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Application Note

Volatile Organic Compounds in bottled water

Gas Chromatography/Mass Spectrometry using EPA method 524.3

Introduction

Bottled waters have become the most popular beverage in the United States in recent years, even surpassing coffee and soft drinks. A walk down the beverage aisle at the grocery store shows quite an increase in types of bottled water over the years.

The Environmental Protection Agency (EPA) regulates public drinking water while the Food and Drug Administration (FDA) regulates bottled water. The FDA protects consumers through the Federal Food, Drug, and Cosmetic Act. The regulations focus mainly on standard of identity or type, standard of quality which sets maximum levels of contaminants, and current good manufacturing practices which require bottled water to be safe.

Standard of quality regulations include setting maximum contaminant levels which include VOCs listed in 21 CFR Part 165 analyzed by Method 524.2 or updated revisions. Method 524.3 is listed in 40 CFR 141.24 as an approved alternate to analyze drinking water.

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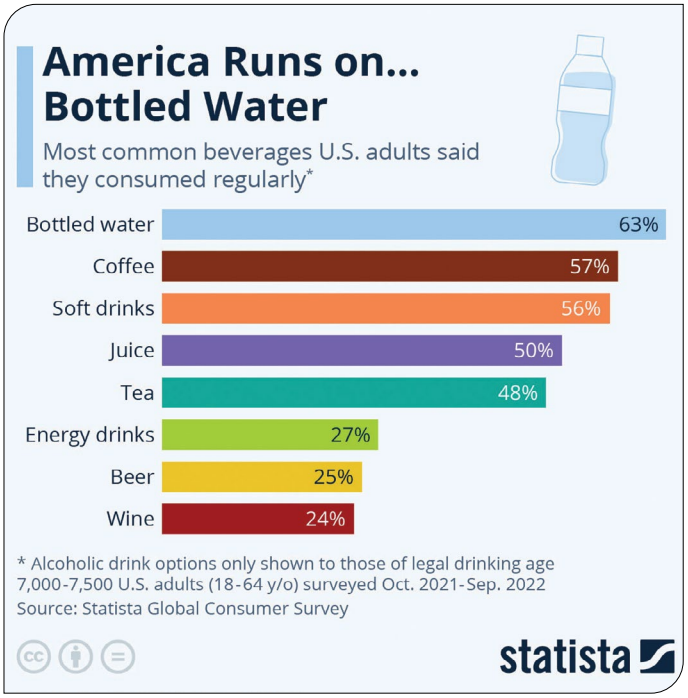
This application note compares various bottled water products for volatile organic compounds using EPA Method 524.3. Contaminants of interest were analyzed in a variety of waters for VOCs using purge and trap concentration (P&T) followed by separation and detection by gas chromatography/ mass spectrometry (GC/MS).

Methodology

In this study some of the different types of bottled water such as purified, spring water, well water, mineral water, and artesian well water were obtained and analyzed using EPA Method 524.3. Local tap water and well water were also analyzed to compare with the bottled waters. While this is a mature method there are various ways to optimize the analysis for fast cycle time and ease of use. The method allows different P&T parameters so the lab can determine which ones work best utilizing existing equipment.



The instrumentation used for concentration was an OI Analytical 4760 P&T with a 4100 soil/water autosampler. An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection. P&T and GC parameters were optimized for best performance and cycle time. Please see Table 1 for instrument parameters.

A calibration of target compounds for Method 524.3 was analyzed at 0.5, 1, 2, 5, 10, 20, and 40 ppb. Internal Standard-Surrogate Standards (IS-SS) were added to all QC and samples to result in a 5 ppb concentration in 5 ml of sample. Calibration levels were requantitated using the calibration after analysis. The lowest standard must be within +/- 50% of the true value and all other levels within +/- 30%. This criteria was met. Seven replicates of 5 ppb and seven replicates of 10 ppb were analyzed for precision and accuracy, Initial Demonstration of Capability (IDC). The QC requirements for relative standard deviation of 20% and accuracy of +/- 20% were met for this. All other QC requirements for reporting level validation, carryover, blank contamination, continuing calibration checks, and IS-SS recovery were met.

Quantitation of QC and samples was achieved using linear and quadratic regression. Average response quantitation was used for surrogates.

