIM)
- US EPA Method 524.3
- Volatiles

Overview

Ever increasing drinking water regulations demonstrate the need for sensitivity and dynamic range of a GC-MS system in order for the laboratory to provide usable data over the long term. The California Department of Public Health published new notification levels for a list of compounds including 1,2,3-trichloropropane (1,2,3-TCP) at 0.005 µg/L.[1] Uses for these compounds includes paint and varnish remover, cleaning and degreasing agent, a cleaning and maintenance solvent, and more currently as a chemical intermediate. Its use as a pesticide was in formulations with dichloropropenes in the manufacture of D-D, a soil fumigant. EPA Method 524.3 allows for the use of Single Ion Monitoring (SIM) to reach ppt levels.[2] The determination of lower level MDLs in compliance with the volatile notification levels listed below was run on a Thermo Scientific ISQ GC-MS with an OI Analytical Eclipse Purge-and-Trap Sample Concentrator.

Experimental

The Thermo Scientific Trace GC Ultra Multi-Channel Gas Chromatograph was configured for use with a purge and trap by installing the purge and trap adapter. A Thermo Scientific TraceGOLD TG-VMS GC 20 meter × 0.18 mm × 1.0 µm capillary column (PN 26080-4950) was installed on the Split/Splitless inlet. The split vent was set to 30 mL/min and the column flow to a constant flow of 1 mL/min. The instrument parameters are listed in Table 1 for the ISQ™ GC-MS and Table 2 for the Eclipse in the analysis of the calibration curve and spiked samples.

GC Parameters

Column	TG-VMS GC 20 meter × 0.18 mm, 1.0 µm
Carrier	1 mL/min constant flow
Oven	40 °C, 4.5 min; 8 °C/min,100 °C, 0.0 min; 25 °C/min, 230 °C, 2 min
Split Inlet	200 °C
Spit Flow	30 mL/min

ISQ MS Parameters

Transferline	200 °C
Ion Source	230 °C
Ionization Mode	EI
Filament Delay	0.5 min
Chrom Filter Width	2.5 sec
Detector Gain	5×10^5

Table 1: GC and MS parameters for EPA Method 524.3

Purge and Trap Parameters

Sample Volume	5 mL
Sample Purge Temperature	40 °C
Sample Mount	90 °C
Trap	#10 (Tenax, silica gel, cms)
Purge Flow	40 mL/min
Purge Time	11 min
Water Management Temperature	Purge 110 °C, desorb 0 °C, transfer line 150 °C, valve oven 150 °C, bake 240 °C
Desorb Preheat	180 °C
Desorb Temperature	190 °C
Desorb Time	0.5 min
Bake Rinse Cycles	Twice
Bake Cycle	210 °C for 12 min

Table 2: Parameters of the OI Analytical Eclipse for EPA Method 524.3

A 1 µL injection of 25 ng/µL BFB was analyzed based on the 524.3 quality control criteria, before the calibration curve. BFB is no longer required every twelve hours as in previous versions of the method. BFB must pass the tune criteria before any new curve is established, or after any major maintenance is performed on the instrument. Standards were prepared in organic free water. A 5 mL aliquot was transferred from the 40 mL VOA vial into the fritted sparger automatically. The linearity was evaluated from 0.020 to 20 µg/L and MDLs were determined by running seven replicates at 0.1 µg/L and 0.020 µg/L.

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Results

The ISQ GC-MS easily met the QC criteria for the method. Figure 1 demonstrates the results of the BFB tune check criteria.

The entire GC run time was 16 minutes as shown by the TIC of the 2 µg/L standard in Figure 2.

The TIC of the scan segments are shown in Figure 3 along with the SIM ions that were utilized.

The instrumentation and the column provided excellent chromatography which is demonstrated by the Gaussian-shaped peaks for the early eluting gases seen in Figure 4.

