Analytical Trap Comparison for USEPA Method 8260C

Application Note

Abstract

Purge and trap concentration is a technique that is used for the analysis of Volatile Organic Compounds (VOCs). The major component of any purge and trap system is the analytical trap. This trap is responsible for retaining the VOCs during the purge cycle and then releasing them upon heating and transfer to the GC/MS for separation and detection.

While most standard methods define the dimensions of the trap as well as the recommended packing materials, there are multiple packing choices that can be substituted as long as they meet the analytical requirements of the method. For this study, four analytical traps commonly used for purge and trap analysis will be compared using an automated VOC sample prep system. Linear calibrations and Method Detection Limits (MDLs) will be established for US EPA Method 8260C[1] compounds for each trap.

Introduction

A common technique used in the analysis of drinking/waste water is Purge and Trap Concentration (PTC). PTC is used for determining the VOCs that are present in drinking/waste water. The major component of any PTC system is the analytical trap. This allows the analytes to be trapped and concentrated before being desorbed and sent to the GC/MS for separation and detection.

Analytical traps are generally packed with multiple beds of adsorbent materials, to allow for differentiation of a broad range of compounds. The weaker adsorbent bed is placed on the top side of the trap, while the stronger adsorbent bed is placed below the weaker adsorbent bed. The less volatile analytes are not effectively desorbed by the stronger adsorbent material; they are retained in the weaker adsorbent bed. In turn the less volatile analytes fail to reach the stronger adsorbent bed, so only the most volatile analytes reach the stronger adsorbent bed due to the volatility. Desorption is carried out by back-flushing the analytical trap using the Gas Chromatograph (GC) carrier gas flow (Helium).

Key features for an analytical trap are as follows[2]:

1. At low temperatures, it must retain the desired analytes while allowing oxygen and water to pass through unimpeded.
2. Must release the analytes quickly and efficiently upon heating.
3. Must not contribute any volatiles of interest to the analysis.
4. Should have a reasonable price and lifetime.

Most standard methods, such as USEPA Method 8260C[1], define the dimensions of the analytical trap as well as the recommended packing materials. Multiple packing material choices can be substituted as long as they meet the method requirements. In this study, four analytical traps commonly used in P&T analysis (Tekmar #9, “3” analytical trap, Vocarb 3000 and Vocarb 4000) will be compared using USEPA Method 8260C. **Table 1** outlines the selected traps and their characteristics.

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Trap Name.	Adsorbent Material	Analytes that are retained	Dry Purge Capability	Desorb preheat temp	Desorb temp	Bake temp
3	Tenax Silica Gel Charcoal	Everything including freons	No	180 ˚C	185˚C	230 ˚C
9	Proprietary	Everything including freons	Yes	245 ˚C	250 ˚C	260 ˚C
Supelco Vocarb 3000	Carbopak B Carboxen 1000 Carboxen 1001	Everything including freons	Yes	245 ˚C	240-250 ˚C	260 ˚C
Supelco Vocarb 4000	Carbopak C Carbopak B Carboxen 1000 Carboxen 1001	Everything except 2-chloro-ethyl-vinyl-ether	Yes	245 ˚C	250 ˚C	260 ˚C

Table 1: Characteristics and operating parameters for selected Analytical Traps.[2]

For this study, Teledyne Tekmar's Atomx, an automated VOC sample prep system, was used in conjunction with an Agilent 7890/5975 GC/MS to evaluate each trap presented in **Table 1** for USEPA Method 8260C. Different compound classes (gases, polar compounds, halogens, aromatics, and high boiling point/ late eluting compounds) will be evaluated for each trap.

Experimental-Instrument Conditions

The Atomx, equipped with each trap, and an Agilent 7890A GC with a 5975C inert XL MSD were utilized for this study. **Tables 2-4** show the GCMS and PTC parameters for this study.

