

Application Note

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Abstract

US EPA Method 8260 is used primarily by environmental labs for the analysis of Volatile Organic Compounds (VOCs) in soils and water. While this method is effective at concentrating the trace levels of VOCs sometimes found in water and wet soils, it also tends to transfer significant quantities of water vapor to Gas Chromatograph/Mass Spectrometer (GC/MS) instruments.

To reduce the amount of water transferred during desorb, the Teledyne Tekmar Lumin Purge and Trap (P&T) concentrator incorporates a specially designed Moisture Control System (MCS) to significantly improve water vapor removal in comparison to other P&T instruments. The MCS's superior water vapor removal efficiency allows for excellent chromatography without dry purge. Additionally, an efficient trap cooling design reduces sample cycle times, resulting in more samples tested per 12 hour period.



Introduction

The process of purge and trap concentration of toxic VOCs begins with aqueous samples that inherently convey water vapor to Gas Chromatograph/Mass Spectrometer (GC/MS) systems used for detection. Traditionally, purge and trap instruments have reduced the amount of water transferred to GC/MS instruments through a variety of water management techniques, including dry purging of the analytical trap. Recognizing the need for improvement, the Teledyne Tekmar Lumin incorporates a unique MCS that achieves significant water vapor reduction prior to transferring the sample to the GC/MS system.

US EPA Method 8260, when used in conjunction with US EPA Method 5030, transfers significant amounts of water vapor to GC/MS systems. This leads to poor chromatography for early eluting gases. Both methods will be used to demonstrate the ability of the Lumin to reduce the amount of water transferred to the GC/MS, while eliminating the dry purging of the trap.

Sample Preparation

Calibration standards were prepared from Restek® standards using 8260B MegaMix®, 8260B Acetate, California Oxygenates, VOA (Ketones) and 502.2 Calibration Mixes. The ketones mix compounds were present at 2.5 times the concentration of other compounds in the mix. The oxygenate compound, t-butanol, was present at 5 times the concentration of other compounds in the mix.

A calibration curve was prepared from 0.5 ppb to 200 ppb for all of the compounds except the ketones and t-butanol. The ketones range from 1.25 ppb to 500 ppb. The t-butanol range was 2.5 ppb to 10,000 ppb. The relative Response Factor (RF) was calculated for each VOC using one of three internal standards: 1,4-difluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4. Surrogate standards consisted of: Dibromofluoromethane, 1,2 Dichloroethane-d4, Toluene-d8, Pentafluorobenzene, Fluorobenzene, and Bromofluorobenzene.

Seven 0.5 ppb and seven 2 ppb standards were prepared to calculate the Method Detection Limit (MDL), accuracy and precision data. All calibration and MDL samples were analyzed with the Lumin conditions in [Table I](#) and the GC/MS conditions in [Table II](#).

Experimental Instrument Conditions

Table I Lumin and AQUATek 100 Conditions			
Standby	Variable	Bake	Variable
Valve Oven Temp	150 °C	Bake Time	2.00 min
Transfer Line Temp	150 °C	Bake Temp	280 °C
Sample Mount Temp	90 °C	Condenser Bake Temp	180 °C
Standby Flow	20 mL/min	Bake Flow	200 mL/min
Purge Ready Temp	35 °C	AQUATek 100	Variable
MCS Purge Temp	20 °C	Sample Loop Time	0.35 min
Purge	Variable	Sample Transfer Time	0.35 min
Purge Temp	20 °C	Rinse Loop Time	0.30 min
Purge Time	11.00 min	Sweep Needle Time	0.30 min
Purge Flow	40 mL/min	Presweep Time	0.25 min
Dry Purge Temp	20 °C	Water Temp	90 °C
Dry Purge Time	No Dry Purge, 0 min	Bake Rinse Drain Cycles	1
Dry Purge Flow	0 mL/min	Bake Rinse Drain Time	0.35 min
Desorb	Variable		
Desorb Preheat Temp	245 °C	Trap	#9
Desorb Temp	250 °C		
Desorb Time	2.00 min		
Drain Flow	300 mL/min		

Table II Agilent 7890B GC / 5977A MS	
Agilent 7890B Conditions	
Column	DB-624 UI, 20 m x 0.18 mm, 1 µm Film, Helium – 0.8 mL/min
Oven Profile	35 °C, 4 min, 16 °C/min to 85 °C, 30 °C/min to 210 °C, 3 min hold, Run Time 14.3 min
Inlet	150 °C, 120:1 Split, Helium Saver 20 mL/min after 4 min
Agilent 5977A Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 <i>m/z</i> to 270 <i>m/z</i> , Delay 0.9 min, Normal Scanning
Gain	Gain Factor 10, BFB Autotune, Trace Ion Detection Off

Results

The Relative Standard Deviation (%RSD) of the RFs for the calibration curve points, MDL, accuracy, and precision data are shown in Table III. Table IV lists the data for t-butanol and the ketones present at a higher concentration for their calibration curve.

