US EPA Method 8260 with the Tekmar Lumin P&T Concentrator and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ MS

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 chromatography-mass spectrometry instruments (GC-MS).

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 GC-MS systems used for detection. Traditionally, purge and trap instruments have reduced the amount of water transferred to GC-MS instruments though 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 was 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 four internal standards: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4. Surrogate standards consisted of: dibromofluoromethane, toluene-d8, and 4-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.

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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	160 °C	Bake Temp	260 °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	3
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	1.20 min		
Drain Flow	300 mL/min		

Table II Thermo Scientific TRACE 1310 GC and ISQ LT MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	Rtx® -VMS, 20 m x 0.18 mm ID, 1 µm Film; Helium – 0.8 mL/min
Oven Profile	35 °C, 2 min, 10 °C/min to 100 °C, 25 °C/min to 225 °C, 2 min hold, Run Time 15.5 min
Inlet	200 °C, 65:1 Split, P&T Adapter, Helium Saver 20 mL/min after 1 min
Thermo Scientific ISQ LT MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 300 °C
Scan	Range 35 amu to 260 amu, Time 0.15 sec; Delay 0.8 min
Current	Emission Current 25 µA, Gain 3E +5

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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 29 samples tested over approximately 9.5 hours is graphed in Figure 3. The drift of the surrogate standards and their %RSD for 29 samples tested over approximately 9.5 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)
Dichlorodifluoromethane	8.1	0.11	1.162	0.49	97	6.8
Chloromethane	7.6	0.11	1.782	0.54	107	6.7
Vinyl Chloride	4.4	0.12	1.211	0.49	97	7.6
Bromomethane	6.1	0.22	0.466	0.64	128	10.7
Chloroethane	15.9	0.22	0.371	0.56	111	12.8
Trichlorofluoromethane	6.8	0.13	0.840	0.50	99	8.1
Diethyl Ether	3.6	0.12	0.509	0.46	92	8.0
1,1-Dichloroethene	4.6	0.14	0.612	0.53	105	8.5
Carbon Disulfide	5.5	0.20	2.335	0.57	115	10.8
1,1,2-Trichlorotrifluoroethane	5.9	0.14	0.585	0.50	100	8.7
Iodomethane	7.3	0.08	1.262	0.44	88	5.9
Allyl Chloride	2.7	0.14	0.550	0.46	93	9.4
Methylene Chloride	4.2	0.13	0.845	0.52	104	8.1
trans-1,2-Dichloroethene	3.5	0.11	0.769	0.51	101	6.7
Methyl Acetate	3.3	0.08	0.871	0.53	105	4.6
Methyl tert-Butyl Ether (MTBE)	3.1	0.07	3.171	0.49	99	4.6
Acetonitrile[1]	12.6	0.40	0.168	2.22[1]	111[1]	4.8[1]
Diisopropyl Ether (DIPE)	3.2	0.12	3.402	0.50	100	7.4
Chloroprene	5.2	0.13	1.439	0.48	96	8.5
1,1-Dichloroethane	3.9	0.10	1.841	0.50	101	6.3
Acrylonitrile	3.4	0.08	0.391	0.53	106	4.8
Ethyl tert-Butyl Ether (ETBE)	2.1	0.06	3.297	0.48	96	4.1
Vinyl Acetate	3.4	0.08	2.392	0.47	95	5.4

