



USEPA 524.2 Method Validation Using the Evolution Purge and Trap Concentrator and the Centurion WS Autosampler

Application Note

Environmental

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Abstract

In order to measure low level purgeable volatile organic compounds in water, the United States Environmental Protection Agency (USEPA) developed the 524.2 method. This method requires a 5mL or 25mL purge volume and can be further complicated by the mandatory lower detection limits and an extended four minute desorb time. These constraints can be problematic for laboratories due to the large amount of water the system is exposed to. This application will utilize the requisite method parameters and examine the linearity, detection, precision and accuracy of the EST Analytical Evolution and Centurion purge and trap sampling system.

Introduction:

USEPA Method 524.2 calls for purge and trap sampling coupled with a Gas Chromatograph (GC) and Mass Spectrometer (MS) for separation and analysis. It has an extensive list of compounds and requires lower detection limits due to its use in drinking water testing. A 20% relative standard deviation for compound response factors is required across the calibration curve while the calibration check standard analytes have to be within 30% of the expected concentration.

Currently, this method calls for a 5mL or 25mL purge volume and a four minute desorb time. These method requirements can pose a challenge for the analyst due to the amount of moisture that is created. The negative effects of the increased water vapor include instability of the chromatography, band eluting and poor peak shape to name a few. A side effect of this instability is sample re-runs and lost laboratory productivity. In addition, a common practice for mitigating moisture is increasing the GC inlet split rate. This poses yet another difficulty as the increased split rate can result in reduced sensitivity. EST Analytical's eight port valve in the Evolution purge and trap concentrator aids in limiting the water exposure because the water management of the system is not part of the desorb pathway. This feature also enables laboratories to use a smaller split ratio at the GC inlet thus increasing sensitivity.

Experimental:

The sampling system used for this study was the EST Analytical Evolution purge and trap concentrator and the Centurion WS autosampler. The concentrator was affixed with a Vocab 3000 trap and connected to an Agilent 7890A GC and 5975C inert XL MS. The GC was configured with a Restek Rxi-624 Sil MS 30m x 0.25mm x 1.4µm column. Sampling parameters are listed in Table 1 while Table 2 enumerates the GC/MS parameters.

Purge and Trap Concentrator	EST Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	130°C
Transfer Line Temp.	130°C
Trap Temp.	35°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 Control	On
Desorb Pressure	5psi
Desorb Time	4 min
Desorb Preheat Delay	15 sec
Desorb Temp.	250°C
Moisture Reduction Trap (MoRT) Bake Temp.	210°C
Bake Temp	260°C
Sparge Vessel Bake Temp.	110°C
Bake Time	6 min
Bake Flow	70mL/min
Purge and Trap Auto-Sampler	EST Centurion WS
Sample Type	Water
Water Volume	25ml
Internal Standard Vol.	5µl

Table 1: Purge and Trap Parameters

GC/MS	Agilent 7890A/5975C inert XL
Inlet	Split/Splitless
Inlet Temp.	220°C
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45°C hold for 1 min, ramp 15°C/min to 220°C, hold for 1.33 min, 14 min run time
Column Flow Rate	1mL/min
Gas	Helium
Total Flow	44mL/min
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Scan Range	m/z 35-300
Scans	5.2 scans/sec
Solvent Delay	0.7 min

Table 2: GC/MS Experimental Parameters

A calibration curve was established with a linear range of 0.25 to 40µg/L using the USEPA Method 524.2 standards from Restek. After the curve was determined, method detection limits were ascertained by running a series of seven replicate 0.25 µg/L standards and calculated using the procedure outlined in 40 CFR Part 136 Appendix B. Finally, seven 20 µg/L standards were examined in order to verify the precision and accuracy of the analysis. The results of this study are displayed in Tables 3 and 4 while Figure 1 presents a 20 µg/L standard GC/MS chromatogram