A 0.5 ppb standard was analyzed to indicate the initial six gases were unencumbered by excessive water (Figure 1). Figure 2 displays a 30 ppb standard, indicating excellent peak resolution for all of the VOCs.

The drift of the internal standards and their %RSD for 30 samples tested over 9 hours is graphed in Figure 3. The drift of the surrogate standards and their %RSD for 30 samples tested over 9 hours is depicted in Figure 3.

Table III US EPA Method 8260 Calibration, Accuracy and Precision Data						
Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. RF	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
1,4-Difluorobenzene (IS1)	3.6 ¹					
Dichlorodifluoromethane	4.1	0.18	0.305	0.50	100	11.8
Chloromethane	15.6	0.13	0.236	0.71	142	5.7
Vinyl Chloride	7.2	0.14	0.228	0.51	101	8.6
Bromomethane	12.7	0.18	0.177	0.77	155	7.3
Chloroethane	4.8	0.23	0.150	0.58	116	12.5
Trichlorofluoromethane	3.1	0.09	0.474	0.51	101	5.8
Diethyl Ether	4.9	0.15	0.154	0.54	108	8.6
1,1-Dichloroethene	6.3	0.11	0.256	0.54	108	6.3
1,1,2-Trichlorotrifluoroethane	5.2	0.08	0.289	0.50	100	4.9
Carbon Disulfide	5.7	0.23	0.635	0.58	117	12.5
Iodomethane	4.3	0.04	0.585	0.45	90	3.0
Allyl Chloride	6.4	0.33	0.126	0.59	117	17.9
Acetonitrile	4.7	0.21	0.245	0.56	113	11.6
Methyl Acetate	11.9	0.24	0.160	0.60	119	12.6
Methylene Chloride	9.3	0.12	0.273	0.64	128	5.7
Methyl-tert-Butyl Ether (MTBE)	3.6	0.07	0.726	0.49	99	4.3
trans-1,2-Dichloroethene	4.2	0.09	0.272	0.56	112	4.8
Acrylonitrile	9.6	0.25	0.087	0.56	111	14.6
1,1-Dichloroethane	5.0	0.13	0.386	0.52	104	7.9
Chloroprene (2-Chloro-1,3-butadiene)	5.7	0.14	0.308	0.53	105	8.7
Diisopropyl Ether (DIPE)	5.0	0.08	0.582	0.50	101	5.2
Vinyl Acetate	7.5	0.14	0.363	0.49	98	9.1

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Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. RF	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
Ethyl-tert-butyl Ether (ETBE)	4.0	0.10	0.640	0.51	101	6.0
2,2-Dichloropropane	2.7	0.14	0.358	0.46	93	9.4
cis-1,2-Dichloroethene	4.0	0.11	0.309	0.50	101	6.7
Methyl Acrylate	6.1	0.06	0.202	0.55	111	3.4
Ethyl Acetate ²	6.2	0.59	0.013	1.91	95	9.8
Propionitrile	10.5	0.72	0.032	0.62	125	36.9
Bromochloromethane	4.7	0.07	0.182	0.59	117	3.9
Tetrahydrofuran	6.7	0.36	0.060	0.51	101	22.5
Chloroform	3.5	0.11	0.470	0.52	104	7.0
Methacrylonitrile	9.0	0.23	0.123	0.53	106	13.5
1,1,1-Trichloroethane	4.1	0.07	0.445	0.50	99	4.5
Dibromofluoromethane (Surrogate)	1.4		0.307	25.01	100	1.1
Pentafluorobenzene (Surrogate)	2.7		0.763	24.27	97	0.9
Carbon Tetrachloride	6.9	0.08	0.431	0.48	96	5.2
1,1-Dichloropropene	5.6	0.11	0.340	0.55	111	6.2
Benzene	3.2	0.08	0.999	0.52	104	5.0
1,2-Dichloroethane-d4 (Surrogate)	1.6	1.35	0.068	25.34	101	1.7
1,2-Dichloroethane	3.2	0.09	0.319	0.51	102	5.4
tert-Amyl Methyl Ether (TAME)	3.9	0.08	0.696	0.50	100	5.1
Isopropyl Acetate	9.5	0.21	0.085	0.47	94	14.1
Fluorobenzene (Surrogate)	0.8	0.66	0.823	25.13	101	0.8
Trichloroethylene	4.0	0.15	0.296	0.55	111	8.3
1,2-Dichloropropane	9.2	0.27	0.210	0.54	109	15.5
Dibromomethane	3.1	0.07	0.184	0.53	107	4.3
Methyl Methacrylate	6.1	0.15	0.183	0.52	105	9.0
n-Propyl Acetate	4.9	0.11	0.267	0.49	99	7.0
Bromodichloromethane	4.9	0.07	0.340	0.49	99	4.8
2-Nitropropane (43)	15.7	0.15	0.052	0.42	83	11.2
2-Chloroethyl Vinyl Ether (CLEVE)	5.3	0.11	0.160	0.50	101	6.7
cis-1,3-Dichloropropene	5.9	0.11	0.389	0.46	92	7.7

