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Optimal Conditions for USEPA Method 8260B Analysis using the EST Analytical Sampling system and the Shimadzu GCMS-QP2010s

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Introduction:

The USEPA developed Method 8260B for the determination of Volatile Organic Compounds (VOCs) in an array of waste matrices.[1] Over the years, there have been many advances in purge and trap sampling and GCMS analysis. These advances have aided in carryover reduction, water management and reduced method detection levels. This paper will present the optimum pur e and trap and GCMS parameters used to generate both soil and water USEPA Method 8260B data.

Discussion:

As part of the process of purging the volatile target compounds from a water or soil matrix, water vapor can also be carried along with the purge gas. This moisture can trigger interference in the GCMS total ion chromatograms causing elevated detection levels, poor vacuum readings, and inconsistent analytical results. The management of this moisture prior to GC introduction is crucial in obtaining consistent and reliable data.

The EST Encon Evolution Purge and Trap Concentrator employs a unique Moisture Reduction Trap (MoRT) to decrease the amount of water vapor introduced to the GC. Unlike other concentrators, the Evolution positions the moisture management device before the analytical trap to remove the water from the purge gas as illustrated in Figure 1. Through the use of an 8-port valve, the Evolution's MoRT is excluded from the desorb pathway during the transfer of analytes to the GC as displayed in Figure 2.

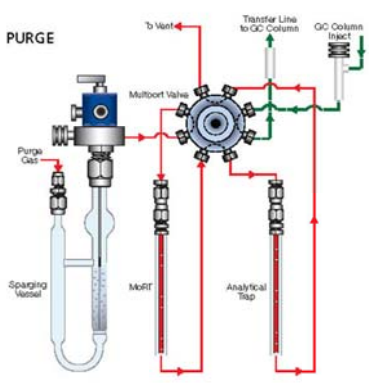

Figure 1: Purge Flow Path

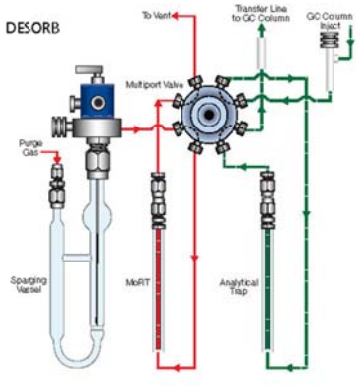

Figure 2: Desorb Flow Path

The Evolution's desorb pathway minimizes "dead volume" between the analytical trap and GC injection port to deliver superb peak resolutions and sensitivity over the entire chromatogram as shown in Figures 3 and 4.