GC Parameters	
GC:	Agilent 7890A
Column	Restek RTX-VMS 20 m x 0.18mmID x 1µm
Oven Program:	40 °C for 4min; 16 °C/min to 100 °C for 0min; 30 °C /min to 200 °C for 4min, 15.083min runtime
Inlet:	220 °C
Column Flow	0.9mL/min
Gas:	Helium
Split:	100:1
Pressure:	21.542psi
Inlet:	Split/Split less

MSD Parameters	
MSD:	5975C TAD
Source:	250 °C
Quad:	200 °C
Solvent Delay:	0.5min
Scan Range:	m/z 35-270
Scans:	5.76 scans/sec
Threshold:	150
MS Transfer Line Temp:	230 °C

Tables 2 & 3: GC and MSD Parameters

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Atomx Water Parameters			
Variable	**Value**	**Variable**	**Value**
Valve oven Temp	140 °C	Dry Purge Time	2.00min
Transfer Line Temp	140 °C	Dry Purge Flow	100mL/min
Sample Mount Temp	90 °C	Dry Purge Temp	20 °C
Water Heater Temp	90 °C	Methanol Needle Rinse	Off
Sample Vial Temp	20 °C	Methanol Needle Rinse Volume	3.0mL
Sample Equilibrate Time	0.00min	Water Needle Rinse Volume	7.0mL
Soil Valve Temp	100 °C	Sweep Needle Time	0.50min
Standby Flow	10mL/min	GC Start Signal	Start of Desorb
Purge Ready Temp	40 °C	Desorb Time	1.50min
Condensate Ready Temp	45 °C	Drain Flow	300mL/min
Presweep Time	0.25min	Methanol Glass rinse	Off
Prime Sample Fill Volume	3.0mL	Number of Methanol Glass Rinses	1
Sample Volume	5.0mL	Methanol Glass Rinse Volume	3.0mL
Sweep Sample Time	0.25min	Number of Bake Rinses	1
Sweep Sample Flow	100mL/min	Water Bake Rinse Volume	7.0mL
Sparge Vessel Heater	On	Bake Rinse Sweep Time	0.25min
Sparge Vessel Temp	40 °C	Bake Rinse Sweep Flow	100mL/min
Prepurge Time	0.00min	Bake Rinse Drain Time	0.40min
Prepurge Flow	0mL/min	Bake Time	2.00min
Purge Time	11.00min	Bake Temp	280 °C
Purge Flow	40mL/min	Bake Flow	400mL/min
Purge Temp	20 °C	Condensate Bake Temp	200 °C
Condensate Purge Temp	20 °C		

Table 4: Atomx Water Parameters (Parameters highlighted in yellow were not used.) ***
Specific parameters were applied to each trap regarding dry purge, desorb preheat temperature, desorb temperature, and bake temperature from ***Table 1.***

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Calibration-Minimum Detection Limits (MDL)

A 50ppm working calibration standard was prepared in methanol. Calibration standards were then serially diluted with de-ionized water to the final calibration concentration level. The water calibration ranged from 0.5-200ppb. A 25ppm internal standard (IS) was prepared in methanol and transferred to one of the three standard addition vessels on the Atomx. Using the standard addition feature, the Atomx transferred the internal standard in 5µL aliquots to the sample providing a constant 25ppb final concentration.

Aglient ChemStation software was used to process the calibration and MDL data. The relative response factors (RRF) of all target analytes were evaluated for average RRF and percent relative standard deviation (%RSD) over the calibrated range. MDLs were established for all compounds by analyzing seven replicates at a 1.0 and 5.0ppb. The percent carry over was also evaluated for each analytical trap.

Results and Chromatograms

A. Gases

When comparing the analytical traps for the gaseous compounds, i.e.: dichlorodifluoromethane, chloromethane, vinyl chloride, bromomethane, chloromethane and trichloromonofluoromethane, there were clear differences between the four analytical traps. The biggest difference observed when utilizing the #3 analytical trap is that the low level (0.5ppb) is hindered by the water front. This issue correlates the lack of dry purge utilized with the #3 trap. The #3 analytical trap cannot be dry purged due to the trapping material present in the trap. This issue is presented in **Table 5** when comparing the MDL for all the traps. The #3 analytical trap had MDL ranging from 0.143-1.316ppb, while all the other traps were below 0.50ppb.