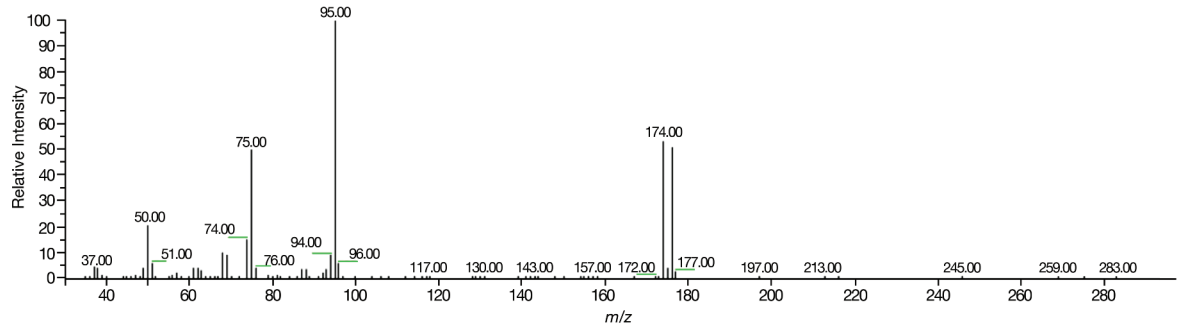
A comparison of the MDLs from EPA Method 524.2 and those produced by EPA Method 524.3 are shown in Table 3.

Conclusion

The ISQ GC-MS easily met the quality control requirements and the lower detection limit requirements for this drinking water method. The average MDL for drinking water was 0.035 µg/L. The following three compounds were run in SIM with MDLs: dibromomethane – 2 ppt, 1,2,3-trichloropropane – 2 ppt, and 1,2-dibromo-3-chloropropane – 4 ppt.

References

1. Drinking Water Notification levels and Response Levels: An Overview, California Department of Public Health Drinking Water Program, Nov. 2010 ***http://www.cdph.ca.gov/certlic/drinkingwater/Pages/default.aspx***
2. EPA Method 524.3, Measurement of Purgeable Organic Compounds in Water by Capillary Column by Gas Chromatography/Mass Spectrometry (GC-MS), Revision 1.0 Jan. 2009



m/z	Ion Abundance Criteria	% Relative Abundance	Pass/Fail
95	equals 100% of Base Peak	100.0	Pass
96	greater than or equal to 5% AND less than or equal to 9% of *m/z* 95	5.9	Pass
173	less than 2% of *m/z* 174	0.6	Pass
174	greater than 50% of *m/z* 95	52.9	Pass
175	greater than or equal to 5% AND less than or equal to 9% of *m/z* 174	7.0	Pass
176	greater than 95% AND less than 105% of *m/z* 174	95.5	Pass
177	greater than or equal to 5% AND less than or equal to 10% of *m/z* 176	5.4	Pass

