USEPA 524.2 Method Validation Using the Evolution 2 Purge and Trap Concentrator

Application Note

Environmental

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Abstract

The United States Environmental Protection Agency (USEPA) created Method 524.2 for the examination of purgeable organic compounds in surface, ground and drinking water. There are a wide range of compounds listed in the method including four trihalomethanes which form when water is chlorinated. This application will examine USEPA Method 524.2 employing the new Evolution 2 purge and trap concentrator.

Introduction:

Through the years, many labs have used a 25mL sample volume to determine the analytes for Method 524.2. The larger volume was employed in order to meet the detection limits of the compounds listed in the method. Unfortunately, when combining the 25mL sample volume with the required four minute desorb time, there was an enhanced possibility of water transfer to the Gas Chromatograph/Mass Spectrometer (GC/MS). For this reason, the EST Analytical Evolution was designed with an 8-port valve. The 8-port valve works to bypass the moisture control trap during desorb so as to limit water transfer.

Currently, most GC/MS systems are sensitive enough to meet method detection limits using a 5mL purge volume. However, the four minute desorb time can still be problematic. Thus, the Evolution 2 (EV2) has retained the 8-port valve for water management. Furthermore, the EV2 has new software, easy access to the concentrator for routine maintenance, a smaller footprint for increased lab bench space and was also designed with better air circulation for an over 25% faster cool down time. Employing the EV2, USEPA Method 524.2 will be examined.

Experimental:

The EV2 and Centurion W/S autosampler were set up to run in water mode. A Vocarb 3000 analytical trap was employed for the study. The GC was configured with a Rxi-624Sil MS 30m x 0.25mm I.D. x 1.4µm film thickness column for analyte separation. While scan mode from 35 to 300m/z was applied for compound analysis. Once the system was ready, a Bromofluorobenzene sample was examined in order to verify that the system passed method tune parameter requirements. Operational parameters are listed in Tables 1 and 2, Figure 1 displays a passing tune graphic.

AutoFind: Scans 2354, 2355, 2356; Background Corrected with Scan 2340

Target Mass	Rel. to Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn	Result Pass/Fail
50	95	15	40	20.3	28475	PASS
75	95	30	60	52.1	73099	PASS
95	95	100	100	100.0	140395	PASS
96	95	5	9	6.5	9119	PASS
173	174	0.00	2	0.6	626	PASS
174	95	50	100	73.9	103805	PASS
175	174	5	9	7.5	7752	PASS
176	174	95	101	97.7	101440	PASS
177	176	5	9	6.8	6849	PASS

Figure 1: Bromofluorobenzene Tune Graphic

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	140°C
Transfer Line Temp.	140°C
Trap Temp.	40°C
Moisture Reduction Trap (MoRT) Temp.	39°C
Purge Time	11 min
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	1.0 min
Desorb Pressure	5.0 psi
Desorb Time	4.0 min
Desorb Preheat Delay	5 sec
Desorb Temp.	250°C
Moisture Reduction Trap (MoRT) Bake Temp.	210°C
Bake Temp	250°C
Sparge Vessel Bake Temp.	110°C
Bake Time	6 min
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Type	Water
Water Volume	5ml
Internal Standard Vol.	5µl

Table 1: Purge and Trap Parameters

GC/MS	Parameter Setting
Inlet	Split/Splitless
Inlet Temp.	220ºC
Inlet Head Pressure	7.774 psi
Mode	Split
Split Ratio	40:1
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45ºC hold for 1.0 min, ramp 15ºC/min to 220ºC, hold for 1.33 min, 14.0 min run time
Column Flow Rate	1mL/min
Gas	Helium
Total Flow	44.0 mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 35-300
Scans	5.2 scans/sec
Solvent Delay	0.7 min

Table 2: GC/MS Experimental Parameters

Certified reference materials were obtained for the Internal Standard, Surrogates and method analytes. Internal Standard and Surrogate mixes were combined in order to create a 25µg/mL standard. The Internal Standard/Surrogate mix was then added to the Internal Standard vessels of the Centurion W/S for sample addition. A seven-point calibration curve from 0.5 to 50µg/L was formulated and sampled using the EV2/Centurion WS system and analyzed with a GC/MS. After the calibration curve was determined, seven blanks and 0.5µg/L standards were examined over three days in order to determine the method detection limits. Next a series of seven 20µg/L samples were sampled and analyzed in order to establish the precision and accuracy of the analysis. Tables 3 and 4 display summaries of the calibration curve, detection limits and precision and accuracy data. A 20 µg/L standard chromatogram is presented in Figure 2.