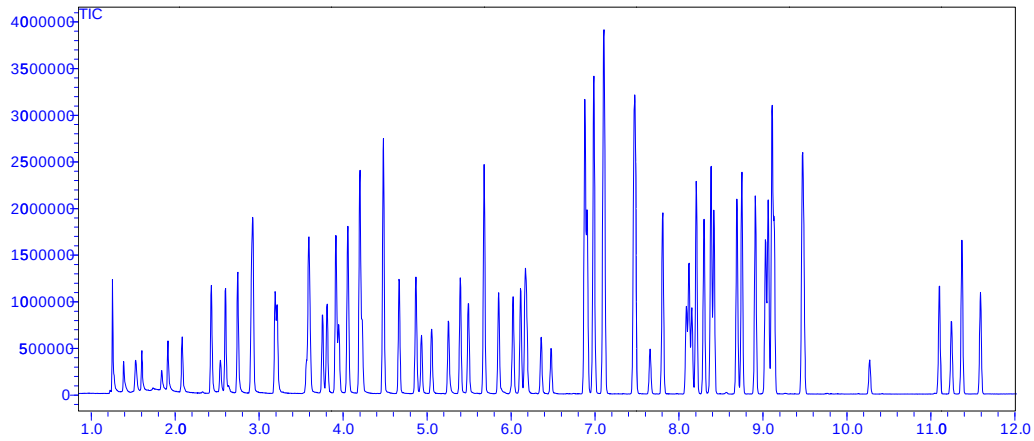

Figure 3: Total ion chromatogram of the 50ppb 8260B Water standard

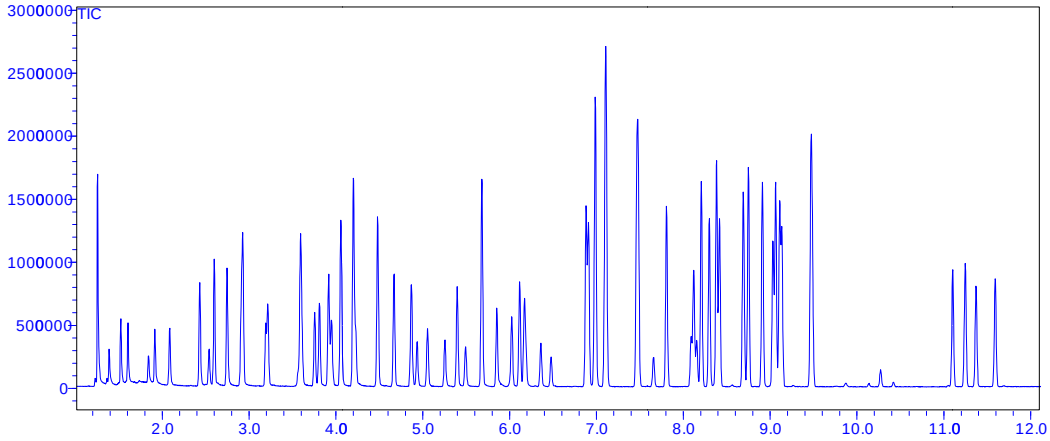

Figure 4: Total ion chromatogram of the 50ppb 8260B Soil standard

Another feature incorporated in the Encon Evolution which enables superior peak resolution is the Desorb Pressure Control (DPC) parameter. This feature allows the analytical trap to be pressurized prior to desorb. The balance of pressure between the trap and GC inlet assures the analytes are transferred in a tight band eliminating the surge in gas flow commonly associated with systems which do not balance pressure and use water management procedures during the critical desorb step.

Figure 5: Heated Sparge Vessel

As detection limits are pushed lower, carryover within the purge and trap system has become of greater concern. In the past, efforts have been made to reduce carryover with new tubing materials and programmable flow rates during the bake cycle, but little has been done to deal with primary cause of the carryover… the sparge vessel itself. The Evolution employs a patented mode which heats the sparge vessel during the bake process as shown in Figure 5. Since this heating takes place during the normal Evolution bake cycle, no additional time is added to the overall cycle time. The result is lower carryover which aids in superior analytical results.

Experimental Results:

The EST Analytical Centurion WS Autosampler and Encon Evolution Purge and Trap Concentrator were interfaced to a Shimadzu GCMS-QP2010s in order to determine the optimal conditions required to achieve the desired chromatographic resolution and sensitivity over the entire compound list in compliance with all USEPA Method 8260B criteria[1]. The system conditions used to obtain the results are shown in Tables 1, 2 and 3.

The linear range of the system was first established by analyzing a nine point calibration curve (0.5-200ppb) according to the outlined procedures in the method, while the internal standard concentration was held constant at 50ppb. The data were analyzed using GCMS Solution software. The percent Relative Standard Deviation (%RSD) for most of the compounds was below the method criteria of <15%. For the compounds with a %RSD >15%, linear calibration was used with a result of greater than 0.998. These calibration results are listed in Table 5.

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	150ºC
Transfer Line Temp.	150ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	11 min
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	50mL/min
Dry Purge Time	2.0 min
Desorb Pressure Control	On
Desorb Pressure	5psi
Desorb Time	0.5 min
Desorb Preheat Delay	5 sec.
Desorb Temp.	260ºC
Moisture Reduction Trap (MoRT) Bake Temp.	230ºC
Bake Temp	260ºC
Sparge Vessel Bake Temp.	120ºC
Bake Time	8
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Type	Water
Sample Fill Mode	Syringe
Sample Volume	5mL
Sample Prime Time	3 sec
Loop Equilibration Time	5 sec
Sample Transfer Time	15 sec
Syringe Rinse	On/25mL
Number of Syringe Rinses	2
Sample Loop Rinse	On/15 sec
Sample Loop Sweep Time	10 sec
Number of Sparge Rinses	Syringe/2
Rinse Volume	7mL
Rinse Transfer Time	20 sec
Rinse Drain Time	20 sec
Number of Foam Rinse Cycles	2
Water Heater Temp.	85°C
Internal Standard Vol.	5µl