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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)
cis-1,2-Dichloroethene	2.5	0.10	0.886	0.51	101	6.0
2,2-Dichloropropane	7.2	0.11	1.384	0.42	83	8.5
Bromochloromethane	3.4	0.17	0.313	0.51	103	10.4
Chloroform	3.6	0.08	1.429	0.50	101	4.9
Carbon Tetrachloride	4.4	0.11	0.837	0.45	90	7.9
Dibromofluoromethane (Surr)	4.2	1.81	0.381	30.2	101	1.9
Methyl Acrylate	5.4	0.08	0.719	0.50	100	5.3
Tetrahydrofuran	2.7	0.12	0.531	0.48	95	8.0
1,1,1-Trichloroethane	4.0	0.12	1.178	0.49	98	7.6
Ethyl Acetate	5.3	0.27	0.040	0.61	122	14.2
1,1-Dichloropropene	4.8	0.08	1.055	0.49	97	5.2
Benzene	4.5	0.12	4.039	0.50	100	8.0
Propionitrile	4.3	0.20	0.163	0.45	91	13.9
Methacrylonitrile	5.7	0.05	0.499	0.50	99	3.3
Pentafluorobenzene (IS)	5.1					3.8
tert-Amyl Methyl Ether (TAME)	3.3	0.07	2.482	0.49	98	4.7
1,2-Dichloroethane	3.2	0.06	1.056	0.50	99	4.1
Isopropyl Acetate	4.6	0.11	1.489	0.51	101	7.2
Trichloroethene	2.9	0.10	0.657	0.48	96	6.8
1,4-Difluorobenzene (IS)	5.4					2.8
Dibromomethane	2.9	0.06	0.412	0.49	98	4.0
1,2-Dichloropropane	4.7	0.09	0.816	0.50	100	5.6
Bromodichloromethane	2.5	0.08	0.842	0.49	97	5.5
Methyl Methacrylate	7.2	0.07	0.598	0.47	93	5.1
Propyl Acetate	6.0	0.12	1.200	0.51	102	7.4
2-Chloroethyl Vinyl Ether	6.6	0.08	0.548	0.47	94	5.6
cis-1,3-Dichloropropene	3.6	0.08	1.471	0.48	95	5.5
Toluene-d8 (Surr)	3.0	1.75	1.523	30.0	100	1.9
Toluene	5.2	0.11	1.805	0.53	106	6.9
2-Nitropropane	7.3	0.17	0.275	0.51	102	10.5

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)
Tetrachloroethylene	6.2	0.16	0.833	0.58	115	8.7
trans-1,3-Dichloropropene	4.0	0.09	1.329	0.49	98	5.5
1,1,2-Trichloroethane	2.8	0.07	0.577	0.52	103	4.3
Ethyl Methacrylate	9.9	0.07	1.215	0.45	90	4.6
Dibromochloromethane	4.6	0.09	0.558	0.47	93	6.3
1,3-Dichloropropane	3.0	0.09	1.444	0.48	97	5.7
1,2-Dibromoethane (EDB)	2.7	0.08	0.631	0.50	101	4.8
Butyl Acetate	7.9	0.11	1.422	0.47	93	7.2
Chlorobenzene-d5 (IS)	5.4					2.8
Chlorobenzene	2.6	0.12	1.716	0.51	101	7.6
Ethylbenzene	2.8	0.10	3.279	0.48	96	6.6
m-, p-Xylene	3.2	0.25	0.513	0.96	96	8.4
1,1,1,2-Tetrachloroethane	8.2	0.13	0.723	0.52	105	7.7
o-Xylene	4.9	0.09	1.198	0.47	95	5.8
Bromoform	9.5	0.12	0.502	0.45	91	8.5
Styrene	7.5	0.09	1.978	0.46	91	6.0
Isopropylbenzene	6.0	0.08	3.019	0.46	93	5.3
Amyl Acetate	12.4	0.17	1.551	0.47	94	11.4
4-Bromofluorobenzene (Surr)	5.3	1.57	0.657	28.5	95	1.8
Bromobenzene	9.9	0.10	2.853	0.54	107	5.9
cis-1,4-Dichloro-2-butene	5.2	0.11	0.742	0.52	104	6.5
n-Propylbenzene	4.8	0.11	5.654	0.50	99	7.2
1,1,2,2-Tetracholorethane	8.3	0.06	0.946	0.47	93	4.2
2-Chlorotoluene	6.7	0.15	3.567	0.52	103	9.0
1,2,3-Trichloropropane	9.3	0.12	1.534	0.55	109	6.9
1,3,5-Trimethylbenzene	5.0	0.09	4.133	0.48	96	6.2
trans-1,4-Dichloro-2-butene	4.7	0.11	0.439	0.56	111	6.3
4-Chlorotoluene	3.8	0.09	3.760	0.49	98	5.8
Pentachloroethane	15.5	0.26	0.485	0.28	56	29.6
tert-Butylbenzene	3.2	0.11	3.400	0.47	93	7.4

