



Purge Flow Effects on USEPA Method 524.3 Compounds

Application Note

Environmental

Authors

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Abstract

During volatile analysis, samples are purged with an inert gas in order for the Volatile Organic Compounds (VOCs) to be swept out of the sample matrix and onto an analytical trap. For years, the established purge flow rate and time has been 40ml/min for 11 minutes. USEPA Method 524.3 changed this. This new method allows for different purge flows and times and outlines recommended and allowable ranges. This application will examine how different purge flows and times affect compound performance for Method 524.3.

Introduction:

When the United States Environmental Protection Agency (USEPA) released Method 524.3 there were allowances for changes to the purge time and flow requirements during the purge and trap sampling. The method outlines recommended and allowable purge flow rates, volumes and total purge volumes. If the method change produces shorter cycle times but poorer method performance, the change may not be used. There are five key parameters that have restrictions to how they can be altered. Method modifications that fall within the allowable ranges can be used with an Initial Demonstration of Capability (IDC), however if the adjustment falls outside the admissible range, but within the allowable range, the lab must show comparable performance.

This application sought to examine how the experimental results were affected by the use of parameters within the recommended range as compared to the allowable range. The consequences of purge flow and volume increases and/or decreases were appraised. The EST Analytical Evolution purge and trap concentrator and the Centurion WS autosampler was the sampling system used for this study.

Experimental:

The Gas Chromatograph (GC) was configured with a 30m x 0.25mm x 1.4µm Rxi 624 Sil MS Column while the Mass Spectrometer was set to run in scan mode with a range of m/z 35 to 300. As stated above, the purge and trap system used for the study was the EST Analytical Evolution purge and trap concentrator and Centurion WS Autosampler. A Vocarb 3000 analytical trap was installed in the Evolution. The purge times, flows and volumes that were examined for this study are outlined in Table 1 while the experimental parameters for the GC/MS and purge and trap sampling system are displayed in Tables 2 and 3.

Parameter	Experiment 1 (Baseline)	Experiment 2	Experiment 3	Experiment 4
Purge Flow Rate	40mL/min	65mL/min	100ml/min	65mL/min
Purge Time	11min	6.5min	4min	4min
Purge Volume	440mL	422.5mL	400mL	260mL
Purge Volume + Dry Purge Volume	480mL	462.5mL	440mL	300mL

Table 1: Purge Flows and Times Evaluated

Purge and Trap Concentrator	EST Analytical 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	Varied
Purge Flow	Varied
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	1.0 min
Desorb Pressure Control	On
Desorb Pressure	5psi
Desorb Time	1.0 min
Desorb Preheat Delay	10 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
Purge and Trap Auto-Sampler	EST Centurion WS
Sample Type	Water
Water Volume	5ml
Sample Prime Time	7 sec
Loop Equilibration Time	5 sec
Sample Transfer Time	10 sec.
Syringe Rinse	On/10 ml
Number of Syringe Rinses	2
Sample Loop Rinse	On/10 sec
Sample Sweep Time	5 sec
Number of Sparge Rinses	On/2
Rinse Volume	5 ml
Rinse Transfer Time	10 sec
Rinse Drain Time	15 sec
Water Heater Temp.	85 sec
Internal Standard Vol.	5 µl

Table 2: Evolution and Centurion WS Experimental Parameters

GC/MS	Parameters
Inlet	Split/Splitless
Inlet Temp.	220°C
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	30m x 0.25mm I.D. 1.4µm film thickness (624)
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 3: GC/MS Parameters

Certified reference standards were procured for the preparation of stock and calibration standards. Maleic Acid and Ascorbic Acid were also obtained for water preservation. Preserved water was employed for the preparation of calibration standards with a range of 0.5 to 40µg/L while a 40ml/min purge flow and 11 min purge time was used to establish a baseline calibration curve. Seven replicate laboratory fortified blanks (LFBs) at the 0.5µg/L minimum reporting limit (MRL) were evaluated to establish the upper and lower Prediction Interval of Results (PIR) while seven replicate mid-level calibration standards were analyzed to demonstrate the precision and accuracy of the experimental parameters. These results were compiled and tabulated using the GC/MS software.

The experimental procedure outlined above was then repeated for the purge flow rates, times and volumes defined in Table 1. The findings of each experiment were then compared to assess how altering the parameters affects the analyte response, upper and lower prediction intervals, precision and accuracy. Tables 4 through 11 display a summary of the experimental results while an overlay of the 20ug/L standard for each experiment is shown in Figure 2. Finally, each experiment was evaluated for moisture control, see Figure 1.