Table 1. Instrument Parameters

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#11; VOCARB
Purge gas	Zero grade Helium at 40 mL/min
Purge time	11 min
Sparge mount temperature	45 ˚C
Sample temperature (purge)	45 ˚C
Sample temperature (bake)	55 ˚C
Desorb time	1.0 min
Bake time	5 min
OI #10 trap temperature	Ambient during purge 240 ˚C during water removal 250 ˚C during desorb 260 ˚C during bake
Water management	120 ˚C during purge Ambient during desorb 240 ˚C during bake
Transfer line temperature	140 ˚C
Six-port valve temperature	140 ˚C

Autosampler	4100 water/soil sample processor
System gas	Zero grade nitrogen
Purge gas	Zero grade helium
LV20 pressure	8.0 psi
Loop-based time settings	Default
Mode	Water
Rinse water	90 ˚C
P&T rinses	3
Rinse water	hot

Gas Chromatograph	Agilent 7890A
Column	Restek Rtx-VMS 30 meter, 0.25mm ID, 1.4 µmdf
Carrier gas	Zero grade helium
Inlet temperature	240 ˚C
Inlet liner	Agilent ultra inert, 1 mm straight taper
Column flow rate	0.8 mL/min
Split ratio	50:1
Oven program	Hold at 40 °C for 2 min 12 °C/minute to 170 °C 40 °C/minute to 220 °C Hold at 220 °C for 2 min Total GC Run is 16.0 min

Mass Spectrometer	Agilent 5975C
Mode	Full scan
Scan Range	35-300 amu
Scans/second	5.19
Solvent delay	1.46 min
Transfer line temperature (AUX)	240 ˚C
Source temperature	230 ˚C
Quadrupole temperature	150 ˚C
Draw out plate	6 mm

Results

All appropriate QA/QC requirements were met. As expected different waters had different results. Of interest is the presence of some Trihalomethanes (THMs) in samples. THMs are formed when organic matter reacts with chorine used to disinfect water. The main THMs are Chloroform, Bromodichloromethane, Chlorodibromomethane, and Bromoform. The limit for total THMs is 80 ppb so all samples were well below that limit. What is interesting is that samples labelled as purified water have any detectable compounds of interest however they are significantly cleaner than tap water that was analyzed. It is probable that most of the samples come from municipal water supplies which may contain THMs. Other compounds were detected which could come from industrial solvents used in manufacturing. One sample from the group, #9, surprisingly had ~3 to 5 ppb aliphatic compounds in it. The levels detected for all samples were well below the maximum allowable limits listed in 21 CFR Part 165. Please see Table 2 for QA/QC results and Table 3 for sample results.

Table 2. 524.3 QAQC

	Compound	Calibration Coefficient (R^2)	AVG. Response Factor	IDC 5ppb % RSD	IDC 5 ppb % Recovery	IDC 10 ppb % RSD	IDC 10 ppb % Recovery
1	1,4-Difluorobenzene (IS)	N/A	N/A	N/A	N/A	N/A	N/A
2	Dichlorofifluoromethane	0.998	0.247	8.12	97.3	7.20	93.6
3	Chlorodifluoromethane	0.994	0.464	2.43	95.3	4.58	96.5
4	Chloromethane	0.996	0.433	3.49	92.3	3.11	91.3
5	Vinyl chloride	0.998	0.313	3.85	98.3	6.29	94.0
6	1,3-Butadiene	0.998	0.508	3.89	99.5	6.65	96.1
7	Bromomethane	0.994	0.179	10.8	104	10.4	103
8	Trichlorofluoromethane	0.999	0.637	6.03	101	5.74	97.1
9	Ethyl ether	0.992	0.217	4.01	92.0	1.97	88.5
10	1,1-Dichloroethene	0.992	0.328	3.93	106	4.53	98.0
11	Carbon disulfide	0.998	0.712	2.20	93.9	5.26	94.7
12	Methyl iodide	0.998	0.339	3.91	104	6.93	104
13	Allyl chloride	0.996	0.117	9.87	110	4.85	107
14	Methylene chloride	0.998	0.192	6.92	104	5.05	104
15	trans-1,2-Dichloroethene	0.991	0.360	4.92	94	3.97	92.5
16	Methyl acetate	0.994	0.251	4.72	104	4.77	97.5
17	Methyl tert-butyl ether-d3(SS)	8.30	0.897	5.07	99.2	3.54	98.5
18	Methyl tert-butyl ether	0.995	0.826	4.05	93.7	1.34	94.3
19	tert-Butyl alcohol	0.999	0.115	5.23	99.0	3.35	96.5
20	Diisopropyl ether	0.999	1.040	2.01	94.6	2.38	96.4
21	1,1-Dichloroethane	0.997	0.631	4.52	96.8	2.88	95.6
22	tert-Butyl ethyl ether	0.997	0.934	3.46	92.6	2.40	94.1
23	cis-1,2-Dichloroethene	0.994	0.361	5.04	91.3	2.83	93.1
24	Bromochloromethane	0.997	0.117	8.73	113	6.26	116
25	Chloroform	0.993	0.611	3.64	91.8	2.26	93.8
26	Carbon tetrachloride	0.995	0.537	6.32	90.8	6.08	95.4
27	Tetrahydrofuran	0.993	0.044	11.8	107	8.20	97.4
28	1,1,1-Trichloroethane	0.996	0.58/1	5.12	92.8	2.37	94.3

