

Introduction

Purge and Trap (P&T) concentrators have been used extensively for the analysis of Volatile Organic Compounds (VOCs) in water since the mid 1970's. By passing a purge gas through the sample, VOCs are swept to an adsorbent analytical trap on which they are collected. The trapped compounds are then released through thermal desorption, separated by gas chromatography, and then quantified by an appropriate detector.

The purge and trap technique excels over other methods of sample concentration allowing detection limits of VOCs in the low parts per billion (ppb). While the method is highly effective at concentrating trace levels of VOCs, it also tends to transfer significant quantities of water vapor that can negatively affect the Gas Chromatograph/Mass Spectrometer (GC/MS) systems used for quantitation. Historically, P&T instruments have employed the use of a condensate trap combined with a period of dry-purge to remove water vapor, which in turn increases total P&T cycle time.

The Moisture Control System (MCS) of the Teledyne Tekmar Lumin Purge and Trap Concentrator (PTC) contains a highly efficient condensate trap capable of removing up to 50% more water than previous designs without the need for dry purging. This study will demonstrate the performance of the Lumin PTC MCS using US EPA Method 524 and a Vocab® 3000 (K) trap.¹ A K type trap was used as some of the absorbents are more hydrophilic than those of a Tenax® trap.

Because the Lumin MCS significantly reduces the amount of moisture transferred, elimination of dry purge time, as well as reduced trap desorb time, become viable analytical options. Variations of US EPA Method 524.3 guidelines were investigated in order to determine the ideal dry purge time and trap desorb time.² The amount of water vapor transferred to the CG/MS under each set of conditions was evaluated.

Reduction of Water Vapor

Previous condensate trap designs, such as that of the Teledyne Tekmar Stratum PTC, rely on dry purging the adsorbent trap with a flow of helium to remove excess moisture. The Lumin MCS design eliminates the need for dry purging by removing more water vapor during the trap desorb cycle. The Lumin MCS still utilizes a temperature gradient to cause condensation of water vapor, but to greater effect than previous designs. The condensed water is separated from the desorb gas stream until the trap desorption is completed, at which point it is then removed from the MCS during the bake cycle.

Lumin Moisture Control System (MCS) Vs. Stratum Condensate Trap & Dry Purge

A comparison of the Lumin MCS to the Stratum condensate trap was accomplished using US EPA 524.2 method parameters. A 5 mL sparge vessel was used to perform seven replicate samples with each instrument. The same Vocab® 3000 (K) trap was also used for both instruments.

The 5 mL deionized water sample was purged with 440 mL of helium for 11 minutes using a 40 mL/minute flow rate. The dry purge time was varied from 0 to 3 minutes, in 1 minute increments. The samples were then desorbed for 4 minutes to transfer the largest quantity of water vapor to the GC/MS instrument. A 20 m x 0.18 µm with a 1 µm thick VMS film was used to identify the water peak with a typical environmental oven temperature program. The MS Gain was lowered to 0.25 to reduce the chance of saturating the detector with water. The MS was scanned from 18 *m/z* to 150 *m/z* to allow for the measurement of the water peak area.



The water mass (18 *m/z*) peak area was quantitated for all samples. The average peak area of the seven samples at each of the four dry purge times was graphed for the Lumin and the Stratum. **Figure 1** compares the chromatogram of the water mass ion, 18 *m/z*, between the Lumin and the Stratum with a 1 min dry purge time.

The average peak area of water vapor transferred was compared and then used to calculate a percentage representing the reduction of water vapor transferred to the GC/MS by the Lumin, in comparison to the Stratum for each dry purge time. A graphic comparison is shown in **Figure 2**. The % water vapor reduction values are shown in **Table I**.

Figure 1 Comparison of the Specific Ion Chromatogram (18 *m/z*) of Water Transferred to the GC/MS by the Stratum and Lumin.