Compound	Curve %RSD	Ave. Curve RF	Compound	Curve %RSD	Ave. Curve RF
Dichlorodifluoromethane	11.26	0.257	ethyl methacrylate	4.21	0.569
Chloromethane	9.13	0.364	trans-1,3-Dichloropropene	4.73	0.533
Vinyl Chloride	6.13	0.371	1,1,2-Trichloroethane	5.47	0.413
Bromomethane	7.03	0.202	Tetrachloroethene	14.69	0.493
Chloroethane	7.28	0.230	1,3-Dichloropropane	6.04	0.715
Trichlorofluoromethane	5.32	0.486	Dibromochloromethane	7.97	0.337
diethyl ether	5.88	0.323	2-Hexanone	12.04	0.374
1,1-Dichloroethene	6.50	0.318	1,2-Dibromoethane	5.89	0.414
Acetone	*0.995	0.334	Chlorobenzene	3.44	1.168
Iodomethane	16.56	0.149	1,1,1,2-Tetrachloroethane	7.21	0.368
Carbon Disulfide	15.08	0.833	Ethylbenzene	5.12	1.994
allyl chloride	9.89	0.492	Xylene (m+p)	5.15	1.533
Methylene Chloride	10.20	0.409	Styrene	5.02	1.268
MTBE	3.19	1.197	Xylene (o)	3.88	1.269
cis-1,2-Dichloroethene	4.15	0.418	Bromoform	13.28	0.208
acrylonitrile	8.46	0.184	Isopropylbenzene	5.16	1.893
1,1-Dichloroethane	4.05	0.677	BFB SUR	2.15	0.540
trans-1,2-Dichloroethene	6.13	0.374	Bromobenzene	5.96	0.883
2-Butanone	16.91	0.273	1,2,3-Trichloropropane	5.01	0.645
2,2-Dichloropropane	14.81	0.349	1,1,2,2-Tetrachloroethane	8.76	0.586
Bromochloromethane	5.12	0.249	n-Propylbenzene	4.69	2.328
propionitrile	9.66	0.077	trans-1,4-dichloro-2-butene	7.17	0.048
methacrylonitrile	8.91	0.284	2-Chlorotoluene	5.20	0.445
THF	9.29	0.145	4-Chlorotoluene	4.43	0.464
Chloroform	4.86	0.695	1,3,5-Trimethylbenzene	4.34	1.574
methyl acrylate	8.81	0.450	tert-Butylbenzene	8.22	1.368
1,1,1-Trichloroethane	7.49	0.542	sec-Butylbenzene	5.75	0.397
Carbon Tetrachloride	5.89	0.415	1,2,4-Trimethylbenzene	4.73	1.652
1,1-Dichloropropene	2.87	0.508	nitrobenzene	7.54	0.019
1-chlorobutane	5.56	0.753	1,3-Dichlorobenzene	3.70	0.895
Benzene	4.23	1.638	1,4-Dichlorobenzene	6.10	0.912
1,2-Dichloroethane	4.75	0.525	Isopropyltoluene	6.38	1.669
Trichloroethene	6.59	0.429	1,2-dichlorobenzene-d4 SUR	2.93	0.530
1,2-Dichloropropane	2.97	0.418	1,2-Dichlorobenzene	3.89	0.911
methyl methacrylate	4.21	0.405	n-Butylbenzene	7.06	1.644
Dibromomethane	4.81	0.247	hexachloroethane	9.85	0.245
Bromodichloromethane	5.23	0.480	1,2-Dibromo-3-chloropropane	7.88	0.098
2-nitropropane	10.45	0.092	1,2,4-Trichlorobenzene	7.29	0.531
cis-1,3-Dichloropropene	3.51	0.572	Naphthalene	4.60	1.701
4-methyl-2-pentanone	9.13	0.481	Hexachlorobutadiene	12.76	0.182
Toluene	7.87	1.077	1,2,3-Trichlorobenzene	5.74	0.482