Figure 1: BFB criteria report from Thermo Scientific EnviroLab Forms 3.1

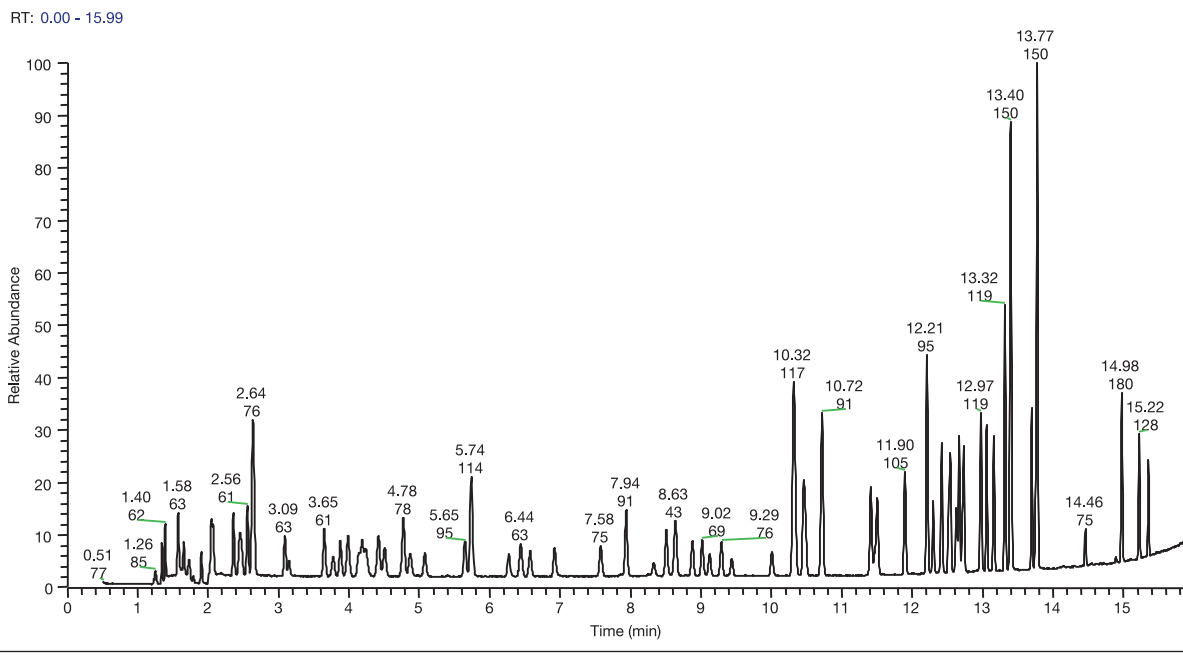


Figure 2: TIC of a 2 µg/L standard in full scan

Component	524.2 Avg Conc (µg/L)	524.3 Avg Conc (µg/L)	524.2 Std Dev	524.3 Std Dev	524.2 % RSD	524.3 % RSD	524.2 MDL (µg/L)	524.3 MDL (µg/L)
dichlorodifluoromethane	0.34	0.024	0.016	0.004	5	17	0.051	0.012
chloromethane	0.43	0.094	0.028	0.008	7	9	0.087	0.026
vinylchloride	0.40	0.020	0.020	0.004	5	20	0.062	0.012
bromomethane	0.45	0.091	0.047	0.001	11	16	0.148	0.045
chloroethane	0.45	0.067	0.077	0.012	17	17	0.242	0.036
trichlorofluoromethane	0.41	0.113	0.039	0.007	9	6	0.121	0.021
diethylether	0.45	0.429	0.031	0.021	7	5	0.097	0.068
1,1-dichloroethylene	0.42	0.116	0.049	0.013	12	11	0.154	0.041
carbon disulfide	0.43	0.400	0.032	0.063	7	16	0.099	0.198
allyl chloride	0.42	–	0.041	–	10	–	0.130	–
methylene chloride	0.46	–	0.032	–	7	–	0.101	–
acetone	4.789*	–	0.399	–	8	–	1.255	–
trans-1,2-dichloroethylene	0.41	0.097	0.046	0.009	11	9	0.144	0.027
methyl tert-butyl ether	0.42	–	0.019	–	4	–	0.058	–
1,1-dichloroethane	0.42	0.021	0.027	0.002	7	8	0.085	0.005
acrylonitrile	0.41	0.118	0.036	0.023	9	20	0.115	0.073
cis-1,2-dichloroethylene	0.41	–	0.029	–	7	–	0.092	–
2,2-dichloropropane	0.38	–	0.026	–	7	–	0.08	–
bromochloromethane	0.39	0.090	0.042	0.007	11	8	0.131	0.021
chloroform	0.41	0.019	0.021	0.004	5	19	0.066	0.011
carbon tetrachloride	0.42	0.104	0.030	0.006	7	6	0.096	0.019
tetrahydrofuran	0.48	0.564	0.087	0.104	18	18	0.272	0.326
methyl acrylate	0.39	0.089	0.041	0.011	11	12	0.128	0.034
1,1,1-trichloroethane	0.43	0.024	0.035	0.004	8	18	0.112	0.014
1,1-dichloropropylene	0.39	0.091	0.030	0.006	8	6	0.093	0.019
2-butanone	0.52	–	0.099	–	19	–	0.310	–
1-chlorobutane	0.35	–	0.096	–	28	–	0.302	–
benzene	0.40	0.092	0.011	0.004	3	4	0.036	0.011
propionitrile	0.43	0.108	0.062	0.027	14	25	0.194	0.085
methacrylonitrile	0.42	0.095	0.053	0.026	13	27	0.166	0.082
1,2-dichloroethane	0.40	0.098	0.024	0.010	6	11	0.076	0.033
fluorobenzene (ISTD)	–	–	–	–	5	4	–	–
trichloroethylene	0.41	0.095	0.025	0.004	6	5	0.077	0.014
dibromomethane	0.39	0.023	0.050	0.001	13	3	0.156	0.002
1,2-dichloropropane	0.40	0.086	0.026	0.007	7	8	0.082	0.021
bromodichloromethane	0.38	0.097	0.024	0.005	6	5	0.075	0.016
methyl methacrylate	0.38	0.100	0.032	0.008	8	9	0.099	0.025
cis-1,3-dichloropropene	0.38	0.094	0.024	0.008	6	9	0.077	0.026
toluene	0.38	0.017	0.008	0.003	2	17	0.025	0.010
chloroacetonitrile	0.31	0.025	0.086	0.005	28	20	0.270	0.015
1,1-dichloro-2-propanone	0.35	0.077	0.082	0.014	23	18	0.257	0.044
tetrachloroethylene	0.39	0.023	0.079	0.004	20	15	0.248	0.011
2-nitropropane	0.41	0.106	0.035	0.010	8	9	0.109	0.031
