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#104

Effect of Split Ratio on USEPA Method 8260 Compounds

Application Note - Environmental

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Abstract

USEPA Method 8260 involves purging analytes out of a water matrix. During a split injection, the sample volatilizes in the inlet and is swept by the carrier gas through the liner onto the GC column with a portion of the sample being split off and sent out the split vent line. The amount of sample reaching the detector is dependent upon the split flow rate. Thus, the higher the split rate, the smaller amount of sample on the column. Furthermore, a higher split ratio minimizes column exposure to moisture. During purge and trap sampling moisture control is crucial to decreasing split flow and enhancing detection limits. This application will explore the effect split ratios have upon USEPA Method 8260 analytes.

Introduction:

Injection size on a GC column is dictated by the diameter of the GC column. Packed columns are usually shorter in length and larger in diameter and are usually filled with a packing coated with stationary phase. Due to their large diameter, packed columns can handle much larger injections. However, since packed columns are shorter in length, compound resolution is more difficult. Capillary columns, on the other hand, are much longer with much smaller diameters. A capillary column has a stationary phase that is coated onto the column wall which in turn makes the diameter even smaller. Overloading is a common problem with capillary columns, thus smaller injections and higher dilutions are required when using a capillary column.

The benefit of a capillary column is that it has substantially more theoretical plates than a packed column. Increasing the number of theoretical plates enhances column efficiency because peaks are narrowed and peak resolution is improved. The disadvantage of the capillary column is column overloading. This is where a split injection is greatly beneficial. A split injection can limit sample overload while taking advantage of the efficiency of the capillary column.

Discussion:

Purge and trap sampling is the method used for purging volatile compounds out of a water matrix for USEPA Method 8260. Due to the large number of analytes and the lower detection limits required in this method, a capillary column is needed for detection and separation. Split injections provide a method to control moisture from the purge and trap sampling while preventing column overloading with the capillary column. However, due to the detection limits required of the method, if the split injection is too large, the detection limits of the method may not be met. On the other hand, if the split injection is too small, there can be moisture problems with the mass spectrometer. This application will provide a comparison of several different split rates and their effect on compound detection for USEPA Method 8260.

Experimental:

The sampling system used for this study was the EST Analytical Encon Evolution concentrator and the Centurion WS autosampler. The concentrator was affixed with a Vocarb 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. Three different split ratios were used for this study. Refer to Table 1 for the sampling method parameters and Table 2 for GC/MS parameters.

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	150°C
Transfer Line Temp.	150°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	4psi
Desorb Time	0.5 min.
Desorb Preheat Delay	10 sec.
Desorb Temp.	260°C
Moisture Reduction Trap (MoRT) Bake Temp.	210°C
Bake Temp	270°C
Sparge Vessel Bake Temp.	120°C
Bake Time	8 min.
Bake Flow	85mL/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	Agilent 7890A/5975C inert XL
Inlet	Split/Splitless
Inlet Temp.	220°C
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1, 80:1, and 100:1
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, 84mL/min, and 104mL/min
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Scan Range	m/z 35-300
Scans	5.10 scans/sec
Solvent Delay	0.7 min

Table 2: GC/MS Experimental Parameters

The USEPA Method 8260 standards were acquired from Restek. The linear range of the split injection experiments were established by running nine point calibration curves with a range of 0.5 to 200ppb. Method detection limits were established for each split rate by examining seven replicate standards of the low calibration point. Tables 3, 4 and 5 display curve linearity, compound response and method detection limits for the three split rates. Table 6 is an average of the experimental results for the split rates. Figure 1 displays chromatograms of the 50ppb calibration point for the split rate, while Figure 2 is an overlay of the last four Method 8260 analytes displaying how split rates effect compound recoveries.