	Compound	Calibration Coefficient (R^2)	AVG. Response Factor	IDC 5ppb % RSD	IDC 5 ppb % Recovery	IDC 10 ppb % RSD	IDC 10 ppb % Recovery
29	1,1-Dichloropropene	0.996	0.434	5.72	89.7	2.69	92.3
30	1-Chlorobutane	0.996	0.705	5.87	90.7	1.61	94.2
31	Benzene	0.999	1.164	4.23	95.9	1.98	97.4
32	tert-Amyl methyl ether	0.999	0.716	3.46	93.5	2.71	95.7
33	1,2-Dichloroethane	0.994	0.415	3.24	93.9	5.30	94.4
34	Trichloroethene	0.998	0.399	6.24	95.1	2.41	95.2
35	tert-Amyl ethyl ether	0.995	0.655	6.73	93.3	5.54	94.8
36	Dibromomethane	0.996	0.196	5.77	95.5	3.94	96.8
37	1,2-Dichloropropane	0.999	0.302	5.19	101	1.54	104
38	Bromodichloromethane	0.995	0.392	4.74	91.7	2.27	95.8
39	cis-1,3-Dichloropropene	0.995	0.390	4.52	89.9	1.13	94.1
40	Chlorobenzene-d5 (IS)	N/A	N/A	N/A	N/A	N/A	N/A
41	Toluene	0.999	0.792	3.89	96.3	3.12	95.4
42	Tetrachloroethene	0.996	0.470	4.09	103	9.75	116
43	trans-1,3-Dichloropropane	0.997	0.445	12.5	94.1	6.10	93.4
44	1,1,2-Trichloroethane	0.996	0.267	10.4	102	5.50	98.7
45	Ethyl methacrylate	0.997	0.315	6.26	96.1	3.06	102
46	Chlorodibromomethane	0.998	0.373	13.6	92.9	5.47	92.6
47	1,3-Dichloropropane	0.997	0.506	9.55	103	5.41	98.8
48	1,2-Dibromoethane	0.996	0.332	13.0	102	6.06	99.7
49	Chlorobenzene	0.999	0.944	3.43	95.5	4.26	97.5
50	Ethylbenzene	0.999	1.785	5.61	94.3	4.29	91.9
51	1,1,1,2-Tetrachloroethene	0.999	0.361	8.45	100	5.38	97.8
52	m,p-Xylenes	0.999	0.763	8.01	95.3	3.14	92.5
53	o-Xylene	0.999	0.731	7.97	96.1	3.98	92.7
54	Styrene	0.999	1.037	7.15	92.9	3.95	91.6
55	Bromoform	0.997	0.227	10.7	85.6	4.69	89.2
56	Isopropylbenzene	0.999	1.901	8.88	92.6	3.39	90.9
57	1,4-Dichlorobenzene-d4 (IS)	N/A	N/A	N/A	N/A	N/A	N/A
58	4-Bromofluorobenzene (SS)	12.73	0.850	8.98	107	2.99	97.4
59	Bromobenzene	0.998	0.774	8.05	111	1.79	103
60	n-Propylbenzene	0.997	2.952	6.62	86.1	3.09	93.4
61	1,1,2,2-Tetrachlroethane	0.997	0.782	10.2	115	3.19	107
62	2-Chlorotoluene	0.997	2.022	6.50	109	1.82	102
63	1,3,5-Trimethylbenzene	0.997	1.984	5.14	87.0	4.17	93.2
64	1,2,3-Trichloropropane	0.996	0.678	11.9	117	3.32	110
65	4-Chlorotoluene	1.00	1.99	2.44	101	1.37	101