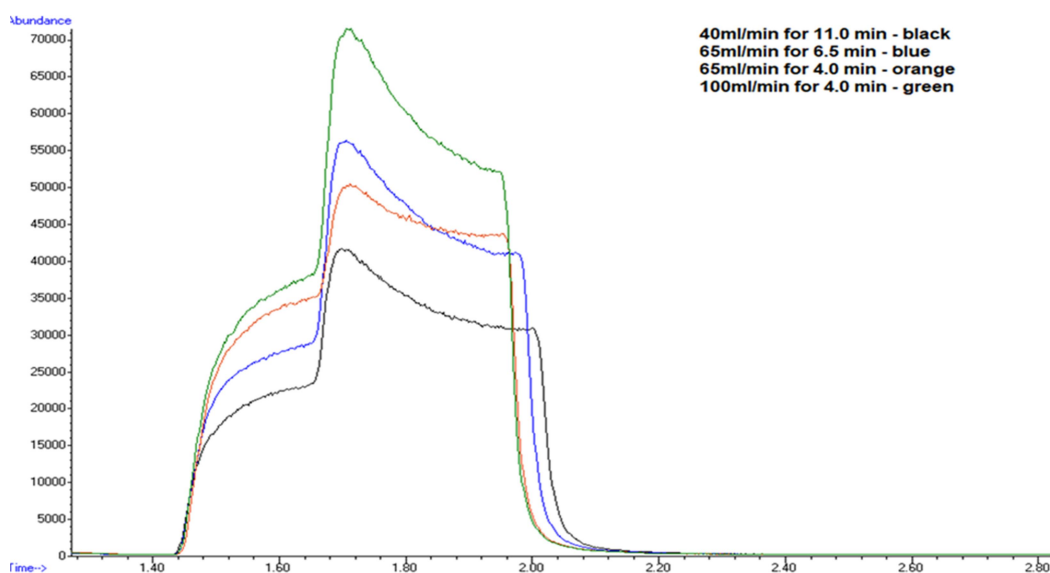


Figure 2: Water Abundance Overlay

Compound	40ml/min for 11min		65ml/min for 6.5min		Compound	100ml/min for 4min		65ml/min for 6.5min	
	Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF		Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF
dichlorodifluoromethane	0.999	0.393	0.998	0.356	tetrachloroethene	0.999	0.683	1.000	0.545
chlorodifluoromethane	0.999	0.473	0.999	0.507	trans-1,3-dichloropropene	1.000	0.777	0.999	0.609
chloromethane	0.999	0.431	0.998	0.436	ethyl methacrylate	1.000	0.722	1.000	0.513
vinyl chloride	0.999	0.456	1.000	0.483	1,1,2-trichloroethane	0.998	0.431	1.000	0.319
1,3-butadiene	0.999	0.368	0.999	0.395	dibromochloromethane	1.000	0.487	0.999	0.380
bromomethane	0.997	0.278	1.000	0.332	1,3-dichloropropane	0.998	0.913	1.000	0.687
trichlorofluoromethane	0.999	0.632	0.999	0.688	1,2-dibromomethane	0.999	0.500	1.000	0.357
diethyl ether	1.000	0.338	0.999	0.361	chlorobenzene	0.999	1.645	1.000	1.347
1,1-dichloroethene	1.000	0.361	1.000	0.400	ethylbenzene	0.999	2.822	1.000	2.268
carbon disulfide	0.999	1.042	0.998	1.140	1,1,1,2-tetrachloroethane	1.000	0.528	0.999	0.435
methyl iodide	0.998	0.620	0.996	0.681	xylene (m+p)	0.999	1.079	1.000	0.869
allyl chloride	0.999	0.226	0.998	0.252	xylene (o)	0.999	1.027	1.000	0.850
methylene chloride	1.000	0.433	0.999	0.472	styrene	1.000	1.658	0.999	1.359
trans-1,2-dichloroethene	1.000	0.423	0.999	0.470	bromoform	0.999	0.284	0.990	0.197
methyl acetate	1.000	0.360	1.000	0.347	isopropylbenzene	1.000	2.693	1.000	2.138
methyl-t-butyl ether (MtBE)	1.000	1.327	1.000	1.416	bromobenzene	0.998	1.354	1.000	1.092
t-butyl alcohol (TBA)	1.000	0.264	0.999	0.289	n-propylbenzene	0.999	6.811	1.000	5.387
diisopropyl ether (DIPE)	1.000	1.269	0.999	1.406	1,1,2,2-tetrachloroethane	0.999	1.308	1.000	0.870
1,1-dichloroethane	1.000	0.767	0.999	0.855	2-chlorotoluene	0.999	1.332	1.000	1.061
t-butyl ethyl ether (ETBE)	1.000	1.319	0.999	1.445	1,3,5-trimethylbenzene	0.999	4.629	1.000	3.663
cis-1,2-dichloroethene	1.000	0.477	0.999	0.527	1,2,3-trichloropropane	0.999	0.420	1.000	0.269
bromochloromethane	0.999	0.219	0.999	0.241	4-chlorotoluene	1.000	1.377	1.000	1.090
chloroform	1.000	0.769	0.999	0.848	t-butylbenzene	1.000	1.147	1.000	0.892
carbon tetrachloride	0.999	0.400	0.999	0.496	pentachloroethane	1.000	0.683	0.999	0.549
tetrahydrofuran	0.998	0.086	0.999	0.080	1,2,4-trimethylbenzene	1.000	4.778	1.000	3.793
1,1,1-trichloroethane	1.000	0.640	0.999	0.721	sec-butylbenzene	0.999	5.833	1.000	4.538
1,1-dichloropropene	0.999	0.334	1.000	0.385	4-isopropyltoluene	1.000	4.955	1.000	3.898
1-chlorobutane	0.999	0.835	0.999	0.942	1,3-dichlorobenzene	0.999	2.543	1.000	2.037
benzene	1.000	1.758	0.999	1.939	1,4-dichlorobenzene	0.998	2.529	0.999	2.040
t-amyl methyl ether (TAME)	1.000	1.291	0.999	1.383	n-butylbenzene	1.000	1.185	1.000	0.932
1,2-dichloroethane	1.000	0.638	0.999	0.704	hexachloroethane	0.999	0.526	0.999	0.419
trichloroethene	1.000	0.489	0.999	0.531	1,2-dichlorobenzene	0.998	2.343	0.999	1.847
t-amyl ethyl ether (TAEE)	1.000	1.019	0.999	1.121	1,2-dibromo-3-chloropropane	1.000	0.227	0.998	0.138
dibromomethane	1.000	0.282	0.999	0.304	hexachlorobutadiene	0.998	0.606	1.000	0.471
1,2-dichloropropane	0.999	0.427	0.999	0.474	1,2,4-trichlorobenzene	0.999	1.490	0.998	1.164
bromodichloromethane	1.000	0.537	0.999	0.590	napthalene	0.999	3.664	1.000	2.385
cis-1,3-dichloropropene	1.000	0.658	0.997	0.723	1,2,3-trichlorobenzene	0.998	1.306	1.000	0.976
toluene	1.000	1.325	0.999	1.467	Average	1.000	1.110	0.999	1.220