Table III US EPA Method 8260 Calibration, Accuracy and Precision Data

Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. RF	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
Chlorobenzene-d5 (IS2)	4.0 ¹					
Toluene-d8 (Surrogate)	1.2	0.56	1.127	24.88	100	0.7
Toluene	3.0	0.10	0.720	0.51	103	6.4
trans-1,3-Dichloropropene	8.4	0.11	0.370	0.46	92	7.7
Ethyl Methacrylate	6.7	0.11	0.338	0.46	92	7.5
Tetrachloroethylene	3.7	0.10	0.409	0.54	108	6.0
1,1,2-Trichloroethane	3.1	0.12	0.216	0.54	108	6.8
1,3-Dichloropropane	2.6	0.11	0.417	0.51	102	6.7
Dibromochloromethane	10.9	0.07	0.368	0.45	91	5.1
Butyl Acetate	4.7	0.12	0.307	0.46	92	8.0
1,2-Dibromoethane (EDB)	3.2	0.13	0.303	0.53	105	7.7
Chlorobenzene	2.9	0.09	0.892	0.52	104	5.4
1,1,1,2-Tetrachloroethane	7.7	0.09	0.335	0.49	97	5.6
Ethylbenzene	4.2	0.10	1.324	0.49	99	6.5
m-, p-Xylene	5.8	0.14	0.552	0.97	194	4.7
o-Xylene	3.8	0.08	0.551	0.48	96	5.0
Styrene	6.5	0.07	0.911	0.49	97	4.3
Bromoform	12.4	0.08	0.295	0.47	94	5.4
n-Amyl Acetate	10.0	0.13	0.302	0.43	87	9.7
Isopropylbenzene (Cumene)	5.3	0.06	1.382	0.50	101	3.9
cis-1,4-Dichloro-2-butene	11.5	0.17	0.100	0.45	91	11.6
Bromofluorobenzene (Surrogate)	0.5	0.47	0.430	25.01	100	0.6
1,4-Dichlorobenzene-d4 (IS3)	4.0 ¹					
Bromobenzene	3.9	0.14	0.735	0.53	106	8.7
n-Propylbenzene	6.5	0.10	2.375	0.51	102	6.0
1,1,1,2-Tetrachloroethane	2.7	0.10	0.524	0.51	103	5.9
1,2,3-Trichloropropane	3.2	0.16	0.619	0.54	109	9.6
trans-1,4-Dichloro-2-butene	4.9	0.18	0.119	0.54	107	10.4
2-Chlorotoluene	2.9	0.14	1.403	0.52	104	8.5
1,3,5-Trimethylbenzene	4.2	0.05	1.800	0.49	98	3.4