Table 1: Purge and Trap Water Parameters

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	150ºC
Transfer Line Temp.	150ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	11 min
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	50mL/min
Dry Purge Time	2.0 min
Desorb Pressure Control	On
Desorb Pressure	5psi
Desorb Time	0.5 min
Desorb Preheat Delay	5 sec.
Desorb Temp.	260ºC
Moisture Reduction Trap (MoRT) Bake Temp.	230ºC
Bake Temp	260ºC
Sparge Vessel Bake Temp.	120ºC
Bake Time	8
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Type	Soil
Sample Fill Mode	Syringe
Sample Volume	10mL
Sample Prime Time	5 sec
Loop Equilibration Time	10 sec
Sample Transfer Time	15 sec
Syringe Rinse	On/25mL
Number of Syringe Rinses	1
Sample Loop Rinse	Off
Sample Loop Sweep Time	15 sec
Number of Sparge Rinses	Syringe/1
Rinse Volume	7mL
Rinse Transfer Time	20 sec
Rinse Drain Time	20 sec
Number of Foam Rinse Cycles	1
Water Heater Temp.	85°C
Sample Preheat Temp.	40°C
Soil Valve Temp.	85°C
Soil Transfer Line Temp.	150°C
Minimizer Time	2 min
Internal Standard Vol.	5µl

Table 2: Purge and Trap Soil Parameters

GC/MS	Shimadzu QP2010S
Injection Mode	Split
Injection Temp.	200ºC
Flow Control mode	Linear Velocity
Linear Velocity	45 cm/sec
Split Ratio	40:1
Purge Flow	0.0 ml/min
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Progra	45ºC hold for 1 min, ramp 15ºC/min to 220ºC, hold for 1.5 min
Ion Source Temp.	185ºC
Interface Temp.	180ºC
Solvent Cut Time	0.7 min
Event Time	0.20 sec
ACQ Mode	Scan
Scan Speed	1250
Start m/z	35
End m/z	265

Table 3: GCMS Parameters

The precision and accuracy of the method was determined by analyzing seven replicate standards spiked at 50ppb. Method Detection Limits (MDLs) were established by running seven replicate standards at 0.5ppb for all of the compounds with the exception of Acetone and 2-Butanone; these MDLs were run at 5ppb. Both the MDLs and the precision and accuracy results are listed in Table 5.

To demonstrate the Encon Evolution's ability to virtually eliminate carryover; two blank samples were analyzed immediately following a 200ppb standard. The carryover results of the last four heavy compounds in the first blank after the 200ppb standard are displayed in Table 4.

Compound	% Carryover
1,2,4-Trichlorobenzene	0.27
Naphthalene	0.20
Hexachlorobutadiene	0.24
1,2,3-Trichlorobenzene	0.27