Table 3: Compound Linearity and Response Factor Table

Compound	MDL	%RSD 50 µg/L	%Recovery 50 µg/L	Compound	MDL	%RSD 50 µg/L	%Recovery 50 µg/L
Dichlorodifluoromethane	0.12	7.86	116.05	ethyl methacrylate	0.05	1.64	96.81
Chloromethane	0.08	6.97	94.89	trans-1,3-Dichloropropene	0.04	1.93	107.84
Vinyl Chloride	0.06	7.91	99.84	1,1,2-Trichloroethane	0.06	1.99	98.64
Bromomethane	0.17	7.02	102.66	Tetrachloroethene	0.08	7.23	110.27
Chloroethane	0.13	6.32	99.85	1,3-Dichloropropane	0.02	2.47	97.06
Trichlorofluoromethane	0.02	7.58	108.74	Dibromochloromethane	0.09	3.42	112.94
diethyl ether	0.05	2.84	97.97	2-Hexanone	0.14	2.69	95.36
1,1-Dichloroethene	0.10	7.56	99.39	1,2-Dibromoethane	0.06	2.21	99.82
Acetone	0.46	4.89	92.85	Chlorobenzene	0.03	3.98	100.84
Iodomethane	0.11	4.95	127.35	1,1,1,2-Tetrachloroethane	0.05	3.83	104.70
Carbon Disulfide	0.05	7.98	97.66	Ethylbenzene	0.05	4.73	101.71
allyl chloride	0.10	6.46	98.06	Xylene (m+p)	0.07	5.24	101.79
Methylene Chloride	0.06	5.22	94.92	Styrene	0.05	4.16	101.36
MTBE	0.04	2.28	99.45	Xylene (o)	0.02	4.04	100.75
cis-1,2-Dichloroethene	0.08	4.87	100.14	Bromoform	0.08	1.95	116.62
acrylonitrile	0.14	2.04	91.91	Isopropylbenzene	0.04	6.54	104.34
1,1-Dichloroethane	0.07	5.21	97.34	BFB SUR	NA	2.66	108.87
trans-1,2-Dichloroethene	0.08	6.21	99.31	Bromobenzene	0.03	5.79	99.35
2-Butanone	0.10	3.14	91.91	1,2,3-Trichloropropane	0.04	3.64	102.22
2,2-Dichloropropane	0.06	5.89	127.89	1,1,2,2-Tetrachloroethane	0.06	3.13	97.50
Bromochloromethane	0.07	4.01	100.94	n-Propylbenzene	0.04	8.04	104.79
propionitrile	0.32	3.58	92.81	trans-1,4-dichloro-2-butene	0.51	3.61	92.54
methacrylonitrile	0.14	12.96	97.22	2-Chlorotoluene	0.04	6.08	106.91
THF	0.48	3.58	89.16	4-Chlorotoluene	0.05	5.93	108.69
Chloroform	0.05	3.97	101.95	1,3,5-Trimethylbenzene	0.03	7.42	103.94
methyl acrylate	0.05	1.93	91.16	tert-Butylbenzene	0.02	7.46	102.90
1,1,1-Trichloroethane	0.06	6.93	103.58	sec-Butylbenzene	0.06	8.24	104.71
Carbon Tetrachloride	0.07	8.27	107.12	1,2,4-Trimethylbenzene	0.03	6.56	104.94
1,1-Dichloropropene	0.05	7.08	101.81	nitrobenzene	0.53	4.19	120.54
1-chlorobutane	0.05	6.88	97.66	1,3-Dichlorobenzene	0.06	5.47	105.16
Benzene	0.04	5.69	98.94	1,4-Dichlorobenzene	0.06	5.41	107.59
1,2-Dichloroethane	0.06	4.45	101.36	Isopropyltoluene	0.04	7.59	105.76
Trichloroethene	0.06	6.73	99.44	1,2-dichlorobenzene-d4 SUR	NA	2.91	111.68
1,2-Dichloropropane	0.05	4.12	97.46	1,2-Dichlorobenzene	0.04	5.15	102.89
methyl methacrylate	0.09	1.57	96.32	n-Butylbenzene	0.04	7.84	103.19
Dibromomethane	0.05	2.50	104.72	hexachloroethane	0.06	7.55	109.44
Bromodichloromethane	0.10	3.67	108.11	1,2-Dibromo-3-chloropropane	0.18	3.39	102.19
2-nitropropane	0.34	2.45	98.16	1,2,4-Trichlorobenzene	0.06	4.04	108.64
cis-1,3-Dichloropropene	0.04	3.64	109.37	Naphthalene	0.05	2.96	107.11
4-methyl-2-pentanone	0.12	2.34	88.56	Hexachlorobutadiene	0.14	6.83	106.76
Toluene	0.05	5.50	95.72	1,2,3-Trichlorobenzene	0.08	3.39	111.93