Curve Linearity Summary							
Compound	40 to 1	80 to 1	100 to 1	Compound	40 to 1	80 to 1	100 to 1
Dichlorodifluoromethane	13.22	6.28	14.66	2-nitropropane	4.81	7.25	9.90
Chloromethane	11.20	8.36	6.74	cis-1,3-Dichloropropene	4.88	2.07	8.63
Vinyl Chloride	11.15	6.44	11.55	4-methyl-2-pentanone	3.55	5.38	5.77
Bromomethane	11.97	13.94	11.81	Toluene-d8 SUR	4.87	4.20	6.77
Chloroethane	7.51	11.20	14.42	Toluene	6.86	6.01	6.03
Trichlorofluoromethane	6.43	5.55	4.69	ethyl methacrylate	4.43	4.22	10.11
diethyl ether	5.13	3.77	9.74	trans-1,3-Dichloropropene	4.99	2.85	5.27
1,1,2-trichlorofluoroethane	6.43	5.55	4.69	1,1,2-Trichloroethane	5.56	5.73	5.64
1,1-Dichloroethene	88	5.17	7.97	Tetrachloroethene	13.44	14.67	13.78
Acetone	8.12	8.19	11.65	1,3-Dichloropropane	3.23	4.88	6.26
Iodomethane	*0.996	*1.000	*0.997	isopropyl acetate	4.93	9.30	6.96
Carbon Disulfide	8.95	11.44	8.74	butyl acetate	4.06	4.35	4.81
allyl chloride	5.44	10.18	6.82	Dibromochloromethane	5.61	8.79	12.54
Methylene Chloride	10.14	13.42	6.90	2-Hexanone	4.21	4.44	7.09
acetonitrile	1	9.60	8.64	1,2-Dibromoethane	5.08	5.13	5.6
Tert Butyl Alcohol	5.33	7.33	8.26	Chlorobenzene	5.81	5.09	5.52
MTBE	5.02	8.71	6.81	1,1,1,2-Tetrachloroethane	4.71	7.69	5.59
cis-1,2-Dichloroethene	5.66	6.08	9.57	Ethylbenzene	5.22	5.04	6.19
acrylonitrile	36	4.22	13.44	Xylene (m + p)	5.35	5.24	7.49
Isopropylether	5.18	5.79	6.77	Styrene	4.61	5.14	7.08
Vinyl acetate	4.94	5.82	8.7	Xylene (o)	4.45	5.50	5.4
1,1-Dichloroethane	5.55	7.81	5.81	n-amyl acetate	3.58	5.46	8.10
Ethyl Tert Butyl Ether	5.33	7.33	8.26	Bromoform	4.93	12.01	10.72
trans-1,2-Dichloroethene	5.76	9.90	9.82	Isopropylbenzene	4.26	4.65	8.10
ethyl acetate	11.81	12.02	4.88	cis-1,4-dichloro-2-butene	4.36	5.71	11
2-Butanone	3.98	3.49	6.03	BFB SUR	8.73	13.62	7.89
2,2-Dichloropropane	90	13.82	5.71	Bromobenzene	6.70	9.60	5.80
Bromochloromethane	6.88	10.99	8.90	1,2,3-Trichloropropane	5.29	8.07	9.02
propionitrile	10.17	8.20	6.10	1,1,2,2-Tetrachloroethane	5.34	8.85	7.59
methacrylonitrile	6.46	5.18	8.49	n-Propylbenzene	5.22	9.53	8.36
THF	31	5.17	7.72	trans-1,4-dichloro-2-butene	5.87	10.34	11.90
Chloroform	9.40	8.21	4.82	2-Chlorotoluene	5.07	7.72	12.99
methyl acrylate	4.43	1.89	6.72	4-Chlorotoluene	5.47	6.91	11.03
Dibromofluoromethane SUR	12.78	14.50	9.90	1,3,5-Trimethylbenzene	5.12	8.16	7.05
1,1,1-Trichloroethane	6.57	4.89	7.47	tert-Butylbenzene	6.22	8.37	10.19
2-Chloroethylvinylether	2.63	10.65	11.55	sec-Butylbenzene	4.75	7.73	9.63
Carbon Tetrachloride	9.54	8.80	11.69	1,2,4-Trimethylbenzene	4.53	9.00	7.87
1,1-Dichloropropene	8.40	7.70	11.81	nitrobenzene	10.25	*0.997	*0.997
methyl acetate	4.66	4.06	5.53	1,3-Dichlorobenzene	5.42	9.67	6.3
isobutyl alcohol	4.16	7.89	8.09	1,4-Dichlorobenzene	10.59	7.52	8.84
Tert Amyl Methyl Ether	5.06	6.15	7.75	Isopropyltoluene	5.96	10.75	8.68
Benzene	5.23	5.99	8.21	1,2,-Dichlorobenzene	5.25	9.23	5.20
1,4-Dioxane	17	11.47	*0.998	n-Butylbenzene	5.35	9.98	10.81
1,2-Dichloroethane	4.65	5.21	6.29	1,2-Dibromo-3-chloropropane	9.67	9.31	5.65
propyl acetate	3.37	5.73	5.43	1,2,4-Trichlorobenzene	4.05	10.88	11.66
Trichloroethene	4.99	6.87	7.51	Naphthalene	5.05	10.93	9.73
1,2-Dichloropropane	88	3.41	12.78	Hexachlorobutadiene	12.64	*0.998	13.18
methyl methacrylate	4.09	2.64	6.11	1,2,3-Trichlorobenzene	5.09	11.83	13.33
Dibromomethane	5.09	13.54	7.49	Ave.	6.36	7.61	8.36
Bromodichloromethane	4.56	3.77	6.19				