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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)
1,2,4-Trimethylbenzene	3.7	0.10	4.206	0.48	96	6.7
sec-Butylbenzene	3.7	0.11	4.982	0.48	97	7.5
p-Isopropyltoluene	3.6	0.12	3.729	0.48	96	8.0
1,3-Dichlorobenzene	2.3	0.12	2.545	0.51	103	7.2
1,4-Dichlorobenzene	3.4	0.12	2.581	0.53	106	7.4
1,4-Dichlorobenzene-d4 (IS)	14.0					3.7
n-Butylbenzene	6.0	0.12	4.157	0.48	96	8.1
1,2-Dichlorobenzene	2.3	0.15	2.482	0.53	107	8.7
1,2-Dibromo-3-chloropropane	5.4	0.14	0.416	0.52	104	8.3
Nitrobenzene	10.7	0.18	0.040	0.69	138	8.1
Hexachlorobutadiene	5.2	0.06	0.703	0.52	105	3.9
1,2,4-Trichlorobenzene	6.5	0.16	1.530	0.56	111	9.2
Naphthalene	5.5	0.13	3.699	0.53	107	7.5
1,2,3-Trichlorobenzene	5.4	0.19	1.540	0.56	112	10.8

1. A laboratory background of this compound biased the 0.5 ppb standard data, which was omitted from the calibration curve. The calibration curve is from 1 ppb to 200 ppb. The accuracy and precision data is for seven 2 ppb standards.

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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)	Avg. RF	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
	Range 2.5 ppb to 10,000 ppb			n=7, 2.5 ppb		
tert-Butanol	5.9	0.43	0.126	2.43	97	5.7
	Range 1.25 ppb to 500 ppb			n=7, 1.25 ppb		
Acetone[1]	4.6	0.54	0.099	5.52[1]	110[1]	6.4[1]
2-Butanone (MEK)	2.2	0.25	0.171	1.22	98	6.4
2-Hexanone	8.1	0.24	0.664	1.22	97	6.3
4-Methyl-2-pentanone (43)	5.4	0.24	0.931	1.24	99	6.0
4-Methyl-2-pentanone (MIBK)	6.1	0.34	0.118	1.25	100	8.5

1. A laboratory background of this compound biased the 0.5 ppb standard data, which was omitted from the calibration curve. The calibration curve is from 1 ppb to 200 ppb. The accuracy and precision data is for seven 2 ppb standards.

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.