4-methyl-2-pentanone	0.41	0.098	0.031	0.009	8	9	0.098	0.029
trans-1,3-dichloropropene	0.38	0.092	0.021	0.008	5	9	0.065	0.025
1,1,2-trichloroethane	0.40	0.098	0.022	0.010	5	10	0.069	0.030
ethyl methacrylate	0.37	0.578	0.022	0.097	6	17	0.069	0.304
dibromochloromethane	0.37	0.019	0.027	0.003	7	16	0.084	0.010
1,3-dichloropropane	0.38	0.016	0.019	0.003	5	18	0.059	0.009
1,2-dibromoethane	0.38	0.095	0.019	0.009	5	10	0.061	0.030
2-hexanone	0.47	0.100	0.061	0.010	13	10	0.193	0.030
chlorobenzene	0.39	0.022	0.016	0.003	4	14	0.052	0.100
ethylbenzene	0.40	0.020	0.019	0.004	5	22	0.059	0.014
1,1,1,2-tetrachloroethane	0.42	0.092	0.038	0.005	9	6	0.119	0.016
m&p-xylene	0.79	0.021	0.041	0.002	5	10	0.130	0.006
o-xylene	0.40	0.021	0.009	0.002	2	12	0.030	0.008
bromoform	0.37	0.019	0.047	0.003	13	17	0.147	0.010
styrene	0.39	0.092	0.017	0.006	5	6	0.055	0.018
isopropylbenzene	0.39	0.017	0.018	0.001	5	9	0.057	0.005
4-bromofluorobenzene (surr)	5.27	–	0.234	–	4	–	0.735	–
bromobenzene	0.40	0.081	0.029	0.011	7	13	0.092	0.034
n-propylbenzene	0.39	0.022	0.020	0.003	5	13	0.064	0.009
1,1,2,2-tetrachloroethane	0.38	0.085	0.022	0.010	6	11	0.069	0.030
2-chlorotoluene	0.40	0.016	0.022	0.002	6	13	0.069	0.006
1,2,3-trichloropropane	0.41	0.020	0.017	0.001	4	4	0.053	0.002
1,3,5-trimethylbenzene	0.39	0.019	0.018	0.004	5	20	0.057	0.012
trans-1,4-dichloro-2-butene	0.40	0.094	0.025	0.011	6	12	0.078	0.036
4-chlorotoluene	0.36	0.017	0.014	0.002	4	12	0.045	0.007
p-isopropyltoluene	0.36	0.080	0.014	0.005	4	6	0.045	0.016
tert-butylbenzene	0.36	0.089	0.012	0.008	3	9	0.039	0.024
1,2,4-trimethylbenzene	0.40	0.023	0.017	0.002	4	8	0.053	0.006
pentachloroethane	0.40	0.337	0.051	0.013	13	4	0.160	0.041
sec-butylbenzene	0.39	0.019	0.017	0.002	4	8	0.053	0.005
1,3-dichlorobenzene	0.44	0.017	0.013	0.003	3	18	0.042	0.010
1,4-dichlorobenzene	0.52	0.075	0.019	0.005	4	7	0.061	0.017
n-butylbenzene	0.39	0.026	0.017	0.003	4	12	0.054	0.010
hexachloroethane	0.37	0.511	0.019	0.045	5	9	0.059	0.142
1,2-dichlorobenzene	0.42	0.023	0.025	0.003	6	14	0.078	0.010
1,2-dichlorobenzene-d_4 (surr)	5.44	–	0.435	–	8	–	1.369	–
1,2-dibromo-3-chloropropane	0.38	0.026	0.046	0.001	12	5	0.144	0.004
nitrobenzene	0.02	–	0.046	–	19	–	0.144	–
hexachlorobutadiene	0.39	0.091	0.039	0.006	10	6	0.122	0.018
1,2,4-trichlorobenzene	0.42	0.018	0.023	0.002	5	12	0.071	0.006
naphthalene	0.38	0.020	0.012	0.003	3	13	0.038	0.008
1,2,3-trichlorobenzene	0.42	0.020	0.025	0.003	6	15	0.079	0.009
					Average	**12**	**0.140**	**0.035**

Table 3: Comparison of the MDL results from EPA Method 524.2 and EPA Method 524.3

**lab air contamination*

Figure 3: TICs showing the full scan and SIM segments used to analyze for the compounds in EPA Method 524.3