Table 3: Curve Linearity Summary

Compound Response Factor Summary							
Compound	40 to 1	80 to 1	100 to 1	Compound	40 to 1	80 to 1	100 to 1
Dichlorodifluoromethane	0.613	0.563	0.493	2-nitropropane	0.912	0.181	0.180
Chloromethane	0.833	0.776	0.622	cis-1,3-Dichloropropene	0.663	0.679	0.640
Vinyl Chloride	0.659	0.720	0.592	4-methyl-2-pentanone	0.666	0.697	0.665
Bromomethane	0.235	0.259	0.234	Toluene-d8 SUR	1.220	1.277	1.215
Chloroethane	0.358	0.383	0.331	Toluene	0.894	0.905	0.860
Trichlorofluoromethane	0.546	0.582	0.553	ethyl methacrylate	0.613	0.632	0.595
diethyl ether	0.615	0.658	0.579	trans-1,3-Dichloropropene	0.613	0.641	0.624
1,1,2-trichlorofluoroethane	0.546	0.582	0.553	1,1,2-Trichloroethane	0.312	0.325	0.307
1,1-Dichloroethene	491	0.513	0.486	Tetrachloroethene	0.364	0.280	0.255
Acetone	0.373	0.375	0.371	1,3-Dichloropropane	0.614	0.659	0.625
Iodomethane	0.341	0.330	0.288	isopropyl acetate	0.122	0.131	0.121
Carbon Disulfide	1.711	1.768	1.521	butyl acetate	0.365	0.379	0.350
allyl chloride	1.523	1.661	1.432	Dibromochloromethane	0.343	0.338	0.333
Methylene Chloride	0.652	0.691	0.604	2-Hexanone	0.488	0.507	0.465
acetonitrile	0	0.131	0.125	1,2-Dibromoethane	0.322	0.339	0.323
Tert Butyl Alcohol	0.479	0.524	0.481	Chlorobenzene	0.964	0.948	0.961
MTBE	2.025	2.213	2.088	1,1,1,2-Tetrachloroethane	0.333	0.334	0.358
cis-1,2-Dichloroethene	0.638	0.693	0.614	Ethylbenzene	1.935	1.978	1.961
acrylonitrile	390	0.406	0.366	Xylene (m + p)	1.500	1.528	1.502
Isopropylether	2.948	3.328	2.912	Styrene	1.082	1.051	1.043
Vinyl acetate	3.275	3.877	3.5	Xylene (o)	1.485	1.526	1.506
1,1-Dichloroethane	1.351	1.510	1.381	n-amyl acetate	1.218	1.183	1.149
Ethyl Tert Butyl Ether	2.393	2.619	2.407	Bromoform	0.256	0.234	0.242
trans-1,2-Dichloroethene	0.575	0.598	0.551	Isopropylbenzene	1.731	1.702	1.702
ethyl acetate	0.162	0.187	0.170	cis-1,4-dichloro-2-butene	0.219	0.204	0.198
2-Butanone	1.745	1.907	1.774	BFB SUR	1.067	1.141	1.121
2,2-Dichloropropane	987	1.088	1.064	Bromobenzene	1.792	1.935	1.929
Bromochloromethane	0.330	0.342	0.313	1,2,3-Trichloropropane	1.076	1.064	0.924
propionitrile	0.159	0.156	0.150	1,1,2,2-Tetrachloroethane	1.077	1.131	1.152
methacrylonitrile	0.760	0.840	0.748	n-Propylbenzene	4.489	4.771	4.811
THF	425	0.418	0.399	trans-1,4-dichloro-2-butene	0.496	0.531	0.547
Chloroform	1.245	1.334	1.248	2-Chlorotoluene	0.738	0.770	0.749
methyl acrylate	0.940	0.995	0.937	4-Chlorotoluene	0.772	0.768	0.767
Dibromofluoromethane SUR	0.600	0.637	0.604	1,3,5-Trimethylbenzene	2.822	2.900	2.995
1,1,1-Trichloroethane	1.026	1.150	1.106	tert-Butylbenzene	2.529	2.726	2.840
2-Chloroethylvinylether	0.569	0.629	0.536	sec-Butylbenzene	0.645	0.634	0.670
Carbon Tetrachloride	0.758	0.797	0.789	1,2,4-Trimethylbenzene	2.855	2.841	2.893
1,1-Dichloropropene	0.948	1.030	0.931	nitrobenzene	0.126	0.078	0.071
methyl acetate	2.108	2.328	2.157	1,3-Dichlorobenzene	1.372	1.346	1.389
isobutyl alcohol	0.069	0.058	0.057	1,4-Dichlorobenzene	1.431	1.340	1.434
Tert Amyl Methyl Ether	2.017	2.163	2.006	Isopropyltoluene	2.887	2.705	2.829
Benzene	2.749	2.936	2.632	1,2,-Dichlorobenzene	1.304	1.257	1.307
1,4-Dioxane	012	0.012	0.011	n-Butylbenzene	2.909	2.852	2.827
1,2-Dichloroethane	1.063	1.216	1.146	1,2-Dibromo-3-chloropropane	0.288	0.256	0.262
propyl acetate	0.977	1.062	0.991	1,2,4-Trichlorobenzene	0.866	0.698	0.663
Trichloroethene	0.334	0.322	0.313	Naphthalene	3.149	2.516	2.380
1,2-Dichloropropane	426	0.462	0.426	Hexachlorobutadiene	0.342	0.247	0.272
methyl methacrylate	0.348	0.374	0.356	1,2,3-Trichlorobenzene	0.840	0.697	0.623
Dibromomethane	0.188	0.184	0.179	Ave.	1.023	1.049	1.003
Bromodichloromethane	0.504	0.533	0.542				

