Optimal Conditions for USEPA Method 8260 Analysis

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Introduction:

Over the past decade, the need for environmental laboratories using purge and trap systems to report at or below the Method Detection Limit (MDL) has created many new challenges. As a result of the required lower detection levels, water management, analyyte migrationand carryover reduction have become a critical concern to meet linear calibration criteria. This paper will present the optimum purge and trap system parameters used to generate USEPA Method 8260B data. The conditions utilized will provide the necessary sensitivity, linearity and accuracy compliant to the method. In particular, the revolutionary advancements used to virtually eliminate carryover and manage the moisture will be highlighted. Analytical results including calibrations factors, method detection limits and reproducibility data will be presented.

Discussion:

As part of the process of purging the volatile target compounds from a water matrix, water vapor can also be carried along with the purge gas. This moisture can trigger interference in the GC/MS 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.

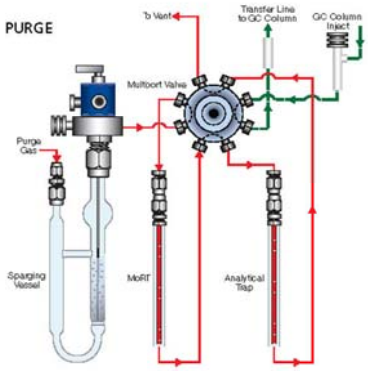

Figure 1: Purge Flow Path

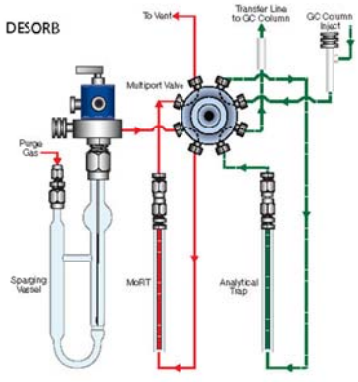

Figure 2: Desorb Flow Path

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 Figure 3.

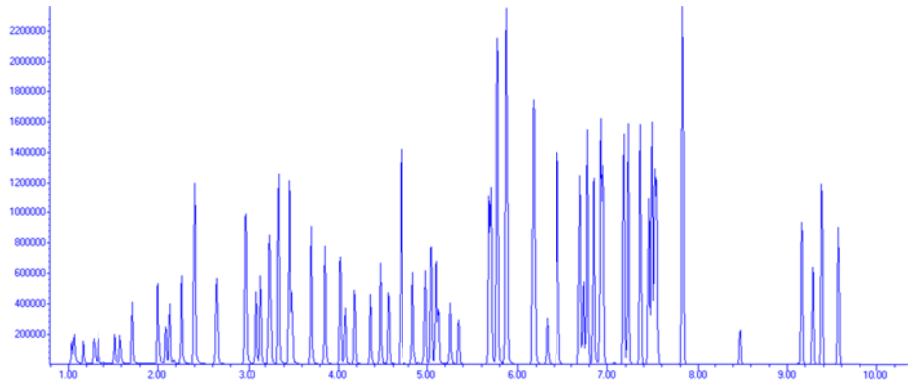

Figure 3: Total ion chromatogram of the 50ppb 8260B standard

Another feature incorporated in the Encon Evolution which enables superior peak resolution is the Desorb Pressure Control (DPC) parameter. This feature allows the trap to be pressurized to near to the GC inlet pressure 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.

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 s arge vessel itself. The Evolution employs a patented mode which heats the sparge vessel during the bake process as shown in Figure 4. Since this heat 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.

Figure 4: Sparge Heater

A further problem associated with producing quality analytical data is internal standard reproducibility. The EST Centurion WS Autosampler eliminates this problem by utilizing a unique delivery mechanism consisting of no moving components. The volume programmable valve injects the internal standard directly into the sample stream rather than passing the sample through a fixed volume loop or valve.

Experimental Results:

The EST Analytical Centurion WS Autosampler and Encon Evolution Purge and Trap Concentrator were interfaced to a GC/MSD in order to determine the optimal conditions required to achieve the desired chromatographic resolutions and sensitivity over the entire compound list in compliance with all USEPA Method 8260B criteria. The system conditions used to obtain the results are shown in Tables 1 and 2.

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. The internal standard concentration was held constant at 50ppb. The perc nt relative standard deviation (%RSD) for each compound were below the method criteria of <15%. These results are listed in Table 4.