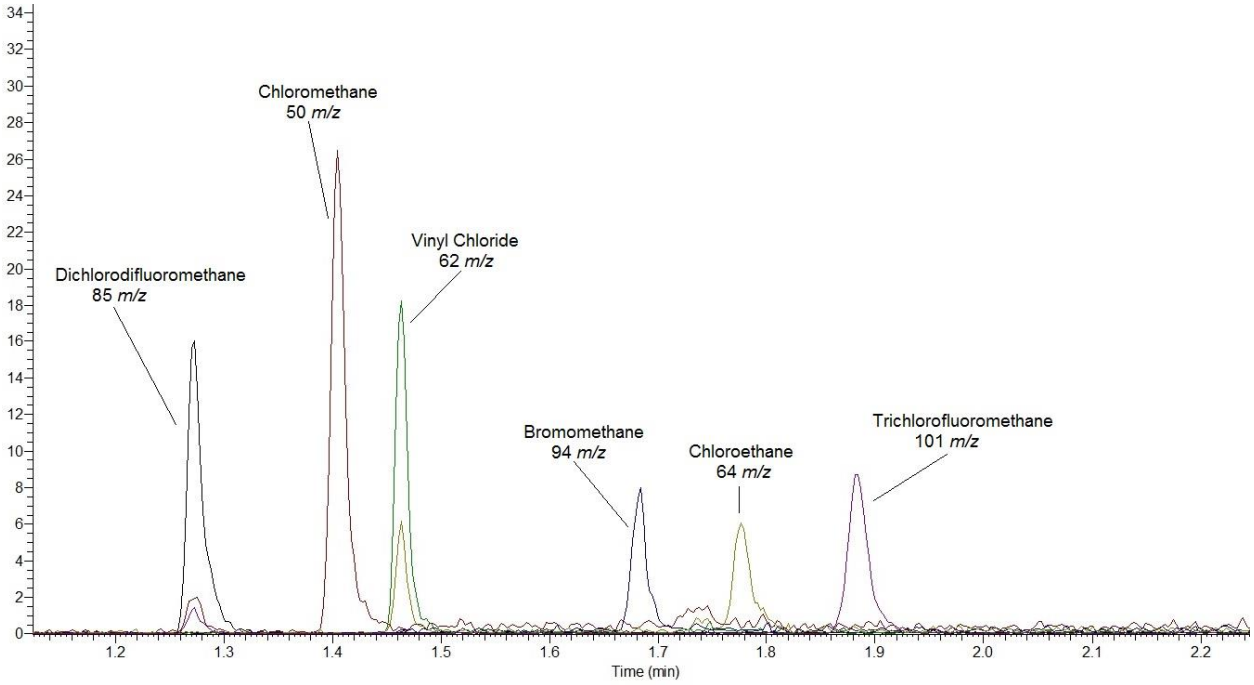

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Figure 2 Total Ion Chromatogram of a 30 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds with No Water Interference.

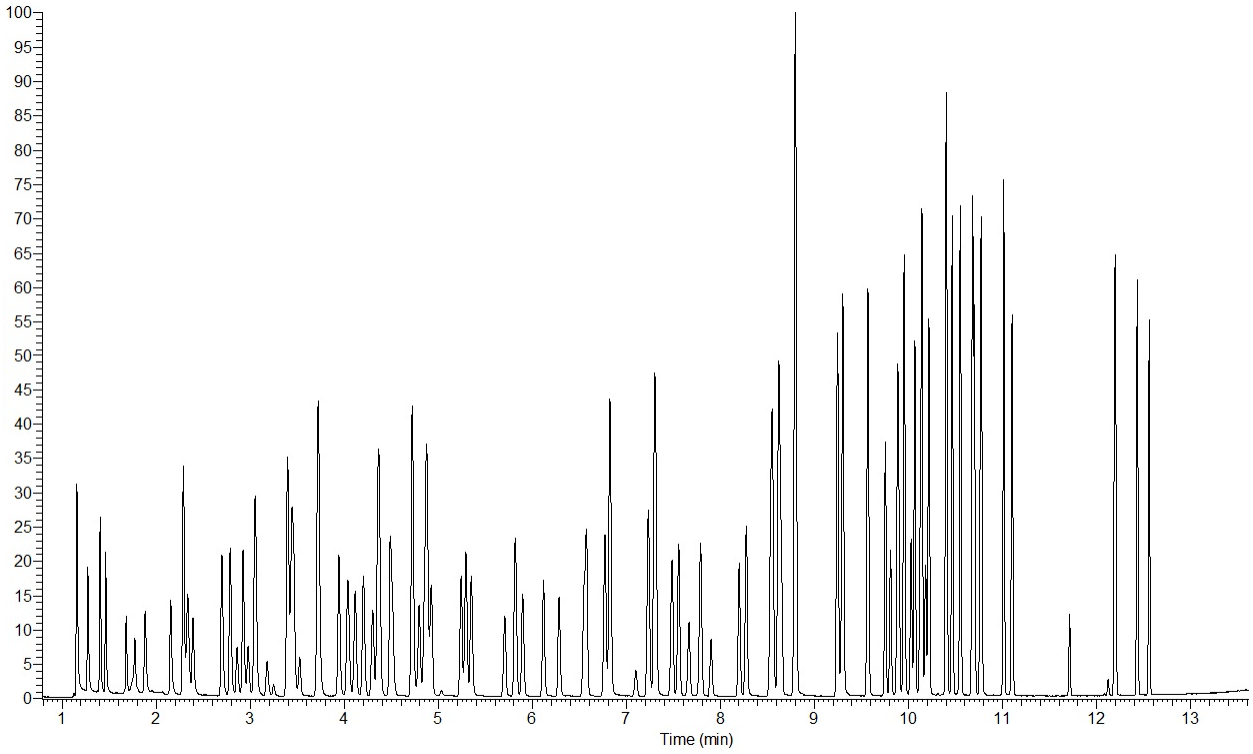

Figure 3 Graph of the Internal Standard Peak Areas and their Respective %RSD from 29 Samples During Approximately 9.5 Hours of Testing.