Table 4: Compound Response Summary

MDL Summary							
Compound	40 to 1	80 to 1	100 to 1	Compound	40 to 1	80 to 1	100 to 1
Dichlorodifluoromethane	0.13	0.28	0.24	2-nitropropane	0.07	0.23	0.71
Chloromethane	0.17	0.21	0.27	cis-1,3-Dichloropropene	0.07	0.12	0.15
Vinyl Chloride	0.12	0.16	0.28	4-methyl-2-pentanone	0.10	0.08	0.25
Bromomethane	0.35	0.27	0.42	Toluene-d8 SUR	0.08	0.06	0.18
Chloroethane	0.18	0.17	0.37	Toluene	0.10	0.10	0.14
Trichlorofluoromethane	0.12	0.14	0.30	ethyl methacrylate	0.07	0.15	0.17
diethyl ether	0.13	0.13	0.32	trans-1,3-Dichloropropene	0.10	0.22	0.29
1,1,2-trichlorofluoroethane	0.12	0.14	0.30	1,1,2-Trichloroethane	0.12	0.20	0.30
1,1-Dichloroethene	17	0.16	0.36	Tetrachloroethene	0.09	0.39	0.37
Acetone	1.53	1.12	1.34	1,3-Dichloropropane	0.12	0.13	0.27
Iodomethane	0.14	0.31	0.78	isopropyl acetate	0.19	0.36	1.08
Carbon Disulfide	0.16	0.19	0.38	butyl acetate	0.14	0.17	0.22
allyl chloride	0.09	0.07	0.29	Dibromochloromethane	0.10	0.17	0.12
Methylene Chloride	0.18	0.15	0.25	2-Hexanone	0.16	0.14	0.22
acetonitrile		1.88	2.05	1,2-Dibromoethane	0.16	0.14	0.2
Tert Butyl Alcohol	0.25	0.30	1.10	Chlorobenzene	0.07	0.14	0.14
MTBE	0.09	0.08	0.19	1,1,1,2-Tetrachloroethane	0.15	0.21	0.18
cis-1,2-Dichloroethene	0.14	0.15	0.36	Ethylbenzene	0.11	0.07	0.17
acrylonitrile	19	0.17	0.29	Xylene (m + p)	0.11	0.17	0.25
Isopropylether	0.08	0.10	0.29	Styrene	0.12	0.11	0.08
Vinyl acetate	0.06	0.15	0.3	Xylene (o)	0.08	0.10	0.0
1,1-Dichloroethane	0.12	0.12	0.22	n-amyl acetate	0.04	0.11	0.23
Ethyl Tert Butyl Ether	0.04	0.06	0.22	Bromoform	0.13	0.27	0.30
trans-1,2-Dichloroethene	0.10	0.21	0.30	Isopropylbenzene	0.08	0.08	0.08
ethyl acetate	0.36	1.68	1.09	cis-1,4-dichloro-2-butene	0.10	0.50	0
2-Butanone	0.05	0.12	0.31	BFB SUR	0.13	0.17	0.23