	Tekmar # 9 Trap				Vocarb 3000				# 3 Trap				Vocarb 4000			
Compound	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike
Dichlorodifluoromethane	0.318	10.02	0.164	1	0.253	10	0.140	1	0.17	8.93	1.092	5	0.417	5.01	0.386	1
Chloromethane	0.425	3.27	0.222	1	0.571	12.89	0.444	1	0.317	5.48	0.143	1	0.639	6.16	0.151	1
Vinyl Chloride	0.471	6.4	0.143	1	0.439	5.4	0.198	1	0.342	7.91	1.046	5	0.535	4.03	0.241	1
Bromomethane	0.464	0.9997*	0.250	1	0.227	9.89	0.364	1	0.279	4.77	0.162	1	0.212	13.93	0.444	1
Chloroethane	0.274	15.67	0.212	1	0.267	16.65	0.279	1	0.239	5.46	1.316	5	0.280	0.9950	0.129	1
Trichloromonofluoromethane	0.695	4.3	0.113	1	0.693	6.01	0.152	1	0.382	13.53	0.278	1	0.712	5.1	0.318	1

Table 5: Calibration and MDL data for gaseous compounds.
**using linear regression (r^2)*

Table 5 shows the Average Response Factor (Avg RF), the %RSD, the MDL and the level the MDL was spiked. Across the board all the gaseous compounds passed on all traps using the USEPA 8260C method except the #3 analytical trap because the low level could not be reached.

Another major difference between the four analytical traps is the recovery of Bromomethane recoveries using the Tekmar #9 trap are almost double that of the other traps. An Extracted Ion Chromatogram Profile (EICP) for the Ion with the m/z at 94 shows (**Figure 1**) the increased response using a Tekmar #9 trap.

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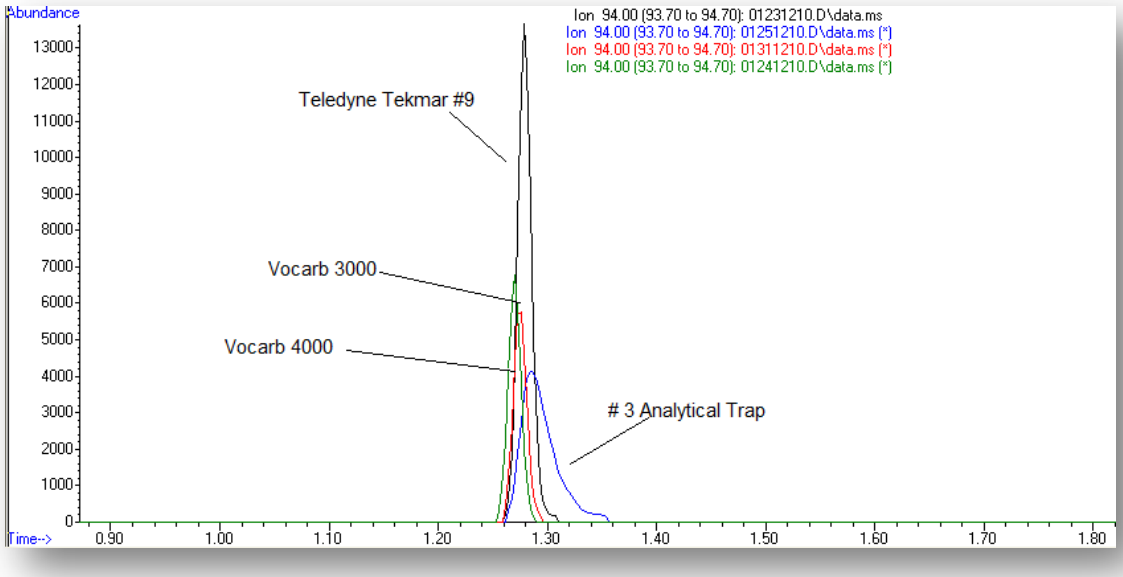

Figure 1: EICP of m/z 94 of Bromomethane for all four analytical traps evaluated at 10ppb.