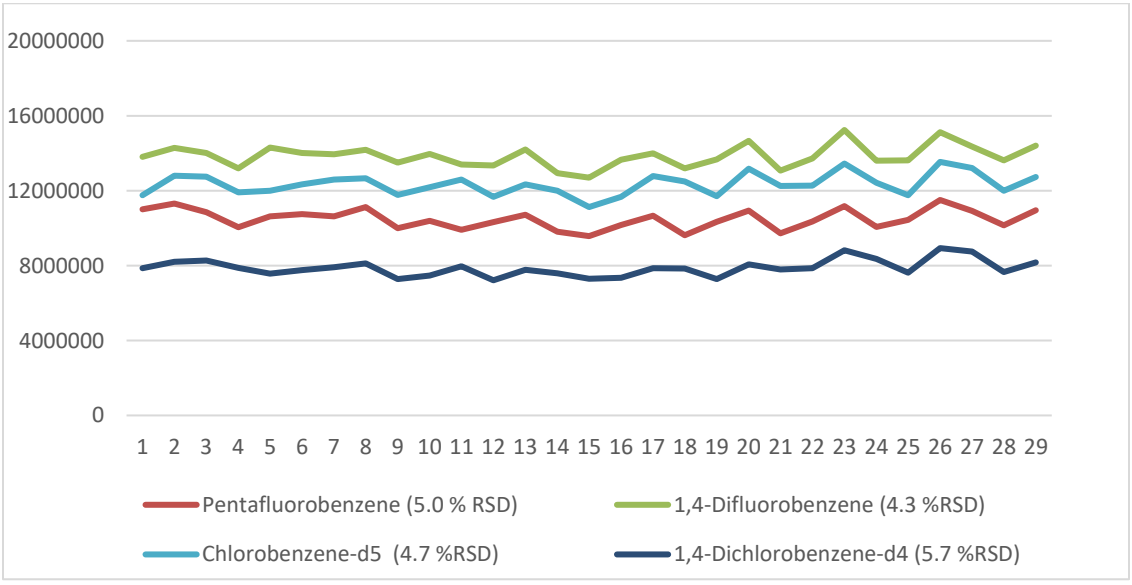

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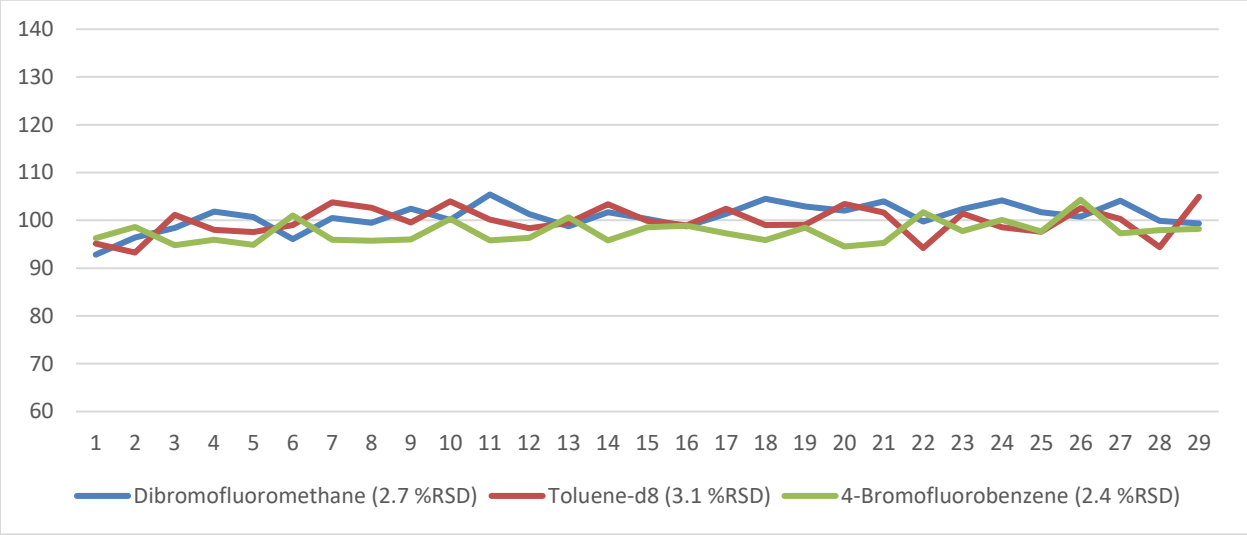
Figure 4 Graph of the Calculated Surrogate Standards as a Percentage of the Expected 30 ppb Concentration and their Respective %RSD from 29 Samples During Approximately 9.5 Hours of Testing.



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 a Thermo Scientific TRACE 1310 GC and ISQ LT MS system. 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.

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