Table III US EPA Method 8260 Calibration, Accuracy and Precision Data

Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. RF	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
4-Chlorotoluene	2.0	0.11	1.640	0.51	101	6.7
tert-Butylbenzene	6.0	0.08	2.120	0.50	100	4.8
Pentachloroethane	8.6	0.19	0.403	0.41	83	14.4
1,2,4-Trimethylbenzene	3.8	0.11	1.867	0.50	101	7.1
sec-Butylbenzene	6.4	0.09	2.318	0.50	101	5.6
1,3-Dichlorobenzene	3.2	0.09	1.329	0.51	101	5.7
p-Isopropyltoluene (p-Cymene)	6.0	0.08	2.120	0.50	100	4.8
1,4-Dichlorobenzene	3.1	0.17	1.327	0.54	108	10.0
n-Butylbenzene	6.3	0.11	1.706	0.48	97	7.3
1,2-Dichlorobenzene	4.6	0.08	1.267	0.55	109	4.9
1,2-Dibromo-3-chloropropane	10.7	0.21	0.100	0.51	102	13.4
Nitrobenzene ²	8.4	1.05	0.016	1.99	99	16.9
1,2,4-Trichlorobenzene	9.0	0.12	1.090	0.52	105	7.1
Hexachlorobutadiene	7.1	0.13	0.615	0.52	104	8.1
Naphthalene	6.5	0.10	2.185	0.51	102	6.2
1,2,3-Trichlorobenzene	8.9	0.11	1.018	0.53	105	6.5

1. %RSD of all peak areas during a 12 hour run, including calibration curve data.
2. Ethyl acetate and nitrobenzene were not detectable below 2 ppb. Their calibration curve is from 2 ppb to 200 ppb. The MDL, accuracy and precision data are from seven replicates of a 2 ppb standard.

Table IV US EPA Method 8260 Calibration, Accuracy and Precision Data for t-Butanol and Ketones						
Compound	Calibration			Accuracy and precision		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
	Range 2.5 ppb to 10,000 ppb			n=7, 2.5 ppb		
tert-Butanol	8.47	1.40	0.022	2.73	109	16.3
	Range 1.25 ppb to 500 ppb			n=7, 1.25 ppb		
Acetone	0.9978	1.17	0.031	1.74	139	21.3
2-Butanone (MEK)	15.59	0.48	0.032	1.19	95	12.8
2-Hexanone	5.70	0.35	0.134	1.22	98	9.0
4-Methyl-2-pentanone (43)	2.66	0.36	0.158	1.24	99	9.2
4-Methyl-2-pentanone (MIBK)	6.68	0.53	0.051	1.24	99	13.6

Figure 1 Primary Characteristic Ions for the First Six Gases of a 0.5 ppb Standard Indicating Excellent Detection Limits with Minimal Interference from Water with No Dry Purge of the Sample.

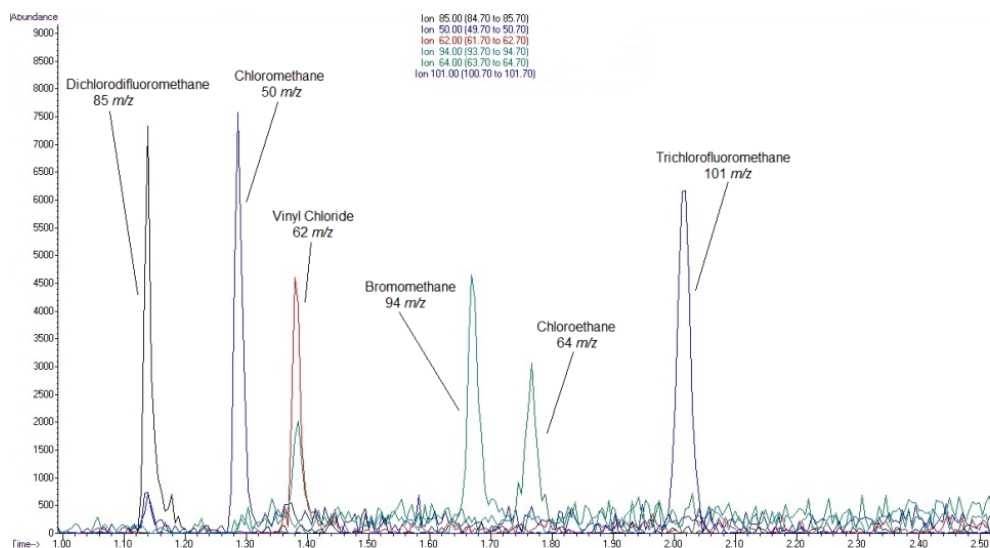


Figure 2 Total Ion Chromatogram of a 30 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds with No Water Interference.