B. Polar Compounds (Ketones and Ethers)

The hardest group of compounds to recover in the Purge and Trap analysis is the polar compound group. The hydrogen bonding associated with these compounds makes them difficult to purge out of water. In USEPA Method 8260C, most of polar compounds are listed as poor purgers (pp), or high temperature (ht, purge 40 ˚C or higher). Because of this all samples were heated to 40 ˚C using the sparge vessel heater to help improve recovery of all polar compounds. **Table 6** shows the calibration and MDL data for the polar compounds that are either ht or pp for the 8260C compound list.[1] All compounds met the USEPA 8260C performance criteria.[1]

	Tekmar # 9 Trap				Vocarb 3000				# 3 Trap				Vocarb 4000			
Compound	**Avg RF**	**%RSD**	**MDL**	**Spike**	**Avg RF**	**%RSD**	**MDL**	**Spike**	**Avg RF**	**%RSD**	**MDL**	**Spike**	**Avg RF**	**%RSD**	**MDL**	**Spike**
Diethyl Ether	0.330	9.49	0.212	1	0.321	8.28	0.297	1	0.286	2.99	0.083	1	0.314	4.87	0.161	1
Acetone	0.439	0.9985*	0.265	1	0.545	0.9992*	0.546	1	0.483	0.9995*	0.310	1	0.630	0.9985*	0.213	1
Methyl-tert-butyl Ether (MTBE)	1.713	4.41	0.068	1	1.74	6.34	0.093	1	0.817	13.5	0.149	1	1.658	6.37	0.061	1
Ethyl-tert-butyl Ether (ETBE)	1.611	2.79	0.026	1	1.582	3.34	0.129	1	1.009	9.46	0.186	1	1.528	3.47	0.146	1
2-Butanone (MEK)	0.165	2.06	0.510	5	0.153	9.95	1.042	5	0.146	7.9	0.788	5	0.151	10.89	0.382	5
Tetrahydrofuran	0.654	17.85	0.174	1	0.6	4.55	0.133	1	0.528	5.05	0.143	1	0.533	8.61	0.202	1
tert-Amyl Methyl Ether (TAME)	1.545	5.69	0.097	1	1.529	2.86	0.079	1	1.189	13.6	0.123	1	1.489	2.34	0.096	1
2-Chloroethyl Vinyl Ether (CLEVE)	0.316	4.63	0.174	1	0.314	7.15	0.166	1	0.277	7.58	0.134	1	0.26	15.98	0.101	1
4-Methyl-2pentanone	0.816	10.46	0.124	1	0.776	4.2	0.189	1	0.683	2.11	0.104	1	0.702	3.65	0.120	1
2-Hexanone	0.778	10.57	0.185	1	0.736	5.72	0.154	1	0.668	4.25	0.162	1	0.66	3.18	0.094	1
Tert-Butyl Alcohol	0.096	6.06	1.467	10	0.077	7.66	2.213	10	0.072	7.5	3.064	10	0.084	3.1	1.131	10

Table 6: Calibration and MDL data for polar compounds.

** using linear regression (r^2)*

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On the USEPA Method 8260C list, 2-Butanone (MEK) and 4-Methyl-2-Pentanone are labeled as poor purgers.[1] **Table 6** shows that MEK data has a better %RSD on the Tekmar #9 trap, while 4-Methyl-2-Pentanone has a better %RSD on the #3 analytical trap.