2,2-Dichloropropane	07	0.18	0.18	Bromobenzene	0.08	0.20	0.22
Bromochloromethane	0.17	0.37	0.34	1,2,3-Trichloropropane	0.23	0.32	0.18
propionitrile	0.92	1.40	1.41	1,1,2,2-Tetrachloroethane	0.07	0.12	0.30
methacrylonitrile	0.09	0.17	0.43	n-Propylbenzene	0.11	0.11	0.19
THF	16	0.25	0.37	trans-1,4-dichloro-2-butene	0.15	0.18	0.30
Chloroform	0.19	0.14	0.35	2-Chlorotoluene	0.16	0.24	0.32
methyl acrylate	0.08	0.14	0.23	4-Chlorotoluene	0.16	0.20	0.12
Dibromofluoromethane SUR	0.11	0.18	0.33	1,3,5-Trimethylbenzene	0.06	0.09	0.12
1,1,1-Trichloroethane	0.13	0.21	0.22	tert-Butylbenzene	0.08	0.15	0.12
2-Chloroethylvinylether	0.15	0.18	0.37	sec-Butylbenzene	0.17	0.18	0.32
Carbon Tetrachloride	0.09	0.14	0.12	1,2,4-Trimethylbenzene	0.09	0.07	0.08
1,1-Dichloropropene	0.14	0.08	0.35	nitrobenzene	1.00	2.01	2.76
methyl acetate	0.06	0.07	0.37	1,3-Dichlorobenzene	0.07	0.17	0.0
isobutyl alcohol	1.23	3.29	1.86	1,4-Dichlorobenzene	0.17	0.16	0.21
Tert Amyl Methyl Ether	0.05	0.07	0.27	Isopropyltoluene	0.10	0.09	0.10
Benzene	0.07	0.14	0.23	1,2,-Dichlorobenzene	0.10	0.17	0.08
1,4-Dioxane	50	9.72	8.49	n-Butylbenzene	0.10	0.13	0.17
1,2-Dichloroethane	0.11	0.15	0.26	1,2-Dibromo-3-chloropropane	0.35	0.99	1.19
propyl acetate	0.06	0.10	0.24	1,2,4-Trichlorobenzene	0.17	0.23	0.42
Trichloroethene	0.11	0.24	0.20	Naphthalene	0.04	0.14	0.15
1,2-Dichloropropane	12	0.20	0.30	Hexachlorobutadiene	0.11	0.26	1.48
methyl methacrylate	0.16	0.18	0.26	1,2,3-Trichlorobenzene	0.16	0.12	0.34
Dibromomethane	0.33	0.46	1.05	Ave.	0.22	0.38	0.48
Bromodichloromethane	0.13	0.13	0.22				

Table 5: Method Detection Limit Summary

Data Summary			
Split	Ave. Curve Linearity	Ave. Compound Response	Ave. MDL
40:1	6.36	1.023	0.22
80:1	7.61	1.049	0.38
100:1	8.36	1.003	0.48