Table 4: Percent Carryover Results

Compound	Water Results					Soil Results				
	Ave RF	Curve %RSD	MDL	50ppb Prec.	50ppb % Rec'y	Ave RF	Curve %RSD	MDL	50ppb Prec.	50ppb % Rec'y
Dichlorofluoromethane	0.303	7.48	0.17	8.89	85.13	0.346	11.81	0.20	8.89	92.33
Chloromethane	0.340	6.32	0.25	5.87	92.76	0.634	8.58	0.15	5.87	101.82
Vinyl Chloride	0.353	4.85	0.18	10.60	81.28	0.497	5.93	0.16	10.60	88.22
Bromomethane	0.108	11.14	0.28	6.06	88.87	0.180	13.77	0.30	6.06	97.75
Chloroethane	0.345	5.32	0.18	10.67	82.14	0.489	7.72	0.18	10.67	89.17
Trichlorofluoroethane	0.371	4.33	0.15	7.61	85.16	0.461	7.05	0.15	7.61	92.56
1,1-Dichloroethene	0.320	6.07	0.18	7.02	84.29	0.425	5.69	0.17	7.02	91.80
Acetone	0.228	12.30	0.50	11.39	98.79	0.665	0.998*	1.16	11.39	108.00
Iodomethane	0.356	13.28	0.16	3.13	76.73	0.410	0.999*	0.11	3.13	84.35
Carbon Disulfide	1.292	9.81	0.30	6.57	80.36	1.881	7.07	0.18	6.57	87.53
Methylene Chloride	0.738	4.92	0.12	4.11	84.65	0.882	4.52	0.12	4.11	93.18
MTBE	1.121	4.81	0.07	3.43	87.57	1.044	7.82	0.09	3.43	96.54
trans-1,2-dichoroethene	0.719	6.11	0.11	3.96	83.96	0.835	6.34	0.07	3.96	92.39
1,1-Dichloroethane	0.809	4.48	0.10	4.67	85.34	0.963	4.53	0.13	4.67	93.66
cis-1,2-dichloroethene	0.627	6.31	0.18	5.52	84.68	0.775	6.82	0.17	5.52	92.63
2-Butanone	0.412	5.15	0.56	7.79	100.80	0.252	6.44	1.13	7.79	110.21
2,2-Dichloropropane	0.431	6.44	0.12	4.73	84.53	0.558	6.26	0.22	4.73	92.68
Bromochloromethane	0.243	3.43	0.17	2.66	88.01	0.264	9.87	0.14	2.66	97.09
Chloroform	0.647	8.69	0.12	3.91	80.25	0.758	6.85	0.13	3.91	88.14
1,1,1-Trichloroethane	0.416	4.09	0.21	5.33	84.00	0.506	4.72	0.13	5.33	91.96
2-Chloroethylvinylether	0.184	7.15	0.11	2.99	80.32	0.142	6.03	0.18	2.99	88.67
Carbon Tetrachloride	0.317	4.67	0.12	6.03	86.45	0.383	8.50	0.18	6.03	94.52
1,1-Dichloropropene	0.530	5.88	0.18	6.46	83.57	0.678	7.08	0.10	6.46	91.06
Benzene	1.799	5.89	0.11	4.66	84.02	2.180	8.36	0.08	4.66	92.17
1,2-Dichloroethane	0.475	4.49	0.13	2.56	81.44	0.468	7.41	0.17	2.56	89.77
Trichloroethene	0.205	7.03	0.19	6.50	93.79	0.286	7.39	0.22	6.50	102.33
1,2-Dichloropropane	0.253	4.81	0.14	4.50	90.20	0.311	6.01	0.13	4.50	99.21
Dibromomethane	0.119	5.96	0.30	3.18	99.34	0.130	9.62	0.23	3.18	109.70
Bromodichloromethane	0.235	2.88	0.13	3.75	91.12	0.275	4.93	0.21	3.75	100.17
cis-1,3-Dichloropropene	0.352	4.46	0.18	3.33	93.42	0.404	8.09	0.11	3.33	103.02
Toluene	0.887	7.68	0.11	5.28	87.33	1.183	9.48	0.09	5.28	95.63
trans-1,3-Dichloropropene	0.281	8.11	0.11	2.33	94.16	0.286	9.45	0.08	2.33	104.10
1,1,2-Trichloroethane	0.183	5.19	0.09	3.48	92.05	0.184	9.61	0.14	3.48	101.37
Tetrachloroethane	0.138	6.08	0.26	6.55	91.04	0.188	6.88	0.16	6.55	99.29
1,3-Dichloropropane	0.355	4.84	0.12	3.22	91.04	0.351	8.06	0.20	3.22	100.38
Dibromochloromethane	0.172	5.85	0.11	2.72	93.77	0.181	6.85	0.28	2.72	103.45
2-Hexanone	0.293	5.76	0.09	5.89	104.23	0.191	9.35	0.17	5.89	114.38
1,2-Dibromoethane	0.195	8.16	0.14	3.51	91.25	0.176	8.77	0.23	3.51	100.56