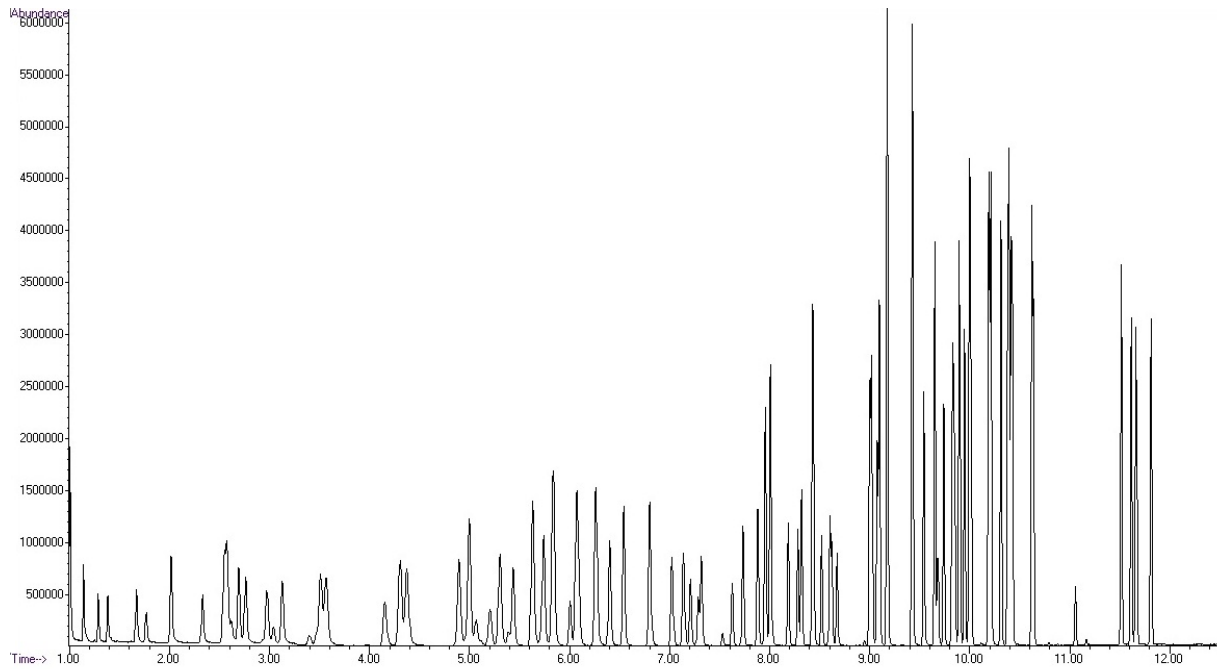


Figure 3 Graph of the Internal Standard Peak Areas and their Respective %RSD from 30 Samples During 9 Hours of Testing.