Table 6: Average Results for Each Split Ratio

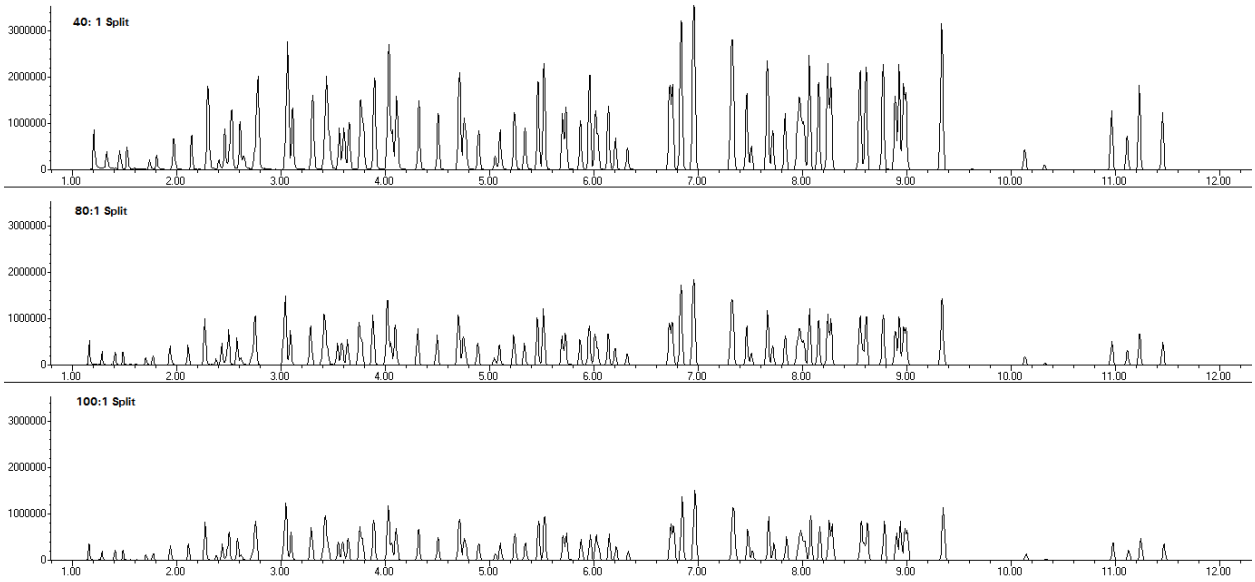

Figure 1: 50ppb Chromatograms of Each Split Ratio

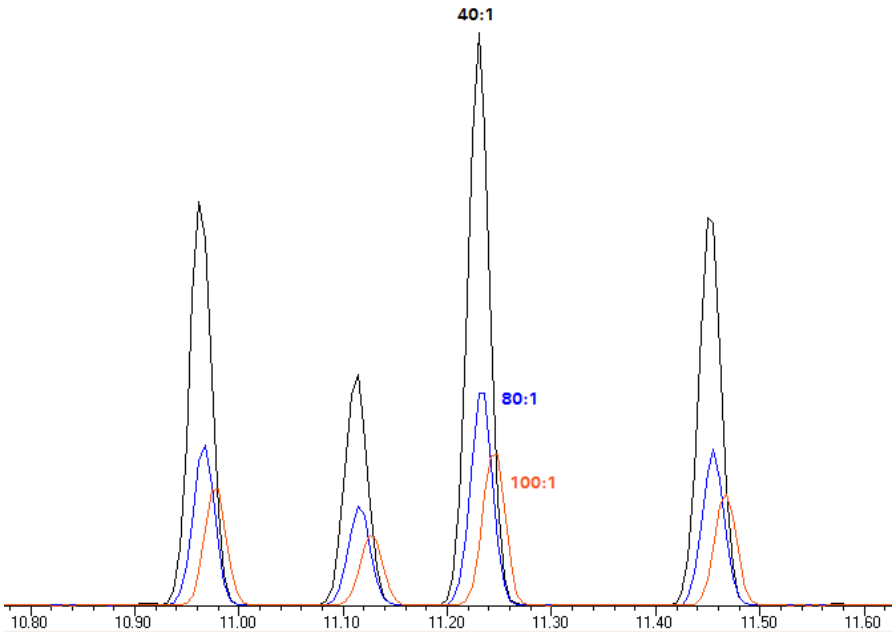

Figure 2: Chromatogram Overlay of the Last Four Analytes

Conclusions:

As USEPA Methods require lower and lower detection limits, split ratios will play a large factor in reaching these new requirements. This study demonstrated that all three split ratios met USEPA Method 8260 requirements for linearity, compound response and method detection limits. However, there was a remarkable difference in compound detection limits as the split ratio was increased. The 40 to 1 split rate had much lower detection limits due to an increase in compound response. The Encon Evolution purge and trap concentrator has a unique feature for moisture control using an eight port valve to avoid desorbing through the moisture trap. This feature enables better moisture control when using a lower split rate, thus using a larger split rate to control moisture is unnecessary.

References:

1. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); United States Environmental Protection Agency Method 8260B, Revision 2, December 1996.

For More Information

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