Table 4: Curve Results Summary 1

Compound	100ml/min for 4min		65ml/min for 4min		Compound	100ml/min for 4min		65ml/min for 4min	
	Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF		Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF
dichlorodifluoromethane	1.000	0.527	0.996	0.307	tetrachloroethene	0.999	0.683	1.000	0.545
chlorodifluoromethane	1.000	0.607	0.999	0.442	trans-1,3-dichloropropene	1.000	0.777	0.999	0.609
chloromethane	1.000	0.519	1.000	0.382	ethyl methacrylate	1.000	0.722	1.000	0.513
vinyl chloride	1.000	0.580	1.000	0.421	1,1,2-trichloroethane	0.998	0.431	1.000	0.319
1,3-butadiene	1.000	0.490	0.990	0.340	dibromochloromethane	1.000	0.487	0.999	0.380
bromomethane	0.999	0.351	0.995	0.317	1,3-dichloropropane	0.998	0.913	1.000	0.687
trichlorofluoromethane	1.000	0.787	0.999	0.597	1,2-dibromomethane	0.999	0.500	1.000	0.357
diethyl ether	0.999	0.380	1.000	0.298	chlorobenzene	0.999	1.645	1.000	1.347
1,1-dichloroethene	0.999	0.433	1.000	0.341	ethylbenzene	0.999	2.822	1.000	2.268
carbon disulfide	1.000	1.226	1.000	0.998	1,1,1,2-tetrachloroethane	1.000	0.528	0.999	0.435
methyl iodide	1.000	0.814	0.999	0.665	xylene (m+p)	0.999	1.079	1.000	0.869
allyl chloride	1.000	0.269	1.000	0.223	xylene (o)	0.999	1.027	1.000	0.850
methylene chloride	1.000	0.499	1.000	0.426	styrene	1.000	1.658	0.999	1.359
trans-1,2-dichloroethene	0.999	0.499	1.000	0.413	bromoform	0.999	0.284	0.990	0.197
methyl acetate	0.999	0.329	1.000	0.203	isopropylbenzene	1.000	2.693	1.000	2.138
methyl-t-butyl ether (MtBE)	1.000	1.415	1.000	1.090	bromobenzene	0.998	1.354	1.000	1.092
t-butyl alcohol (TBA)	1.000	0.302	1.000	0.251	n-propylbenzene	0.999	6.811	1.000	5.387
diisopropyl ether (DIPE)	1.000	1.517	1.000	1.286	1,1,2,2-tetrachloroethane	0.999	1.308	1.000	0.870
1,1-dichloroethane	1.000	0.916	1.000	0.783	2-chlorotoluene	0.999	1.332	1.000	1.061
t-butyl ethyl ether (ETBE)	1.000	1.510	1.000	1.254	1,3,5-trimethylbenzene	0.999	4.629	1.000	3.663
cis-1,2-dichloroethene	1.000	0.560	1.000	0.467	1,2,3-trichloropropane	0.999	0.420	1.000	0.269
bromochloromethane	1.000	0.253	1.000	0.207	4-chlorotoluene	1.000	1.377	1.000	1.090
chloroform	0.999	0.906	1.000	0.765	t-butylbenzene	1.000	1.147	1.000	0.892
carbon tetrachloride	1.000	0.540	0.999	0.432	pentachloroethane	1.000	0.683	0.999	0.549
tetrahydrofuran	0.997	0.075	0.999	0.044	1,2,4-trimethylbenzene	1.000	4.778	1.000	3.793
1,1,1-trichloroethane	0.999	0.766	1.000	0.619	sec-butylbenzene	0.999	5.833	1.000	4.538
1,1-dichloropropene	0.999	0.409	0.997	0.336	4-isopropyltoluene	1.000	4.955	1.000	3.898
1-chlorobutane	0.999	1.013	1.000	0.825	1,3-dichlorobenzene	0.999	2.543	1.000	2.037
benzene	1.000	2.077	1.000	1.741	1,4-dichlorobenzene	0.998	2.529	0.999	2.040
t-amyl methyl ether (TAME)	1.000	1.419	1.000	1.134	n-butylbenzene	1.000	1.185	1.000	0.932
1,2-dichloroethane	0.998	0.724	1.000	0.572	hexachloroethane	0.999	0.526	0.999	0.419
trichloroethene	1.000	0.565	1.000	0.464	1,2-dichlorobenzene	0.998	2.343	0.999	1.847
t-amyl ethyl ether (TAEE)	0.999	1.193	1.000	1.002	1,2-dibromo-3-chloropropane	1.000	0.227	0.998	0.138
dibromomethane	1.000	0.304	1.000	0.232	hexachlorobutadiene	0.998	0.606	1.000	0.471
1,2-dichloropropane	1.000	0.510	1.000	0.436	1,2,4-trichlorobenzene	0.999	1.490	0.998	1.164
bromodichloromethane	0.999	0.615	1.000	0.527	naphthalene	0.999	3.664	1.000	2.385
cis-1,3-dichloropropene	0.999	0.756	1.000	0.636	1,2,3-trichlorobenzene	0.998	1.306	1.000	0.976
toluene	0.999	1.522	1.000	1.245	Average	0.999	1.819	0.999	1.416