Compound	Curve RF	Curve %RSD	Compound	Curve RF	Curve %RSD
Dichlorodifluoromethane	0.226	9.06	ethyl methacrylate	0.423	6.20
Chloromethane	0.310	11.13	trans-1,3-Dichloropropene	0.405	6.88
Vinyl Chloride	0.289	6.04	1,1,2-Trichloroethane	0.247	8.16
Bromomethane	0.165	13.80	Tetrachloroethene	0.215	6.91
Chloroethane	0.192	7.21	1,3-Dichloropropane	0.445	6.06
Trichlorofluoromethane	0.395	4.05	Dibromochloromethane	0.255	7.56
diethyl ether	0.223	5.02	2-Hexanone	0.334	8.14
1,1-Dichloroethene	0.219	5.34	1,2-Dibromoethane	0.264	6.26
Acetone	0.163	12.84	Chlorobenzene	0.662	6.03
Iodomethane	0.213	9.90	1,1,1,2-Tetrachloroethane	0.241	4.22
Carbon Disulfide	0.619	7.74	Ethylbenzene	1.170	6.72
allyl chloride	0.405	8.58	Xylene (m+p)	0.898	6.91
Methylene Chloride	0.263	9.22	Styrene	0.715	5.29
MTBE	0.776	5.87	Xylene (o)	0.919	5.90
cis-1,2-Dichloroethene	0.284	9.87	Bromoform	0.180	7.07
acrylonitrile	0.182	7.77	Isopropylbenzene	1.051	5.68
1,1-Dichloroethane	0.489	6.35	BFB	0.353	1.84
trans-1,2-Dichloroethene	0.247	7.77	Bromobenzene	0.620	6.75
2-Butanone	0.248	11.86	1,2,3-Trichloropropane	0.370	11.85
2,2-Dichloropropane	0.364	10.37	1,1,2,2-Tetrachloroethane	0.396	7.32
Bromochloromethane	0.158	8.78	n-Propylbenzene	1.252	5.20
propionitrile	0.083	11.53	trans-1,4-dichloro-2-butene	0.032	10.34
methacrylonitrile	0.258	7.75	2-Chlorotoluene	0.244	5.87
THF	0.158	12.97	4-Chlorotoluene	0.252	5.97
Chloroform	0.495	9.14	1,3,5-Trimethylbenzene	0.835	6.35
methyl acrylate	0.406	9.82	tert-Butylbenzene	0.730	8.95
1,1,1-Trichloroethane	0.412	5.23	sec-Butylbenzene	0.199	6.30
Carbon Tetrachloride	0.286	12.96	1,2,4-Trimethylbenzene	0.837	6.94
1,1-Dichloropropene	0.366	6.93	nitrobenzene	0.048	17.88
1-chlorobutane	0.539	7.76	1,3-Dichlorobenzene	0.474	6.10
Benzene	1.085	7.79	1,4-Dichlorobenzene	0.480	5.62
1,2-Dichloroethane	0.391	6.81	Isopropyltoluene	0.826	8.25
Trichloroethene	0.255	6.73	1,2-dichlorobenzene-d4	0.327	3.69
1,2-Dichloropropane	0.281	6.22	1,2,-Dichlorobenzene	0.472	7.41
methyl methacrylate	0.267	6.48	n-Butylbenzene	0.793	8.89
Dibromomethane	0.155	4.08	hexachloroethane	0.172	5.14
Bromodichloromethane	0.353	5.24	1,2-Dibromo-3-chloropropa	0.101	9.75
2-nitropropane	0.124	8.49	1,2,4-Trichlorobenzene	0.271	5.89
cis-1,3-Dichloropropene	0.423	7.02	Naphthalene	0.914	10.65
4-methyl-2-pentanone	0.438	8.28	Hexachlorobutadiene	0.116	7.38
Toluene	0.640	4.48	1,2,3-Trichlorobenzene	0.270	6.60