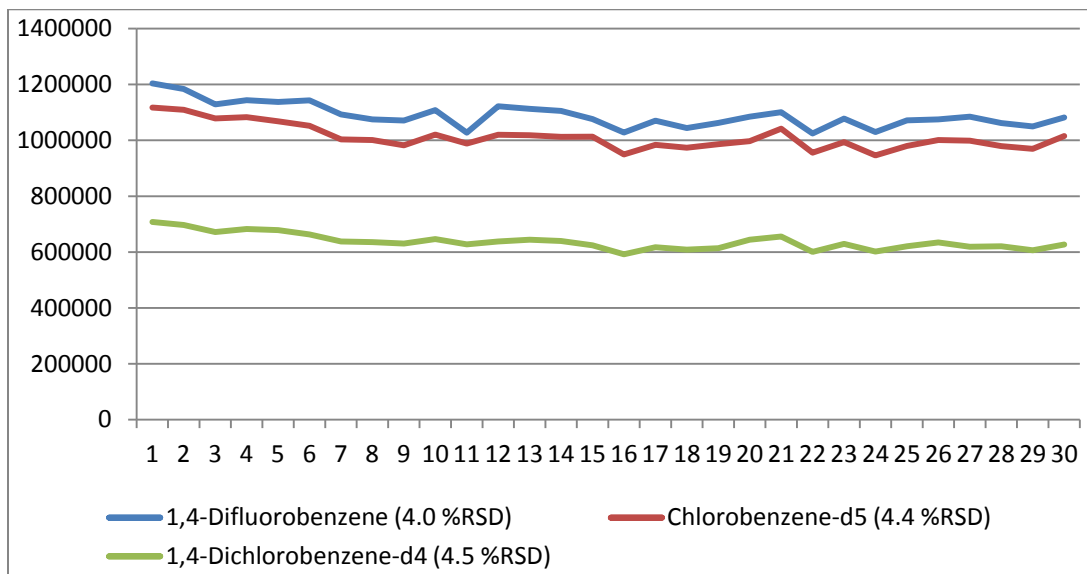
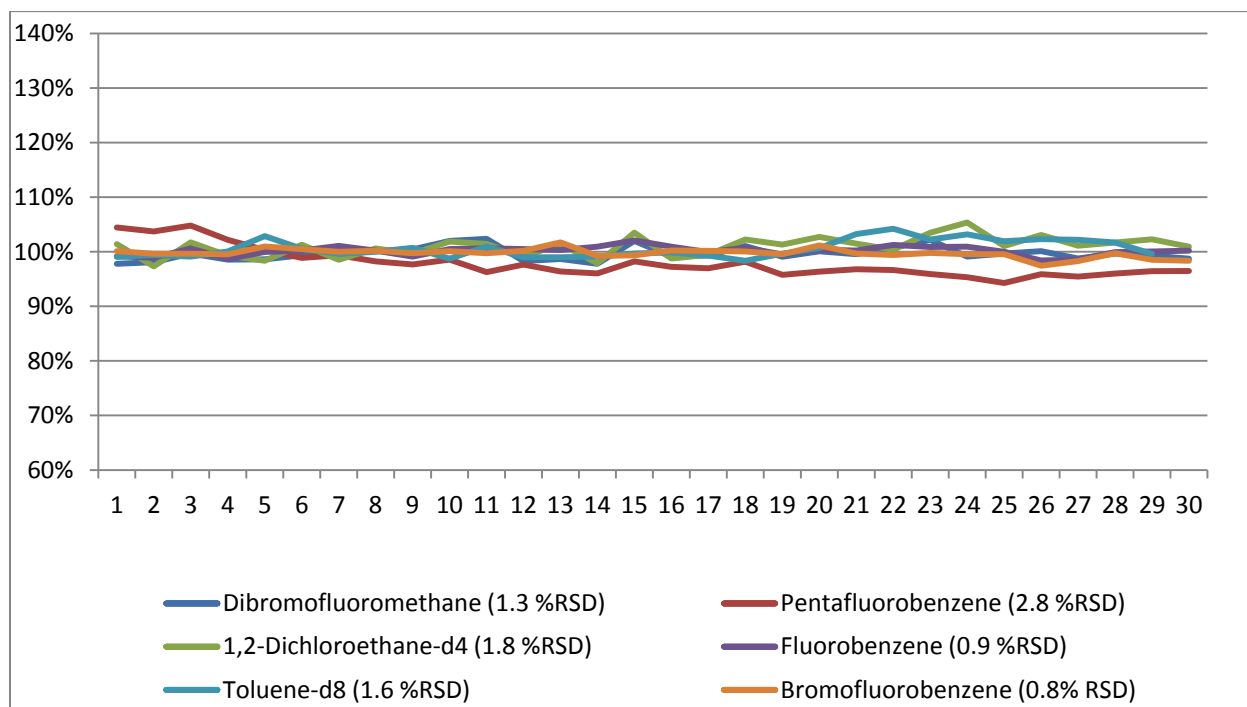


Figure 4 Graph of the Calculated Surrogate Standards as a Percentage of the Expected 25 ppb Concentration and their Respective %RSD from 30 Samples During 9 Hours of Testing.



Conclusion

The Teledyne Tekmar Lumin Purge and Trap Concentrator and AQUATEk 100 was used to process water samples containing VOCs following US EPA Method 8260 and 5030 with detection by an Agilent 7890B GC/5977A MS. The %RSD of the calibration curve passed all method requirements with no interference from excessive water. The MDL, precision and accuracy for seven 0.5 ppb standards also showed no interference from excessive water.

This data indicates that US EPA Method 8260 and 5030 can be performed with the Lumin and AQUATEk 100 using no dry purge time to reduce the purge and trap cycle time. By making additional, appropriate changes to the GC oven temperature program, the GC/MS cycle time may also be reduced, increasing laboratory throughput in a 12 hour period.

References

1. *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*; US EPA, Office of Solid Waste, SW-846 Method 8260B, Revision 2, December 1996.
2. *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*; US EPA, Office of Solid Waste, SW-846 Method 8260C, Revision 3, August 2006.
3. *Purge and Trap for Aqueous Samples*; US EPA, Office of Solid Waste, SW-846 Method 5030B, Revision 2, December 1996.
4. *Purge and Trap for Aqueous Samples*; US EPA, Office of Solid Waste, SW-846 Method 5030C, Revision 3, May 2003.