Table 5: Curve Results Summary 2

Compound	40ml/min for 11min		65ml/min for 6.5min		Compound	40ml/min for 11min		65ml/min for 6.5min	
	Upper PIR	Lower PIR	Upper PIR	Lower PIR		Upper PIR	Lower PIR	Upper PIR	Lower PIR
dichlorodifluoromethane	130.158	103.556	116.388	79.040	tetrachloroethene	122.390	72.467	106.318	65.682
chlorodifluoromethane	123.666	77.477	100.406	78.451	trans-1,3-dichloropropene	109.078	84.065	121.396	100.890
chloromethane	112.252	77.463	115.084	68.344	ethyl methacrylate	116.018	101.696	121.261	98.167
vinyl chloride	104.355	71.073	146.875	101.697	1,1,2-trichloroethane	107.585	87.843	113.678	83.465
1,3-butadiene	124.430	76.713	113.836	72.450	dibromochloromethane	118.408	104.449	137.756	101.101
bromomethane	96.355	63.073	103.142	54.572	1,3-dichloropropane	94.630	76.799	112.710	87.290
trichlorofluoromethane	109.112	68.602	110.608	81.963	1,2-dibromomethane	100.406	78.451	114.051	85.949
diethyl ether	109.103	81.183	106.237	84.049	chlorobenzene	103.549	81.594	118.537	83.748
1,1-dichloroethene	101.974	66.026	138.252	103.463	ethylbenzene	93.594	77.264	115.366	81.777
carbon disulfide	110.334	79.952	119.555	65.017	1,1,1,2-tetrachloroethane	103.551	89.592	128.252	93.463
methyl iodide	133.731	104.554	116.699	96.444	xylene (m+p)	92.480	73.806	115.829	85.028
allyl chloride	109.103	81.183	122.028	72.829	xylene (o)	106.051	77.949	115.072	86.071
methylene chloride	101.935	76.922	112.223	78.634	styrene	100.157	80.415	117.397	90.603
trans-1,2-dichloroethene	97.728	63.986	105.731	76.554	bromoforn	117.549	95.594	132.055	89.088
methyl acetate	121.494	77.934	100.194	81.520	isopropylbenzene	95.196	71.662	118.350	78.222
methyl-t-butyl ether (MtBE)	120.983	66.445	130.627	112.230	bromobenzene	111.078	86.065	118.051	89.949
t-butyl alcohol (TBA)	96.116	84.569	107.521	87.337	n-propylbenzene	124.318	83.682	119.171	79.686
diisopropyl ether (DIPE)	99.770	81.373	106.627	88.230	1,1,2,2-tetrachloroethane	121.770	103.373	122.388	85.040
1,1-dichloroethane	95.201	77.370	113.973	78.599	2-chlorotoluene	108.157	88.415	120.960	83.612
t-butyl ethyl ether (ETBE)	94.152	86.991	107.556	87.301	1,3,5-trimethylbenzene	116.817	88.897	118.403	82.740
cis-1,2-dichloroethene	100.535	70.322	108.338	84.804	1,2,3-trichloropropane	108.456	86.972	108.406	86.451
bromochloromethane	109.396	82.033	121.144	71.427	4-chlorotoluene	110.014	85.415	121.401	86.027
chloroform	98.158	71.556	112.535	82.322	t-butylbenzene	127.224	73.348	117.458	83.114
carbon tetrachloride	119.261	96.167	132.066	88.506	pentachloroethane	136.931	86.497	134.355	101.073
tetrahydrofuran	146.410	53.590	106.408	73.592	1,2,4-trimethylbenzene	111.396	90.890	121.540	84.745
1,1,1-trichloroethane	102.261	70.882	117.650	74.922	sec-butylbenzene	112.628	81.086	116.060	74.797
1,1-dichloropropene	133.055	61.802	107.503	57.069	4-isopropyltoluene	117.196	93.662	122.792	81.779
1-chlorobutane	105.807	73.621	110.654	68.775	1,3-dichlorobenzene	98.631	87.084	116.535	86.322
benzene	97.751	72.534	110.048	79.666	1,4-dichlorobenzene	113.396	92.890	111.078	86.065
t-amyl methyl ether (TAME)	98.018	83.696	108.473	91.527	n-butylbenzene	117.680	85.177	123.099	79.187
1,2-dichloroethane	99.338	84.662	107.072	78.071	hexachloroethane	123.603	80.397	127.171	87.686
trichloroethene	101.296	73.561	115.203	73.940	1,2-dichlorobenzene	110.157	90.415	116.355	83.073
t-amyl ethyl ether (TAEE)	98.473	81.527	108.157	88.415	1,2-dibromo-3-chloropropane	129.112	88.602	123.326	84.103
dibromomethane	110.585	85.986	103.585	83.843	hexachlorobutadiene	115.239	84.189	134.244	65.184
1,2-dichloropropane	111.222	81.350	106.888	93.683	1,2,4-trichlorobenzene	110.630	92.799	111.103	83.183
bromodichloromethane	113.222	83.350	126.608	97.963	naphthalene	115.295	89.277	111.078	86.065
cis-1,3-dichloropropene	106.237	84.049	114.206	75.509	1,2,3-trichlorobenzene	107.217	80.669	110.633	84.224
toluene	96.338	72.804	115.973	80.599	Average	110.225	81.645	116.529	83.307