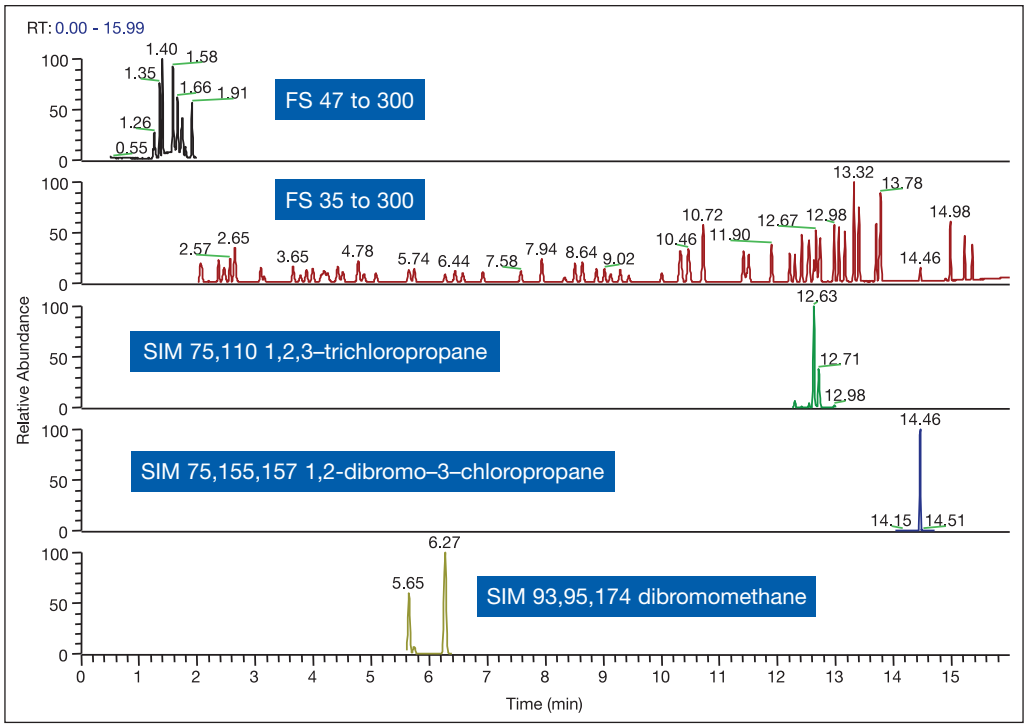
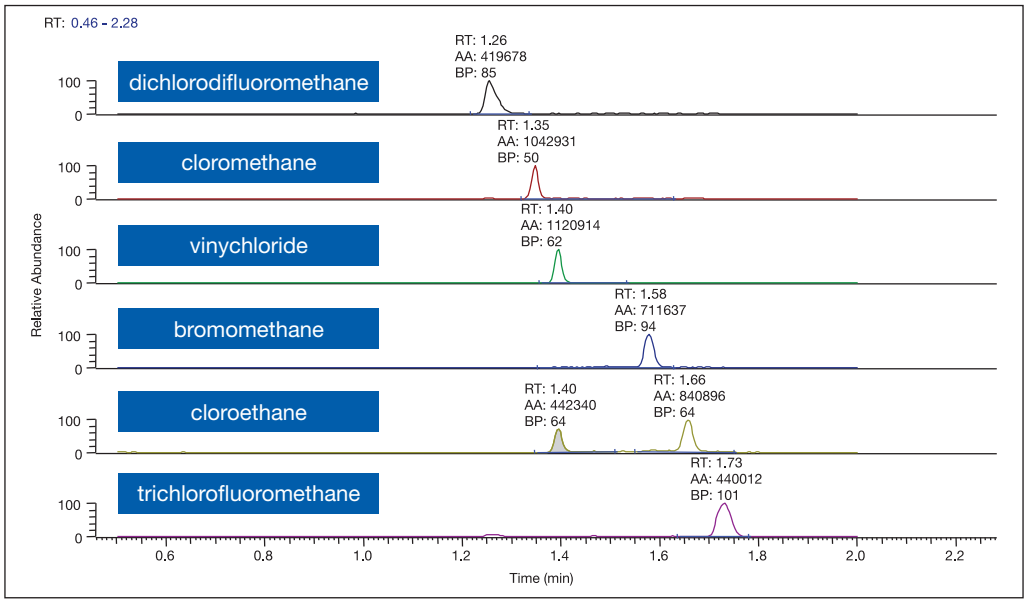


Figure 4: TIC of the early eluting gases from EPA Method 524.3



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