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	130ºC
Transfer Line Temp.	130ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
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	12psi
Desorb Time	1.0 min.
Desorb Temp.	260ºC
Moisture Reduction Trap (MoRT) Ba e Temp.	230ºC
Bake Temp	260ºC
Sparge Vessel Bake Temp.	110ºC
Bake Time	8
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Size	5mL
Internal Standard Volume	5µL

Table 1: Purge and Trap Parameters

GC/MS	Agilent 6890A/5973 inert XL
Inlet	Split/Splitless
Inlet Temp.	200ºC
Inlet Head Pressure	17.311 psi
Mode	Split
Split Ratio	40:1
Column	Rxi-624Sil MS 20m x 0.18mm I.D. 1µm film thickness
Oven Temp. Progra	45ºC hold for 1 min., ramp 18ºC/min to 220ºC, hold for 0.3 min.
Column Flow Rate	0.8mL/min
Gas	Helium
Total Flow	38.8mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 35-265
Scans	3.12 scans/sec
Solvent Delay	0.7 min

Table 2: GC/MS Parameters

The precision and accuracy of the method was determined by analyzing seven replicate standards spiked at 50ppb. Method detection limits were established by running seven replicate standards at 1ppb. Both the MDLs and the precision and accuracy results are listed in Table 4.

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 3.

Compound	% Carryover
1,2,4-Trichlorobenzene	0.20
Naphthalene	0.24
Hexacholorbutadiene	0.19
1,2,3-Trichlorobenzene	0.21

Table 3: Percent Carryover Results

In order to the present the precision of the internal standard delivery system, the internal standard compound response was analyzed over the 10 replicate samples at a concentration of 1ppb. The precision is expressed as %RSD and the results are displayed in Figure 5.