Table 6: Upper and Lower PIR Summary 1

Compound	100ml/min for 4min		65ml/min for 4min		Compound	100ml/min for 4min		65ml/min for 4min	
	Upper PIR	Lower PIR	Upper PIR	Lower PIR		Upper PIR	Lower PIR	Upper PIR	Lower PIR
dichlorodifluoromethane	94.350	54.222	119.434	81.137	tetrachloroethene	101.966	54.034	105.840	57.588
chlorodifluoromethane	107.807	75.621	90.633	64.224	trans-1,3-dichloropropene	88.633	62.224	119.078	76.350
chloromethane	107.196	83.662	119.205	72.795	ethyl methacrylate	89.951	67.763	119.118	87.739
vinyl chloride	93.929	64.928	129.854	91.289	1,1,2-trichloroethane	102.066	58.506	119.833	96.739
1,3-butadiene	91.396	64.033	110.206	71.509	dibromochloromethane	104.960	67.612	111.396	90.890
bromomethane	111.260	75.597	94.795	41.205	1,3-dichloropropane	96.480	77.806	120.473	103.527
trichlorofluoromethane	94.048	63.666	110.749	76.108	1,2-dibromomethane	101.468	66.532	133.854	95.289
diethyl ether	117.401	82.027	111.473	78.813	chlorobenzene	90.676	61.324	98.051	69.949
1,1-dichloroethene	105.807	73.621	115.633	73.510	ethylbenzene	96.051	67.949	106.037	77.392
carbon disulfide	117.778	77.650	108.242	56.901	1,1,1,2-tetrachloroethane	106.131	60.726	115.260	79.597
methyl iodide	126.338	102.804	113.396	86.033	xylene (m+p)	92.828	69.458	102.884	73.401
allyl chloride	113.112	72.602	113.144	63.427	xylene (o)	95.751	70.534	107.650	64.922
methylene chloride	112.158	85.556	108.060	66.797	styrene	101.366	67.777	115.203	73.940
trans-1,2-dichloroethene	106.817	78.897	102.355	69.073	bromoform	90.304	75.982	116.456	94.972
methyl acetate	113.218	68.496	122.676	93.324	isopropylbenzene	96.388	59.040	106.947	69.053
methyl-t-butyl ether (MtBE)	109.326	70.103	103.594	87.264	bromobenzene	103.680	71.177	132.240	94.618
t-butyl alcohol (TBA)	104.031	75.855	102.830	84.827	n-propylbenzene	102.060	60.797	112.060	70.797
diisopropyl ether (DIPE)	104.633	78.224	100.194	81.520	1,1,2,2-tetrachloroethane	99.973	64.599	136.817	108.897
1,1-dichloroethane	117.540	80.745	94.051	65.949	2-chlorotoluene	102.813	58.901	105.935	80.922
t-butyl ethyl ether (ETBE)	105.811	74.761	103.585	83.843	1,3,5-trimethylbenzene	98.823	66.320	112.473	76.099
cis-1,2-dichloroethene	106.823	74.320	100.037	71.392	1,2,3-trichloropropane	124.711	58.146	141.934	87.209
bromochloromethane	108.711	70.146	118.037	89.392	4-chlorotoluene	100.875	55.697	106.608	77.963
chloroform	102.817	74.897	102.899	66.244	t-butylbenzene	91.326	52.103	112.314	72.829
carbon tetrachloride	114.066	70.506	114.899	78.244	pentachloroethane	98.650	68.778	120.022	82.264
tetrahydrofuran	208.458	98.399	146.392	82.180	1,2,4-trimethylbenzene	95.974	60.026	129.359	62.641
1,1,1-trichloroethane	108.314	68.829	99.401	64.027	sec-butylbenzene	97.901	61.527	112.947	79.053
1,1-dichloropropene	122.242	70.901	101.055	53.230	4-isopropyltoluene	96.014	62.272	116.875	71.697
1-chlorobutane	106.650	76.778	98.927	65.645	1,3-dichlorobenzene	95.171	55.686	107.295	81.277
benzene	109.680	77.177	96.444	69.842	1,4-dichlorobenzene	113.171	63.972	109.852	78.148
t-amyl methyl ether (TAME)	100.014	75.415	121.556	101.301	n-butylbenzene	104.317	51.112	130.391	69.038
1,2-dichloroethane	105.118	73.739	123.187	90.527	hexachloroethane	111.084	64.344	118.736	70.597
trichloroethene	105.540	68.745	93.296	65.561	1,2-dichlorobenzene	99.852	68.148	119.937	65.777
t-amyl ethyl ether (TAEE)	105.401	70.027	103.983	80.017	1,2-dibromo-3-chloropropane	114.150	24.135	131.746	47.682
dibromomethane	106.760	70.954	109.261	86.167	hexachlorobutadiene	107.794	58.491	126.521	63.194
1,2-dichloropropane	113.552	60.734	98.676	69.324	1,2,4-trichlorobenzene	99.072	70.071	110.914	79.372
bromodichloromethane	116.763	76.380	102.723	76.705	naphthalene	103.778	63.650	123.732	79.125
cis-1,3-dichloropropene	109.110	88.604	107.833	84.739	1,2,3-trichlorobenzene	102.947	65.053	117.103	89.183
toluene	106.697	60.731	112.650	82.778	Average	105.731	68.568	112.790	76.888