Chlorobenzene	0.661	5.80	0.13	3.84	91.33	0.907	6.18	0.14	3.84	100.51
1,1,1,2-Tetrachloroethane	0.199	8.91	0.14	3.15	94.92	0.268	10.49	0.26	3.15	104.67
Ethylbenzene	1.119	8.86	0.09	5.27	91.09	1.580	9.54	0.14	5.27	99.79
Xylene (p&m)	1.806	8.60	0.09	4.88	90.03	2.591	10.13	0.12	4.88	98.79
Styrene	0.740	10.06	0.08	3.79	95.67	1.025	12.65	0.10	3.79	105.36
Xylene (o)	0.894	8.36	0.06	4.59	91.87	1.243	9.74	0.16	4.59	100.92
Bromoform	0.137	7.18	0.15	2.83	103.63	0.139	9.18	0.20	2.83	114.59
Isopropylbenzene	0.837	5.38	0.07	5.65	94.02	1.243	7.65	0.14	5.65	102.89
Bromobenzene	1.030	9.06	0.17	4.17	84.41	1.254	6.72	0.11	4.17	92.72
1,2,3-Trichloropropane	0.615	6.91	0.13	3.47	86.17	0.516	5.94	0.19	3.47	94.86
1,1,2,2-Tetrachloroethane	0.712	5.21	0.07	3.17	85.38	0.572	4.64	0.09	3.17	94.15
n-Propylbenzene	2.480	6.05	0.12	6.30	87.08	3.463	6.18	0.11	6.30	94.97
2-Chlorotoluene	0.531	6.22	0.15	4.93	86.87	0.735	6.51	0.17	4.93	95.07
4-Chlorotoluene	0.545	7.13	0.14	4.36	88.71	0.732	6.28	0.16	4.36	97.34
1,3,5-Trimethylbenzene	1.806	5.90	0.11	5.79	90.51	2.590	6.33	0.12	5.79	99.00
tert-Butylbenzene	1.406	6.52	0.09	6.62	89.15	1.999	6.78	0.18	6.62	97.16
sec-Butylbenzene	0.430	6.71	0.12	6.63	88.59	0.677	7.64	0.19	6.63	96.54
1,2,4-Trimethylbenzene	1.776	6.22	0.09	4.83	89.22	2.572	6.93	0.14	4.83	97.80
1,3-Dichlorobenzene	0.966	8.86	0.15	4.28	91.76	1.345	5.79	0.14	4.28	100.73
1,4-Dichlorobenzene	1.000	7.14	0.20	3.63	91.95	1.360	5.95	0.18	3.63	101.16
Isopropyltoluene	1.681	7.51	0.15	5.96	87.74	2.499	8.80	0.09	5.96	95.86
1,2-Dichlorobenzene	0.925	9.64	0.16	3.59	92.28	1.228	8.34	0.13	3.59	101.52
n-Butylbenzene	1.652	9.02	0.18	6.20	89.33	2.512	7.76	0.13	6.20	97.59
1,2-Dibromo-3-chloropropane	0.122	9.79	0.18	4.68	89.00	0.087	7.40	0.65	4.68	98.17
1,2,4-Trichlorobenzene	0.525	7.48	0.25	2.81	97.44	0.851	6.41	0.21	2.81	107.64
Naphthalene	1.857	9.92	0.13	3.77	84.44	1.740	7.47	0.25	3.77	93.09
Hexachlorobutadiene	0.283	8.10	0.22	6.29	94.53	0.681	7.35	0.20	6.29	103.14
1,2,3-Trichlorobenzene	0.494	9.21	0.15	3.07	95.79	0.787	6.32	0.16	3.07	105.93

*Curve Results were linear regressed.

Table 5: Curve, MDL and Precision and Accuracy Data

Conclusion:

The instrument configuration and operating conditions described above produced outstanding performance for USEPA Method 8260B. All quality control criteria were easily met or exceeded for both the water and soil matrices. In addition to the superior analytical performance of the Shimadzu GCMS-QP2010s, the EST Encon Evolution/Centurion WS sampling system offers a number of unique features and benefits. The features examined in this study include the patented mode which heats the sparge vessel during bake, Desorb Pressure Control for better peak shape and the Moisture Reduction Trap which reduces the amount of water transferred to the GC.

References:

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

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