Table 4: MDL and Precision and Percent Recovery Table

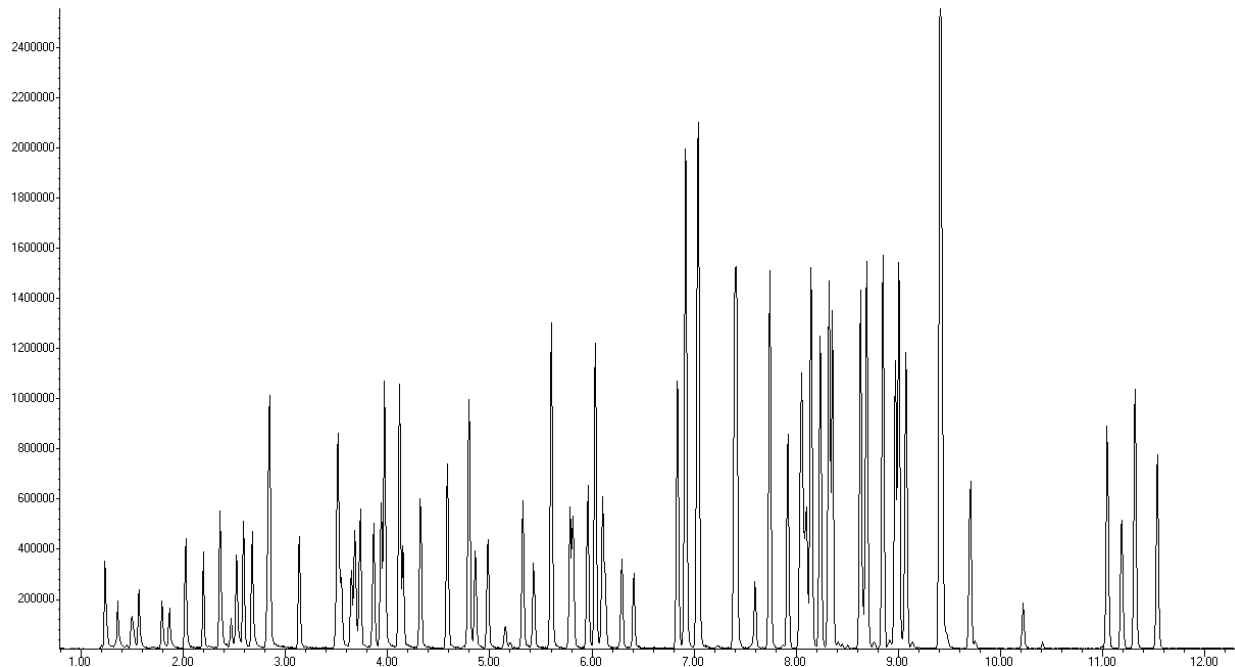


Figure 1: 20µg/L Standard Chromatogram

Conclusions:

This study demonstrated the effectiveness of the Evolution/Centurion purge and trap sampling system. The results passed all of the USEPA Method 524.2 criteria for both linearity and detection limits. Since the Evolution bypasses the water management trap during the four minute desorb process, the amount of water effecting the experiments was limited. Furthermore, the forty to one split ratio at the GC inlet provided excellent detection limits as the system was more sensitive to the low level standard requirements of the method. The lower split rate has an added benefit of reducing laboratory helium consumption when setting it against other system's higher split ratios. Finally, the precision and percent recovery results showed the reliability of the system in producing accurate experimental findings.

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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