C. Halogens (Chlorinated and Brominated)

The most reactive compounds on the USEPA 8260C list are generally the chlorinated and brominated compounds. Typically, these compounds can be used to monitor the performance of the analytical trap. The compounds selected for this study are listed in Table 7. For example declining recoveries of 2,2-dichloropropane might be an indication of an active site in the system or trap wear. Other compounds that are effected by trap condition are bromoform, dibromofluoromethane, 2, 2-dichloropropane, and bromomethane. As Table 7 shows the selected few chlorinated and brominated compounds all pass and exceed the requirements for USEPA Method 8260C.

	Tekmar # 9 Trap				Vocarb 3000				# 3 Trap				Vocarb 4000			
Compound	**Avg RF**	**%RSD**	**MDL**	**Spike**	**Avg RF**	**%RSD**	**MDL**	**Spike**	**Avg RF**	**%RSD**	**MDL**	**Spike**	**Avg RF**	**%RSD**	**MDL**	**Spike**
Chloromethane	0.425	3.27	0.222	1	0.571	12.890	0.444	1	0.317	5.48	0.144	1	0.639	6.16	0.151	1
2,2-Dichloropropane	0.690	4.48	0.219	1	0.682	4.480	0.157	1	0.374	4.63	0.217	1	0.616	8.86	0.317	1
Chloroform	0.858	2.00	0.062	1	0.880	4.840	0.107	1	0.817	1.82	0.118	1	0.860	2.82	0.102	1
Dibromomethane	0.249	3.75	0.163	1	0.229	14.960	0.185	1	0.228	10.46	0.114	1	0.243	7.62	0.149	1
Bromodichloromethane	0.443	4.56	0.170	1	0.450	6.360	0.100	1	0.422	6.22	0.123	1	0.438	5.79	0.194	1
1,1,2-Trichloroethane	0.293	2.63	0.175	1	0.287	11.410	0.119	1	0.272	9.75	0.121	1	0.287	7.83	0.165	1
Bromoform	0.356	10.52	0.205	1	0.344	12.330	0.168	1	0.337	10.48	0.080	1	0.351	11.82	0.096	1
Tetrachloroethylene	0.427	11.14	0.224	1	0.299	6.310	0.159	1	0.286	7.60	0.307	1	0.290	5.29	0.455	1

Table 7: Calibration and MDL data for halogenated compounds.

A major difference between analytical traps is the increased recovery of tetrachloroethylene using the Tekmar #9 trap, almost double that of other traps. An Extracted Ion Chromatogram Profile (EICP) for the Ion with the m/z at 166 shows (**Figure 2**) difference in response for tetrachloroethylene.