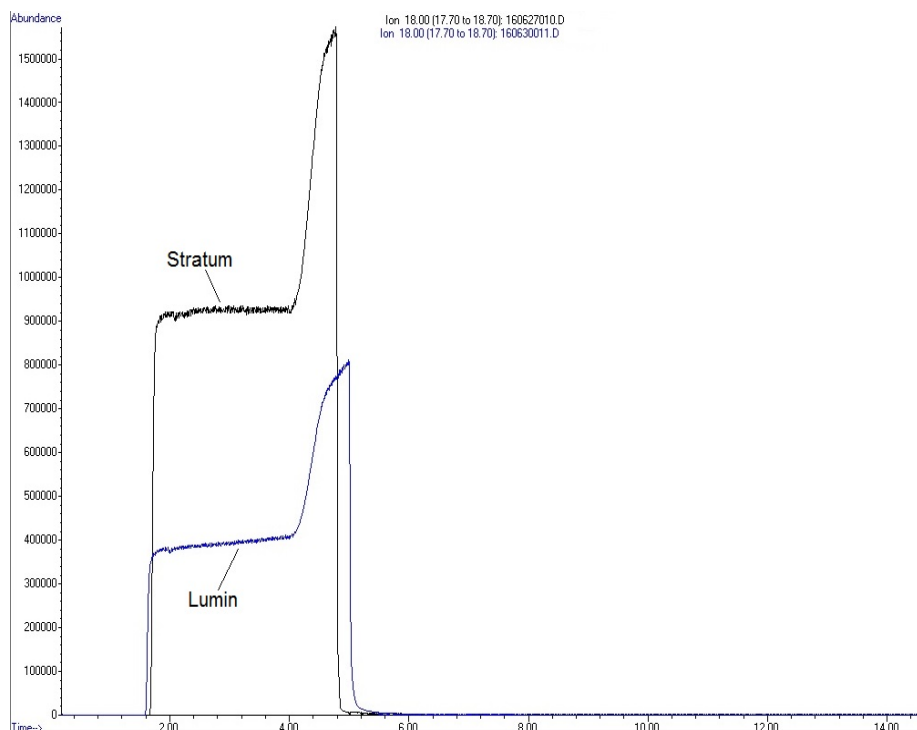


Figure 2 Comparison of the Average Peak Area of Water Transferred to the GC/MS by the Lumin and Stratum with Various Dry Purge Times.

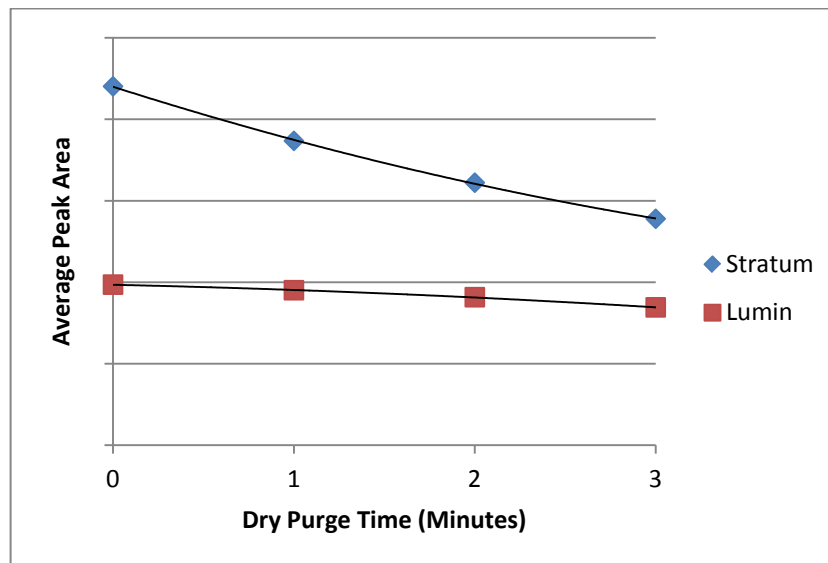


Table I Lumin % Water Vapor Reduction When Compared to the Stratum	
Dry Purge Time (Minutes)	Lumin % Water Vapor Reduction
4	55
3	49
2	44
1	39
0.5	13

Water Vapor Transfer Based on Trap Desorption Time

The trap desorption (desorb) time is one of the variables that can be modified under US EPA Methods 524.3 and 524.4.³ The amount of water vapor transferred according to desorb time was investigated with times ranging from 0.5 to 4 minutes.