Table 7: Upper and Lower PIR Summary 2

Compound	40ml/min for 11min		65ml/min for 6.5min		Compound	40ml/min for 11min		65ml/min for 6.5min	
	Precision %RSD	Accuracy (% Rec'ry)	Precision %RSD	Accuracy (% Rec'ry)		Precision %RSD	Accuracy (% Rec'ry)	Precision %RSD	Accuracy (% Rec'ry)
dichlorodifluoromethane	5.29	95.05	7.81	95.71	tetrachloroethene	5.42	104.93	6.45	93.06
chlorodifluoromethane	4.98	101.67	7.63	95.54	trans-1,3-dichloropropene	3.13	105.14	3.12	95.66
chloromethane	5.94	97.64	6.35	93.50	ethyl methacrylate	2.85	102.19	2.28	94.13
vinyl chloride	4.82	102.27	7.64	94.09	1,1,2-trichloroethane	3.13	101.92	2.95	92.96
1,3-butadiene	5.12	102.46	8.71	97.69	dibromochloromethane	3.25	103.74	2.69	95.60
bromomethane	2.20	104.51	6.10	94.13	1,3-dichloropropane	3.26	103.56	2.94	93.06
trichlorofluoromethane	5.39	107.43	7.37	99.20	1,2-dibromomethane	3.10	103.17	2.49	93.24
diethyl ether	3.23	103.04	2.92	96.21	chlorobenzene	4.45	103.54	4.62	92.66
1,1-dichloroethene	4.68	104.61	7.92	94.86	ethylbenzene	4.42	105.35	5.82	93.71
carbon disulfide	4.47	104.39	6.76	99.42	1,1,1,2-tetrachloroethane	3.94	103.56	4.05	93.57
methyl iodide	3.66	105.60	5.67	101.32	xylene (m+p)	4.55	104.91	5.52	93.75
allyl chloride	4.51	104.52	5.87	97.71	xylene (o)	4.60	103.99	4.92	93.42
methylene chloride	4.08	103.22	3.77	95.51	styrene	4.12	104.00	4.08	94.34
trans-1,2-dichloroethene	4.79	103.72	6.03	95.14	bromoform	2.53	102.54	2.34	91.71
methyl acetate	2.77	102.37	1.76	96.01	isopropylbenzene	4.83	104.96	6.08	94.17
methyl-t-butyl ether (MtBE)	3.34	102.99	2.90	94.19	bromobenzene	4.06	102.28	3.97	93.33
t-butyl alcohol (TBA)	3.77	104.48	3.21	95.44	n-propylbenzene	4.92	105.53	5.83	95.01
diisopropyl ether (DIPE)	3.69	104.21	3.69	96.31	1,1,2,2-tetrachloroethane	2.77	101.54	2.95	93.31
1,1-dichloroethane	4.43	104.40	5.14	95.81	2-chlorotoluene	4.70	103.56	5.20	93.21
t-butyl ethyl ether (ETBE)	3.58	103.62	3.21	95.44	1,3,5-trimethylbenzene	4.68	104.76	5.27	94.25
cis-1,2-dichloroethene	4.33	103.46	4.84	95.14	1,2,3-trichloropropane	2.72	101.97	2.23	92.04
bromochloromethane	4.10	101.81	3.57	96.24	4-chlorotoluene	4.41	103.19	4.34	93.55
chloroform	4.00	103.71	4.43	95.39	t-butylbenzene	4.99	104.66	5.77	94.25
carbon tetrachloride	3.79	107.80	6.89	100.24	pentachloroethane	3.54	104.14	3.84	94.86
tetrahydrofuran	2.15	100.61	2.35	93.62	1,2,4-trimethylbenzene	4.60	103.86	5.06	94.13
1,1,1-trichloroethane	4.48	105.32	6.54	96.97	sec-butylbenzene	4.79	105.67	6.21	95.56
1,1-dichloropropene	5.03	104.38	7.85	98.48	4-isopropyltoluene	4.80	104.74	5.62	95.13
1-chlorobutane	4.86	104.89	6.99	97.21	1,3-dichlorobenzene	4.16	103.33	4.22	93.19
benzene	4.46	103.84	5.19	95.57	1,4-dichlorobenzene	4.45	103.51	3.83	93.34
t-amyl methyl ether (TAME)	3.27	102.99	2.68	95.06	n-butylbenzene	4.89	105.19	5.55	94.53
1,2-dichloroethane	3.15	103.86	3.39	94.86	hexachloroethane	3.99	105.46	5.06	100.24
trichloroethene	5.03	103.49	5.94	95.22	1,2-dichlorobenzene	3.89	102.65	3.54	92.87
t-amyl ethyl ether (TAE)	3.61	103.14	3.53	94.93	1,2-dibromo-3-chloropropane	1.94	101.98	2.38	95.89
dibromomethane	3.24	102.34	2.71	95.94	hexachlorobutadiene	5.05	103.84	5.47	94.41
1,2-dichloropropane	3.70	103.05	4.20	95.10	1,2,4-trichlorobenzene	3.56	103.25	3.33	94.46
bromodichloromethane	3.51	103.41	3.58	96.26	napthalene	2.79	102.63	2.54	93.95
cis-1,3-dichloropropene	3.51	104.53	3.14	98.99	1,2,3-trichlorobenzene	3.25	102.86	3.08	94.28
toluene	4.50	104.99	5.58	94.17	Average	4.03	103.57	4.86	95.11