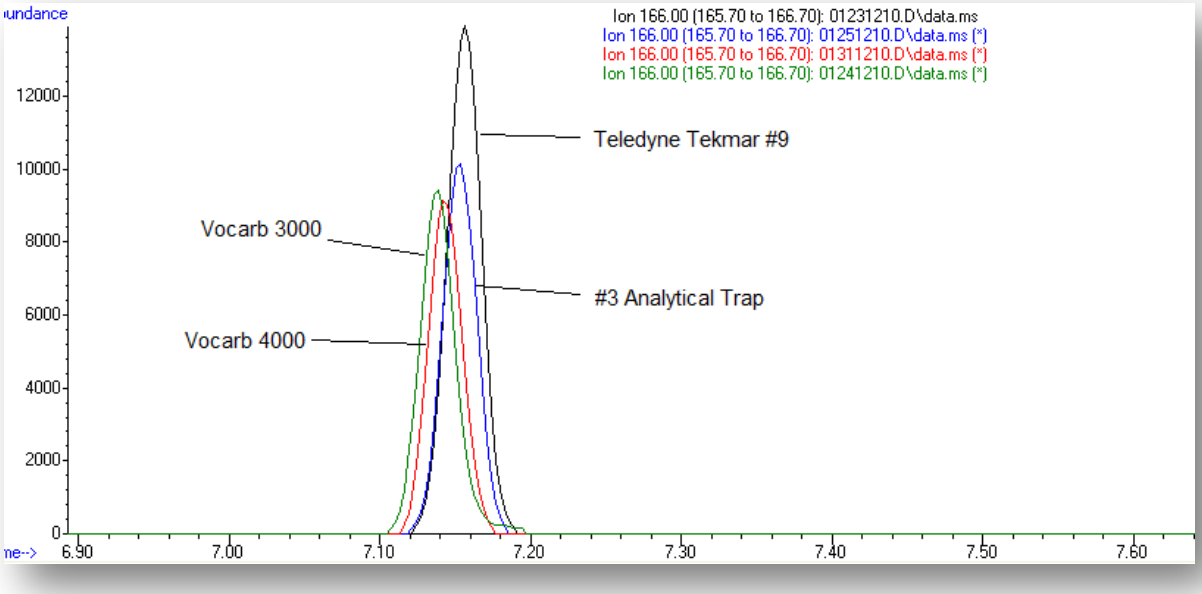

Figure 2: EICP of m/z 166 for Tetrachloroethylene for all four analytical traps evaluated at 10ppb.

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D. Aromatic Compounds

Aromatic compounds are the most stable in the USEPA Method 8260C compound list due to their structures. Since the trapping materials employed for these compounds are similar there are no clear advantages between the traps for these compounds. **Table 8** shows similarities between the Avg RF, %RSD and the MDL across all traps.

	Tekmar # 9 Trap				Vocarb 3000				# 3 Trap				Vocarb 4000			
Compound	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike
Benzene	1.94	4.3	0.131	1	1.942	4.18	0.156	1	1.84	2.4	0.092	1	1.932	2.21	0.154	1
Toluene	1.417	3.51	0.082	1	1.393	2.63	0.104	1	1.377	2.49	0.060	1	1.39	2.86	0.168	1
Ethylbenzene	1.777	2.88	0.094	1	1.752	2.25	0.083	1	1.718	2.12	0.126	1	1.699	3.09	0.199	1
m-,p-Xylene	0.671	3.13	0.132	2	0.65	2.74	0.260	2	0.646	2.89	1.057	2	0.649	4.39	0.386	2
o-Xylene	0.65	3.04	0.144	1	0.636	2.72	0.193	1	0.629	3.28	0.097	1	0.632	4.14	0.192	1
2-Chlorotoluene	2.194	3.69	0.139	1	2.1	4.52	0.140	1	2.038	3.15	0.132	1	1.945	1.93	0.271	1
1,3,5-Trimethylbenzene	2.55	3.93	0.128	1	2.45	3.66	0.097	1	2.398	2.43	0.143	1	2.359	2.73	0.239	1
4-Chlorotoluene	2.283	3.54	0.147	1	2.218	3.78	0.111	1	2.126	3.23	0.149	1	2.057	2.65	0.255	1
1,2,4-Trimethylbenzene	2.611	2.86	0.145	1	2.509	3.51	0.118	1	2.447	3.37	0.089	1	2.415	2.38	0.215	1
1,3-Dichlorobenzene	1.534	1.53	0.157	1	1.524	4.54	0.135	1	1.488	2.54	0.085	1	1.436	1.84	0.502	1
1,4-Dichlorobenzene	1.594	4.4	0.128	1	1.551	2.47	0.136	1	1.508	2.79	0.156	1	1.485	2.7	0.259	1
1,2-Dichlorobenzene	1.527	4.32	0.102	1	1.479	1.55	0.090	1	1.432	3.09	0.088	1	1.422	2.18	0.183	1

Table 8: Calibration and MDL data for aromatic compounds

E. High Boiling Point/Late Eluting Compounds and Carry Over

These perform similarly to the aromatic compounds but the main differences are that they have higher boiling points and late elution times. **Table 9** shows the Avg RF, %RSD and the MDL data for all traps.