	Compound	Calibration Coefficient ($R^{2)}$	AVG. Response Factor	IDC 5ppb % RSD	IDC 5 ppb % Recovery	IDC 10 ppb % RSD	IDC 10 ppb % Recovery
66	tert-Butylbenzene	0.994	1.898	8.71	81.9	8.13	83.9
67	1,2,4-Trimethylbenzene	0.992	1.564	4.25	84.1	10.4	88.8
68	sec-Butylbenzene	0.990	2.052	6.49	109	9.58	87.0
69	p-Isopropyltoluene	0.998	1.657	6.39	95.0	12.1	98.7
70	1,3-Dichlorobenzene	0.999	1.550	8.03	104	1.92	102
71	1,4-Dichlorobenzene	1.00	1.362	2.42	96.8	2.03	97.8
72	n-Butylbenzene	0.994	1.381	7.81	89.8	12.7	89.3
73	Hexachloroethane	0.995	0.223	12.6	105	3.06	106
74	1,2-Dichlorobenzene-d4 (SS)	4.94	1.005	5.76	103	2.75	97.1
75	1,2-Dichlorobenzene	0.999	1.490	5.91	107	1.66	103
76	1,2-Dibromo-3-chloropropane	0.996	0.208	12.0	118	4.44	109
77	Hexachlorobutadiene	0.999	0.304	7.32	91.1	4.70	93.0
78	1,2,4-Trichlorobenzene	0.998	0.606	6.01	97.7	7.20	95.4
79	Naphthalene	0.999	2.150	8.22	103	4.65	99.5
80	1,2,3-Trichlorobenzene	0.997	0.614	7.62	98.8	7.62	96. 3