Table 3: Compound Linearity and Response Factor Table

Compound	MDL	%RSD Precision	% Rec'ry	Compound	MDL	%RSD Precision	% Rec'ry
Dichlorodifluoromethane	0.060	3.581	102.71	ethyl methacrylate	0.140	4.877	107.52
Chloromethane	0.153	4.482	97.42	trans-1,3-Dichloropropen	0.112	4.664	108.68
Vinyl Chloride	0.083	4.310	101.17	1,1,2-Trichloroethane	0.218	4.596	105.26
Bromomethane	0.213	5.198	103.01	Tetrachloroethene	0.152	5.044	95.38
Chloroethane	0.135	4.759	101.11	1,3-Dichloropropane	0.155	4.543	105.90
Trichlorofluoromethane	0.087	3.635	100.41	Dibromochloromethane	0.167	4.314	109.67
diethyl ether	0.134	3.763	107.34	2-Hexanone	0.247	5.680	101.37
1,1-Dichloroethene	0.093	4.486	100.64	1,2-Dibromoethane	0.075	4.520	106.09
Acetone	0.358	4.552	95.61	Chlorobenzene	0.156	5.721	105.64
Iodomethane	0.134	5.558	116.46	1,1,1,2-Tetrachloroethane	0.150	5.091	108.42
Carbon Disulfide	0.118	4.568	104.63	Ethylbenzene	0.088	5.627	104.78
allyl chloride	0.104	5.063	105.44	Xylene (m+p)	0.239	5.573	105.73
Methylene Chloride	0.140	4.495	102.76	Styrene	0.101	5.069	109.97
MTBE	0.147	4.237	106.76	Xylene (o)	0.099	5.138	105.54
cis-1,2-Dichloroethene	0.119	5.141	103.24	Bromoform	0.112	4.365	112.04
acrylonitrile	0.142	4.243	102.37	Isopropylbenzene	0.097	5.711	106.39
1,1-Dichloroethane	0.139	5.939	103.51	BFB	NA	4.889	139.23
trans-1,2-Dichloroethene	0.131	5.347	103.01	Bromobenzene	0.088	4.729	105.76
2-Butanone	0.320	5.588	97.75	1,2,3-Trichloropropane	0.394	5.275	96.02
2,2-Dichloropropane	0.159	3.871	117.01	1,1,2,2-Tetrachloroethane	0.126	4.126	105.49
Bromochloromethane	0.101	4.432	111.59	n-Propylbenzene	0.110	5.591	107.48
propionitrile	0.130	4.303	98.69	trans-1,4-dichloro-2-buten	0.357	5.145	102.25
methacrylonitrile	0.153	4.427	99.89	2-Chlorotoluene	0.172	5.656	107.19
THF	0.202	6.825	96.92	4-Chlorotoluene	0.118	5.904	109.70
Chloroform	0.133	5.437	103.93	1,3,5-Trimethylbenzene	0.118	5.755	109.39
methyl acrylate	0.139	4.789	100.88	tert-Butylbenzene	0.090	5.637	105.04
1,1,1-Trichloroethane	0.140	5.384	102.56	sec-Butylbenzene	0.098	6.086	109.61
Carbon Tetrachloride	0.140	12.189	106.14	1,2,4-Trimethylbenzene	0.099	5.854	111.78
1,1-Dichloropropene	0.138	7.508	97.83	nitrobenzene	0.316	7.567	91.87
1-chlorobutane	0.192	7.597	98.69	1,3-Dichlorobenzene	0.102	6.015	109.38
Benzene	0.160	7.687	98.21	1,4-Dichlorobenzene	0.083	5.466	109.86
1,2-Dichloroethane	0.181	8.204	100.66	Isopropyltoluene	0.101	5.963	113.23
Trichloroethene	0.179	6.490	101.61	1,2-dichlorobenzene-d4	NA	6.315	143.31
1,2-Dichloropropane	0.132	4.592	103.84	1,2,-Dichlorobenzene	0.104	5.728	107.56
methyl methacrylate	0.178	3.369	104.56	n-Butylbenzene	0.097	5.726	109.64
Dibromomethane	0.126	4.326	109.97	hexachloroethane	0.144	6.440	107.61
Bromodichloromethane	0.172	4.790	108.37	1,2-Dibromo-3-chloropro	0.147	5.503	102.18
2-nitropropane	0.206	7.963	97.54	1,2,4-Trichlorobenzene	0.108	5.827	110.62
cis-1,3-Dichloropropene	0.136	4.701	108.35	Naphthalene	0.102	5.309	115.34
4-methyl-2-pentanone	0.303	5.145	101.69	Hexachlorobutadiene	0.180	6.372	109.49
Toluene	0.120	5.545	103.77	1,2,3-Trichlorobenzene	0.104	5.151	111.53