	Tekmar # 9 Trap				Vocarb 3000				# 3 Trap				Vocarb 4000			
Compound	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike	Avg RF	%RSD	MDL	Spike
1,2,4-Trichlorobenzene	1.175	8.98	0.244	1	1.15	6.89	0.120	1	1.174	9.08	0.149	1	1.119	4.85	0.417	1
Hexachlorobutadiene	0.549	10.9	0.202	1	0.558	5.27	0.125	1	0.563	9.89	0.149	1	0.501	7.06	0.424	1
Naphthalene	4.064	6.83	0.092	1	3.823	5.96	0.098	1	3.852	8.02	0.092	1	3.611	5.67	0.097	1
1,2,3-Trichlorobenzene	1.143	9.04	0.146	1	1.118	7.06	0.160	1	1.14	8.55	0.179	1	1.095	4.21	0.286	1

Table 9: Calibration and MDL data for the late eluting compounds

One key difference between all four traps is carry over. Heavier compounds such as Napthalene, 1,2,4 and 1,2,3-Trichlorobenzene exhibit the highest amount of carry over. This is due in part to incomplete desorption and cause a gradual rise in the bake back-pressure. The Vocarb 4000 trap has the highest bake pressure that averaged out to be 32.79psi. This high back-pressure caused the Vocarb 4000 trap to fail the carry over study (**Table10**). The carry over study involved running a blank after the highest calibration point (200ppb). The concentration for each compound in the blank should be less than 1.0ppb (less than 0.5% of 200ppb).

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	Tekmar # 9 Trap			Vocarb 3000			# 3 Trap			Vocarb 4000		
Compound	Carry Over (ppb)	Max Carry Over (ppb)	<1ppb	Carry Over (ppb)	Max Carry Over (ppb)	<1ppb	Carry Over (ppb)	Max Carry Over (ppb)	<1ppb	Carry Over (ppb)	Max Carry Over (ppb)	<1ppb
1,2,4-Trichlorobenzene	0.99	1	Pass	0.84	1	Pass	0.85	1	Pass	2.01	1	Fail
Hexachlorobutadiene	0.89	1	Pass	0.82	1	Pass	0.89	1	Pass	2.00	1	Fail
Naphthalene	0.61	1	Pass	0.41	1	Pass	0.39	1	Pass	0.74	1	Pass
1,2,3-Trichlorobenzene	0.79	1	Pass	0.51	1	Pass	0.6	1	Pass	1.36	1	Fail

Table 10: Carry over evaluation for late eluting compounds

Conclusions

The analytical traps used in Purge and Trap analyses are packed with multiple beds of various adsorbent materials (**Table 1**). This allows high and low molecular weight compounds, polar and non-polar compounds to be trapped in a single analytical trap. When selecting the appropriate trap the most important factor is the ability of the adsorbent material to efficiently trap and release the compounds of interest. Choosing the correct trapping material will help to provide high recoveries and sharp chromatography peaks and allowing accurate quantification of the analytes.

The Tekmar #9 and the Vocarb 3000 trap contain adsorbents that will efficiently trap and release a broad range of analytes in the USEPA Methods 524.2 and 8260C. The #3 analytical trap can also be used for a board range of analytes but does retain a sizeable amount of water which in turn, interferes with the gaseous compounds at low levels. The Vocarb 4000 can be used for samples containing larger molecular size compounds such as the late eluting compounds. This trap can present high back pressure which can lead to higher levels of carry over.

While there are some differences in performance and MDL, all analytical traps test in this study have passed the minimum calibration and MDL requirements set forth by the USEPA 8260C.Whie the unique trapping materials of the Tekmar #9 show improved performance for meeting the requirements of challenging compounds including bromomethane, chloroethane, and the increasing list of added oxygenates, defined by Methods US EPA 8260 and 524.2.

References

1. USEPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3, August 2006
2. Analytical Trap Choices for Stratum PTC and Velocity XPT Purge and Trap Concentrators

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