Figure 2. 10 ppb Standard

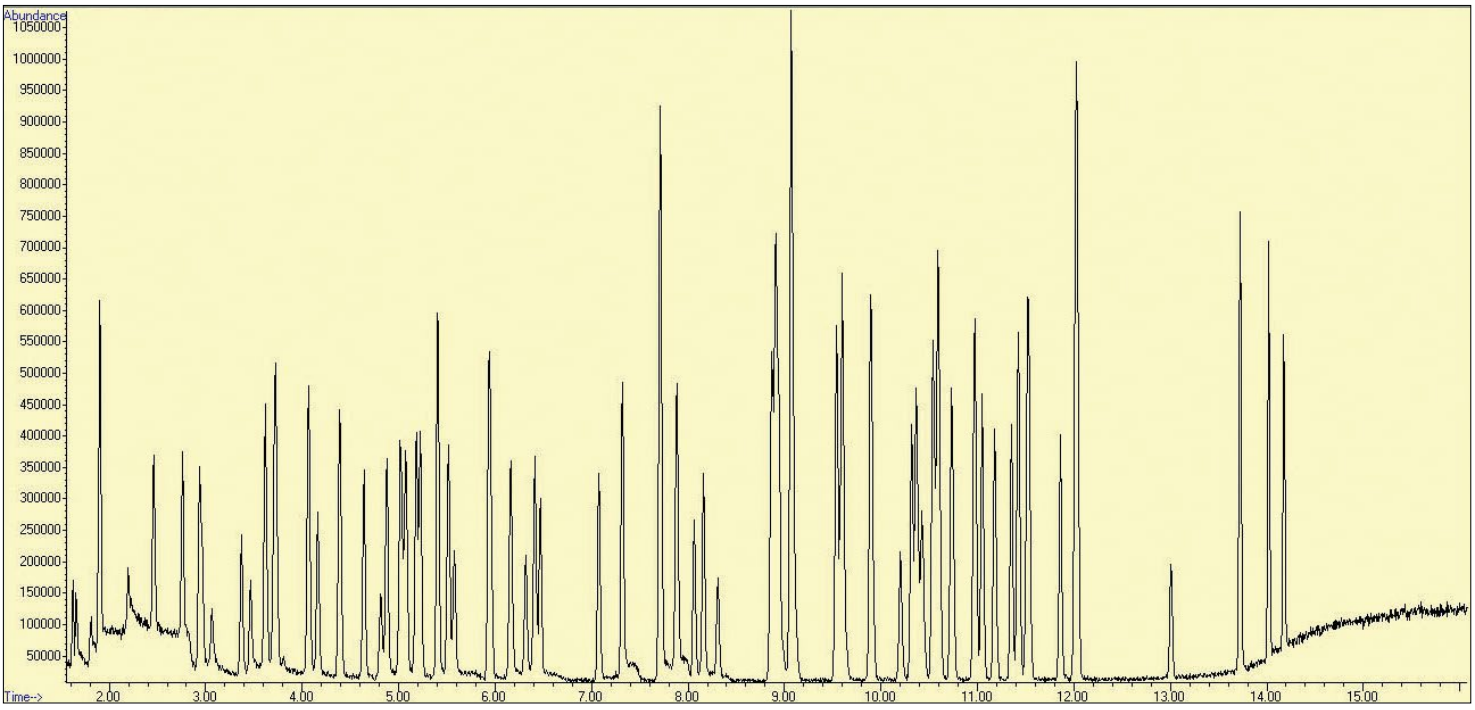


Figure 3. Sample #9

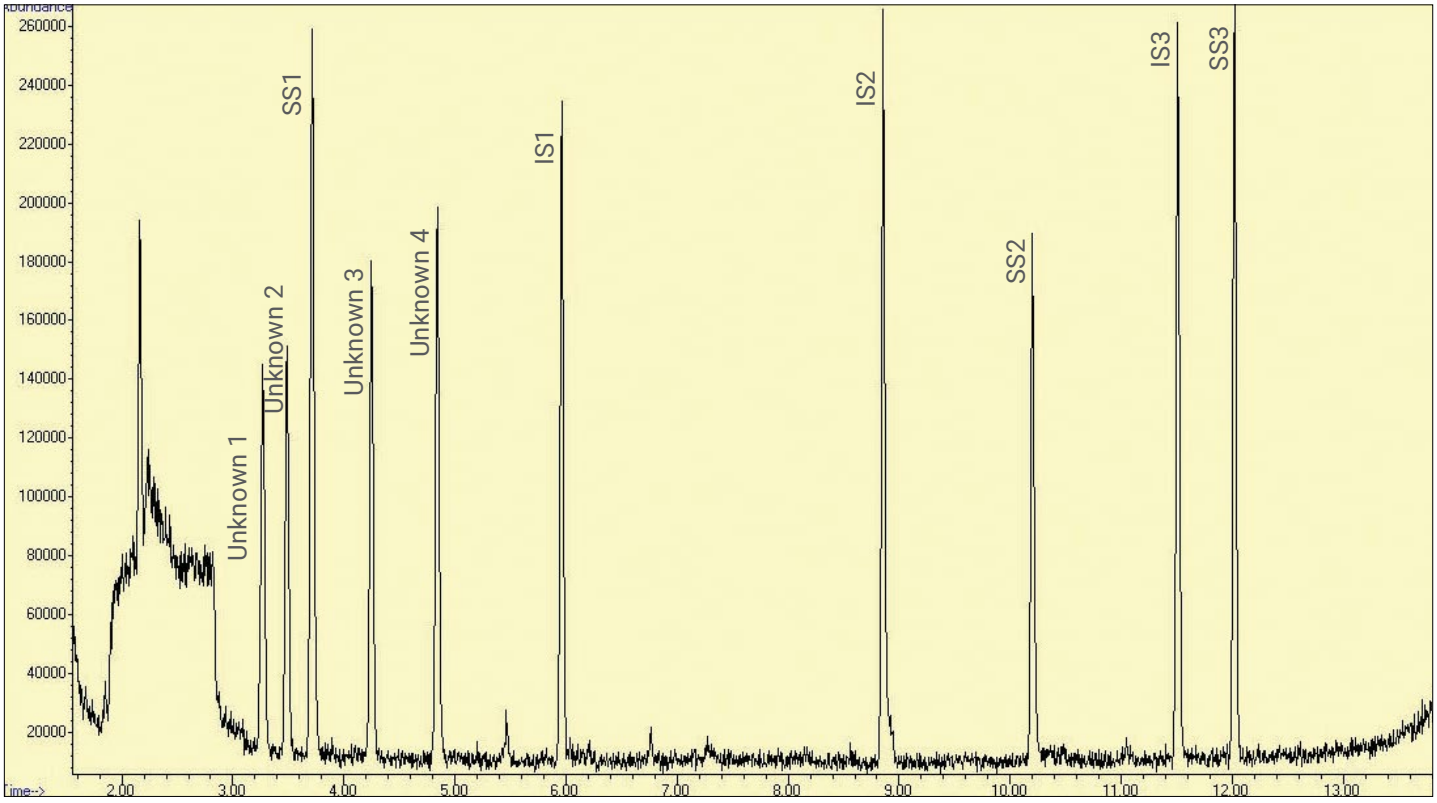


Table 3. Sample Results

	Sample	CH_2BrCl ppb	$CHCl_3$ ppb	THF ppb	C_6H_6 ppb	$CHBrCl_2$ ppb	$CHBr_2Cl$ ppb	$CHBr_3$	1,4-DCB
1	Purified by reverse osmosis; Electrolyte enhanced; Alkaline pH >/=7.5	ND	0.35*	ND	0.33*	ND	ND	ND	ND
2	Purified by reverse osmosis; Electrolyte and mineral enhanced; Alkaline pH >/=9.5	ND	ND	1.16	ND	ND	0.28*	0.50	ND
3	Purified – ionized; Electrolyte enhanced; Alkaline pH >/=9.5	0.50	0.50	ND	ND	0.37*	ND	ND	ND
4	Purified by reverse osmosis; Electrolyte enhanced; "Balanced pH"	ND	0.78	1.82	ND	0.70	ND	ND	ND
5	Purified; Electrolyte enhanced; pH >/=9.5	ND	ND	ND	ND	ND	ND	ND	0.37*
6	Texas spring water	ND	ND	ND	ND	ND	ND	ND	ND
7	Purified by reverse osmosis	ND	1.60	ND	ND	ND	ND	ND	ND
8	Purified by reverse osmosis; Mineral enhanced	ND	0.99	ND	ND	0.78	0.42*	0.49*	0.59

	Sample	CH_2BrCl ppb	$CHCl_3$ ppb	THF ppb	C_6H_6 ppb	$CHBrCl_2$ ppb	$CHBr_2Cl$ ppb	$CHBr_3$	1,4-DCB
9	Artesian water; Naturally filtered through volcanic rock; Natural electrolytes and minerals	ND	ND	ND	ND	ND	ND	ND	ND
10	Artesian water; Naturally filtered through volcanic rock; Natural electrolytes and minerals	ND	ND	ND	ND	ND	ND	4.84	ND
11	Mineral water with natural carbonation	ND	0.33*	ND	ND	0.41*	0.32*	0.38*	ND
12	Naturally alkaline spring water filtered through rock layers; pH 7.8-8.2	ND	ND	ND	ND	ND	ND	ND	ND