Table 8: Precision and Accuracy Summary 1

Compound	100ml/min for 4min		65ml/min for 4min		Compound	40ml/min for 11min		65ml/min for 6.5min	
	Precision %RSD	Accuracy (% Rec'ry)	Precision %RSD	Accuracy (% Rec'ry)		Precision %RSD	Accuracy (% Rec'ry)	Precision %RSD	Accuracy (% Rec'ry)
dichlorodifluoromethane	5.91	98.09	2.16	98.52	tetrachloroethene	5.95	95.99	2.68	107.41
chlorodifluoromethane	5.77	99.59	2.33	103.63	trans-1,3-dichloropropene	4.18	96.01	2.78	105.00
chloromethane	5.94	98.05	2.57	97.39	ethyl methacrylate	3.90	96.41	2.67	105.73
vinyl chloride	5.45	100.31	2.31	101.64	1,1,2-trichloroethane	4.44	93.07	2.59	104.39
1,3-butadiene	5.39	101.31	2.35	104.64	dibromochloromethane	3.76	95.55	2.90	106.34
bromomethane	3.27	100.96	3.61	100.29	1,3-dichloropropane	4.40	92.59	3.02	103.86
trichlorofluoromethane	5.76	101.11	3.17	107.03	1,2-dibromomethane	4.43	93.64	3.21	104.67
diethyl ether	3.87	96.51	2.38	103.45	chlorobenzene	4.95	94.27	3.27	104.71
1,1-dichloroethene	5.40	100.49	2.23	106.14	ethylbenzene	37.30	83.49	2.83	106.25
carbon disulfide	4.53	102.06	2.70	107.57	1,1,1,2-tetrachloroethane	4.53	94.65	3.28	105.34
methyl iodide	3.25	99.03	2.64	106.03	xylene (m+p)	5.39	95.28	2.85	105.78
allyl chloride	4.63	100.12	2.21	102.59	xylene (o)	5.21	94.23	3.26	104.79
methylene chloride	4.35	97.11	2.73	102.39	styrene	4.96	94.64	2.94	105.11
trans-1,2-dichloroethene	5.12	98.51	1.98	104.17	bromoform	3.51	96.15	2.57	106.77
methyl acetate	4.87	96.88	2.45	99.96	isopropylbenzene	5.29	95.44	2.81	106.89
methyl-t-butyl ether (MtBE)	3.80	98.11	2.49	103.39	bromobenzene	5.14	90.66	3.48	106.24
t-butyl alcohol (TBA)	3.64	98.01	2.86	103.12	n-propylbenzene	5.82	94.34	2.94	109.26
diisopropyl ether (DIPE)	4.11	98.47	2.80	102.84	1,1,2,2-tetrachloroethane	5.31	92.30	3.00	106.07
1,1-dichloroethane	4.50	98.08	2.58	102.95	2-chlorotoluene	5.52	92.67	3.16	107.24
t-butyl ethyl ether (ETBE)	3.65	98.02	2.86	103.11	1,3,5-trimethylbenzene	5.36	93.81	3.08	108.69
cis-1,2-dichloroethene	4.76	97.36	2.30	102.98	1,2,3-trichloropropane	4.96	91.31	3.67	106.10
bromochloromethane	4.43	96.99	2.84	102.92	4-chlorotoluene	5.25	92.54	3.25	107.16
chloroform	4.63	97.33	2.79	103.01	t-butylbenzene	5.73	93.76	3.01	109.31
carbon tetrachloride	4.53	102.29	2.31	109.62	pentachloroethane	4.49	93.31	3.24	108.47
tetrahydrofuran	5.61	95.49	2.61	100.59	1,2,4-trimethylbenzene	5.63	93.10	2.88	107.54
1,1,1-trichloroethane	4.72	100.10	2.28	107.34	sec-butylbenzene	5.77	93.99	2.77	109.27
1,1-dichloropropene	4.39	101.21	2.96	106.41	4-isopropyltoluene	5.82	93.76	2.98	108.64
1-chlorobutane	5.06	100.54	2.37	105.69	1,3-dichlorobenzene	5.20	92.01	3.33	107.37
benzene	4.72	98.23	2.52	103.54	1,4-dichlorobenzene	5.24	90.10	3.58	106.89
t-amyl methyl ether (TAME)	3.70	97.71	2.56	102.36	n-butylbenzene	5.82	93.79	3.13	107.57
1,2-dichloroethane	4.92	95.88	2.75	102.04	hexachloroethane	4.80	95.24	2.75	112.48
trichloroethene	4.81	97.88	2.56	104.31	1,2-dichlorobenzene	5.00	89.34	3.33	107.15
t-amyl ethyl ether (TAE)	3.80	97.59	2.71	102.54	1,2-dibromo-3-chloropropane	4.54	95.04	3.30	109.78
dibromomethane	3.94	96.41	2.73	103.56	hexachlorobutadiene	6.15	90.37	2.81	108.27
1,2-dichloropropane	4.02	97.47	2.53	102.23	1,2,4-trichlorobenzene	4.78	90.39	3.38	107.74
bromodichloromethane	3.69	97.89	2.71	103.88	napthalene	4.71	92.05	3.10	109.15
cis-1,3-dichloropropene	3.89	97.02	2.56	102.20	1,2,3-trichlorobenzene	4.55	90.09	2.95	108.45
toluene	5.09	95.46	2.95	105.76	Average	5.89	93.12	3.05	107.08

Table 9: Precision and Accuracy Summary 2

Compound	40 ml/min for 11 min - Response Factors	65 ml/min for 6.5 min - Response Factors	100 ml/min for 4 min - Response Factors	65 ml/min for 4 min - Response Factors
methyl acetate	0.360	0.347	0.329	0.203
MTBE	1.327	1.416	1.415	1.090
THF	0.086	0.080	0.075	0.044
ethylmethacrylate	0.749	0.765	0.722	0.513
1,2-dibromomethane	0.496	0.526	0.500	0.357
bromoform	0.304	0.303	0.284	0.197
1,1,2,2-tetrachloroethane	1.348	1.383	1.308	0.870
1,2,3-trichloropropane	0.458	0.459	0.420	0.269
1,2-dibromo-3-chloropropane	0.283	0.266	0.227	0.138