Table 4: MDL and Precision and Percent Recovery Table

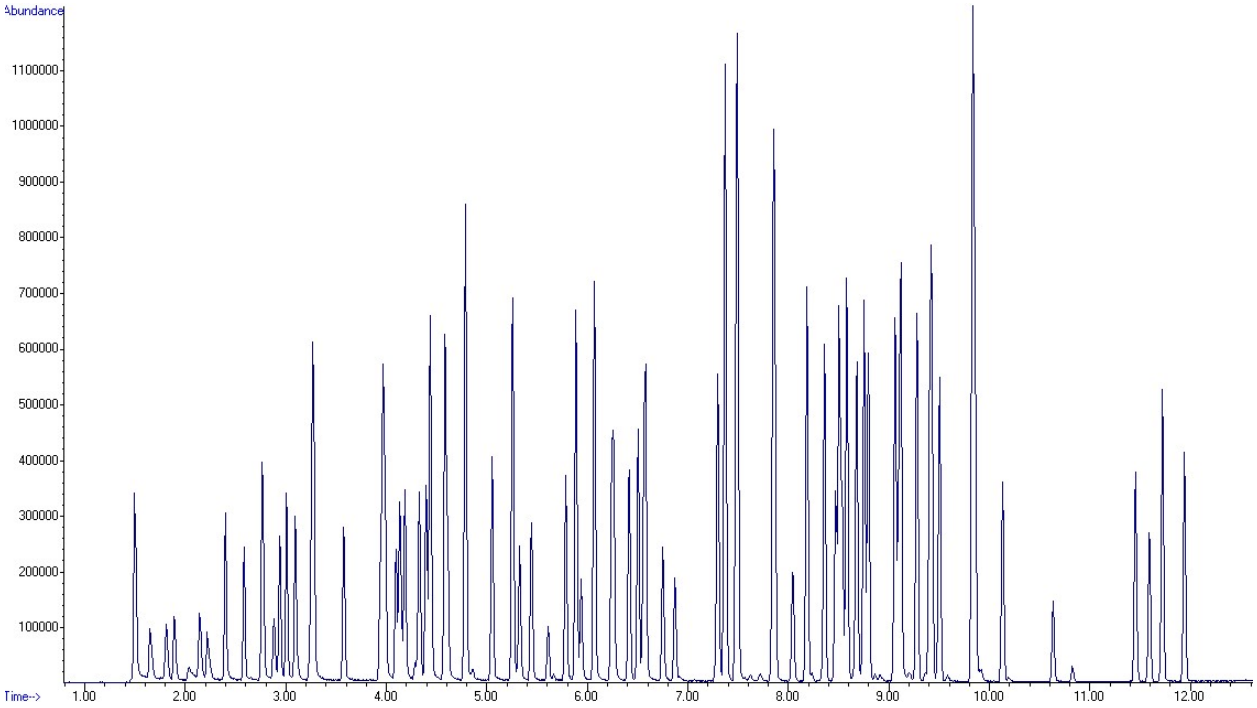

Figure 2: 20µg/L Standard Chromatogram

Conclusions:

The results of the Method 524.2 study using the EV2 purge and trap concentrator were very good. The system met all of the method requirements. The average precision at 20µg/L was 5.4% while the average percent recovery was 106%. The EV2 with its new software, smaller footprint and better ventilation for faster cool down time is an excellent addition to any drinking water lab.

References:

1. USEPA Method 524.2, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1, 1995.

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