13	Texas spring water	ND	0.89	ND	ND	0.39*	ND	ND	ND
14	Vapor distilled water; Electrolyte enhanced	ND	0.26*	ND	ND	0.36*	0.25*	ND	ND
15	Purified by reverse osmosis; Electrolyte and mineral enhanced; pH ~7.4	ND	0.34*	ND	ND	ND	ND	ND	ND
16	Bryan, Texas tap water	ND	1.07	ND	ND	4.52	13.7	14.3	ND
17	Texas well water – Carrizo-Wilcox aquifer	ND	ND	ND	ND	ND	ND	ND	ND
18	Texas well water – Carrizo-Wilcox aquifer	ND	ND	ND	ND	ND	ND	ND	ND
19	College Station, Texas tap water	ND	1.41	ND	ND	5.55	15.0	14.9	ND
20	Carbonated water; Natural electrolytes	ND	ND	ND	ND	ND	ND	0.38*	ND

* Estimated concentration between 0.25 and 0.5 ppb (reporting level)

CH_2BrCl – Bromochloromethane $CHCl_3$ – Chloroform THF – Tetrahydrofuran C_6H_6 - Benzene
$CHBrCl_2$ – Bromodichloromethane $CHBr_2Cl$ – Chlorodibromomethane $CHBr_3$ – Bromoform
1,4-DCB – 1,4-Dichlorobenzene

Results

Consumers love bottled water because it is healthy, safe, convenient, and often times tastes better than tap water. The FDA ensures that these beverages are safe. The parameters used for this study enable a fast, accurate method for analyzing VOCs by Method 524.3.

Reference

1. Prakash, B,; Munch, D.; Pepich, B. Method 524.3.Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0; EPA-815-09-009; U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water: Cincinnati, Ohio, June 2009;

2. Statista Global Consumer Survey

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