Table 10: Curve Results Response Factor Outlier Summary

Compound	40 ml/min for 11 min		65 ml/min for 6.5 min		100 ml/min for 4 min		65 ml/min for 4 min	
	Upper PIR	Lower PIR	Upper PIR	Lower PIR	Upper PIR	Lower PIR	Upper PIR	Lower PIR
bromomethane	96.36	63.07	103.14	54.57	111.26	75.60	94.79	41.21
methyl acetate	121.49	77.93	100.19	81.52	113.22	68.50	122.68	93.32
MTBE	120.98	66.45	130.63	112.23	109.33	70.10	103.59	87.26
THF	146.41	53.59	106.41	73.59	208.46	98.40	146.39	82.18
ethylmethacrylate	116.02	101.70	121.26	98.17	89.95	67.76	119.12	87.74
1,2-dibromomethane	100.41	78.45	114.05	85.95	101.47	66.53	133.85	95.29
bromoform	117.55	95.59	132.06	89.09	90.30	75.98	116.46	94.97
1,1,2,2-tetrachloroethane	121.77	103.37	122.39	85.04	99.97	64.60	136.82	108.90
1,2,3-trichloropropane	108.46	86.97	108.41	86.45	124.71	58.15	141.93	87.21
1,2-dibromo-3-chloropropane	129.11	88.60	123.33	84.10	114.15	24.14	131.75	47.68

Table 11: Upper and Lower PIR Outlier Summary

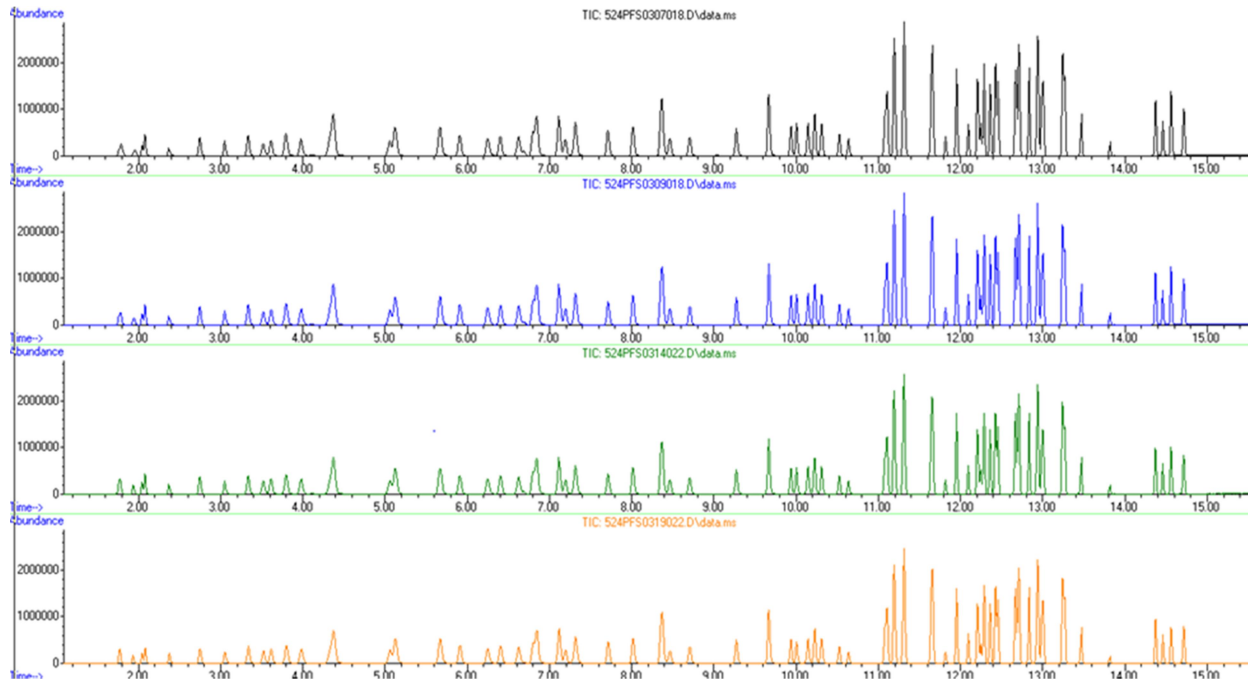


Figure 1: Chromatograms of a 20µg/L standard, 40ml/min for 11 min (Black), 65ml/min for 6.5 min (Blue), 100ml/min for 4 min (Green), and 65ml/min for 4 min (Orange)

Conclusions:

The effect of purge flow and volume can be significant. When following the recommended parameters, the results proved to be consistent with what was seen using the standard 40ml/min purge flow and 11 min purge time. The allowable parameters on the other hand displayed some problems with compound response and prediction intervals. As the purge volume decreased, so did the compound response thus causing the lower PIR to fail for some of the compounds. When the purge flow was increased, the upper and lower PIR failed for two of the compounds due to the purge flow being too high. Furthermore, the standard flow of 40ml/min produced the least amount of water while the 100ml/min flow produced the most. Overall, the 65ml/min purge flow with the 6.5 min purge time proved to be the optimum parameters for USEPA Method 524,3. Since these parameters fell within the recommended range additional demonstration of performance is not needed. Furthermore, lab productivity is increased without sacrificing the quality of the experimental results.

References:

1. Method 524.3, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0, June 2009.
2. Method 524.4 (Draft), Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (Using Nitrogen Purge Gas), Version 1, September 2011.

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