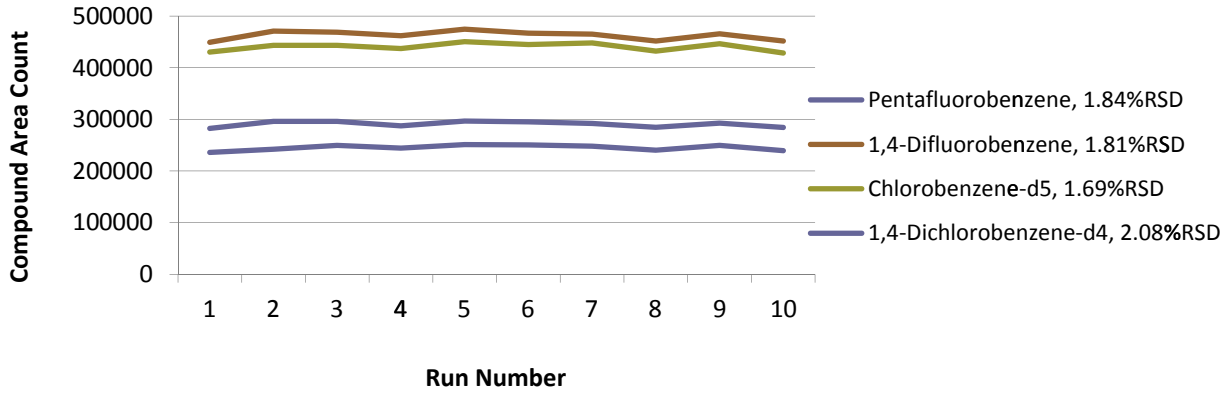

Figure 5: The Internal Standard Delivery Precision

Compound	Curve %RSD	Ave. Curve RF	MDL	50ppb %Recovery	50ppb %RSD
Dichlorodifluoromethane	10.97	0.309	0.18	90.76	4.82
Chloromethane	5.01	0.614	0.09	91.19	4.74
Vinyl Chloride	5.11	0.529	0.13	96.94	5.05
Bromomethane	6.70	0.291	0.22	98.74	4.70
Chloroethane	4.67	0.387	0.16	97.93	4.74
Trichlorofluoromethane	5.77	0.685	0.11	98.28	5.18
1,1-Dichloroethene	6.80	0.400	0.19	100.10	5.05
Acetone	7.22	0.189	0.25	100.01	3.44
Iodomethane	12.65	0.592	0.12	102.45	4.01
Carbon Disulfide	10.42	1.270	0.13	90.28	5.57
Methylene Chloride	3.17	0.514	0.07	97.12	3.63
MTBE	5.43	1.501	0.08	97.60	2.72
trans-1,2-Dichloroethene	5.05	0.576	0.06	98.13	3.70
Vinyl acetate	7.01	1.372	0.21	80.03	9.52
1,1-Dichloroethane	6.04	1.015	0.16	100.33	4.09
cis-1,2-Dichloroethene	4.59	0.496	0.17	98.90	4.90
2-Butanone	6.83	0.367	0.15	92.73	2.65
2,2-Dichloropropane	2.13	0.721	0.06	84.26	5.47
Bromochloromethane	8.24	0.348	0.10	100.38	2.95
Chloroform	3.16	0.910	0.15	98.38	3.78
1,1,1-Trichloroethane	4.04	0.812	0.14	98.22	4.87
2-Chloroethylvinylether	7.15	0.431	0.18	99.80	2.47
Carbon Tetrachloride	8.21	0.677	0.15	102.37	5.20
1,1-Dichloropropene	3.91	0.762	0.13	98.15	5.02
Benzene	1.18	2.301	0.11	96.51	4.27
1,2-Dichloroethane	6.42	0.775	0.07	99.60	2.69
Trichloroethene	3.89	0.384	0.16	101.51	3.32
1,2-Dichloropropane	2.66	0.364	0.09	101.72	3.34
Dibromomethane	4.30	0.210	0.14	102.60	3.14
Bromodichloromethane	3.49	0.436	0.14	101.43	2.95
cis-1,3-Dichloropropene	3.31	0.540	0.08	99.47	2.96
Toluene	2.26	0.905	0.08	98.56	4.16
trans-1,3-Dichloropropane	3.17	0.462	0.09	99.16	2.79

Compound	Curve %RSD	Ave. Curve RF	MDL	50ppb %Recovery	50ppb %RSD
Tetrachloroethene	4.35	0.278	0.15	104.80	4.79
1,3-Dichloropropane	1.46	0.544	0.14	100.64	2.66
Dibromochloromethane	3.51	0.343	0.10	102.65	2.47
2-Hexanone	5.53	0.332	0.09	105.84	2.95
1,2-Dibromoethane	2.44	0.310	0.12	101.88	2.28
Chlorobenzene	2.79	1.043	0.07	96.25	3.40
1,1,1,2-Tetrachloroethane	4.78	0.282	0.18	98.76	4.91
Ethylbenzene	1.94	1.852	0.13	98.61	4.51
Xylene (m+p)	1.81	1.430	0.19	96.73	3.96
Styrene	1.14	1.185	0.09	96.64	3.35
Xylene (o)	1.40	1.431	0.07	97.50	3.71
Bromoform	4.95	0.257	0.07	102.04	2.95
Isopropylbenzene	2.57	1.611	0.10	100.18	4.39
Bromobenzene	2.37	1.240	0.06	94.16	2.84
1,2,3-Trichloropropane	3.30	0.704	0.10	96.26	2.45
1,1,2,2-Tetrachloroethane	1.61	0.818	0.09	91.43	2.37
n-Propylbenzene	2.91	3.800	0.12	96.94	3.92
2-Chlorotoluene	1.73	0.787	0.13	95.78	3.87
4-Chlorotoluene	2.08	0.796	0.13	95.00	3.73
1,3,5-Trimethylbenzene	2.20	2.730	0.07	96.46	3.66
tert-Butylbenzene	1.86	2.394	0.08	96.92	4.32
sec-Butylbenzene	2.27	0.727	0.10	96.98	4.45
1,2,4-Trimethylbenzene	2.02	2.818	0.07	95.72	3.56
1,3-Dichlorobenzene	1.82	1.474	0.08	95.06	3.28
1,4-Dichlorobenzene	5.02	1.537	0.04	92.16	3.06
Isopropyltoluene	1.46	2.965	0.11	96.15	3.94
1,2,-Dichlorobenzene	2.52	1.405	0.09	94.72	2.77
n-Butylbenzene	1.50	2.651	0.10	97.11	4.11
1,2-Dibromo-3-chloropropane	6.99	0.166	0.19	98.12	2.87
1,2,4-Trichlorobenzene	2.19	0.932	0.10	95.18	2.70
Naphthalene	3.25	2.934	0.08	97.86	2.42
Hexachlorobutadiene	2.74	0.387	0.21	94.51	3.96
1,2,3-Trichlorobenzene	1.92	0.891	0.09	96.67	2.80

Table 4: 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. In addition to its superior analytical performance, the EST Encon Evolution and Centurion WS Autosampler also offer a number of other unique features and benefits. These include a patented mode which heats the sparge vessel during bake, the fiber optic foam sensor, and the electronic pressure control system with built in diagnostics including an automatic leak check for guaranteed system integrity assurance.