The same GC/MS conditions and trap used for the [Lumin Moisture Control System \(MCS\) Vs. Stratum Condensate Trap & Dry Purge](#) data were also used for this study. A 1 minute dry purge was used. Five replicate 5 mL deionized water samples were tested at five trap desorb times. The water ion mass 18 *m/z* peak area was calculated for all samples. The peak area for the five samples at each trap desorb time was then averaged.

[Figure 3](#) compares the water mass ion chromatograms for the five different trap desorb times. [Table II](#) compares the water peak area for each trap desorb time as a percent of the water peak area at 4 minutes. [Figure 4](#) graphs the water peak area for the various trap desorb times.

Figure 3 Comparison of the Specific Ion Chromatogram of Water (18 m/z) Transferred by the Lumin to the GC/MS for Trap Desorb Times Ranging from 0.5 to 4 Minutes.

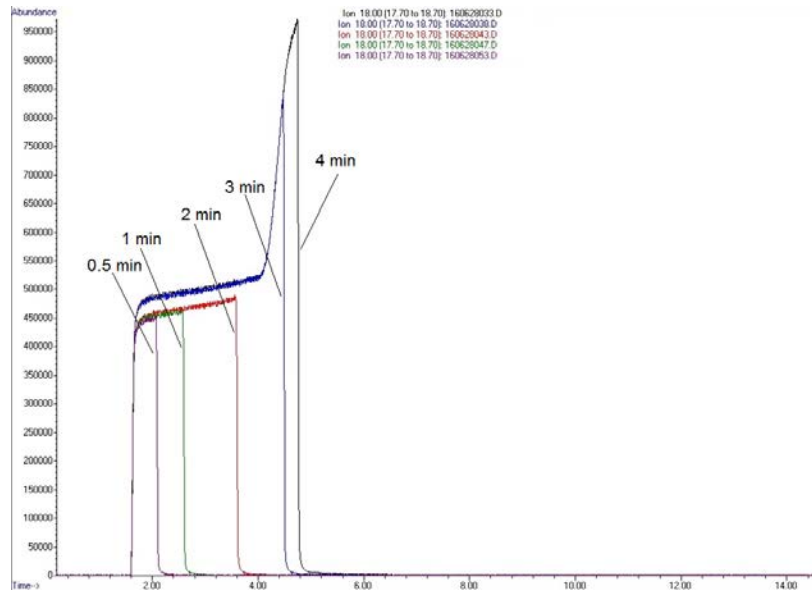
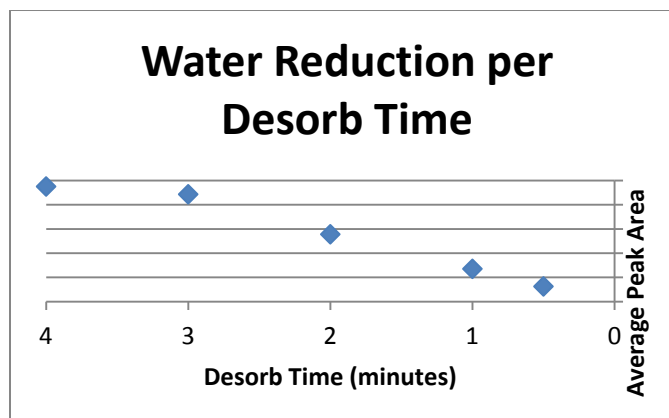


Table II Calculated Values of Water Reduction Based on 4 Minute Lumin Trap Desorb Time		
Desorb Time (Minutes)	Percent of 4 minutes	Percent Reduction
4	100	0
3	93	7
2	58	71
1	28	251
0.5	13	658

Figure 4 Graph of the Peak Area of Water Transferred to the GC/MS by the Lumin by Trap Desorb Time.



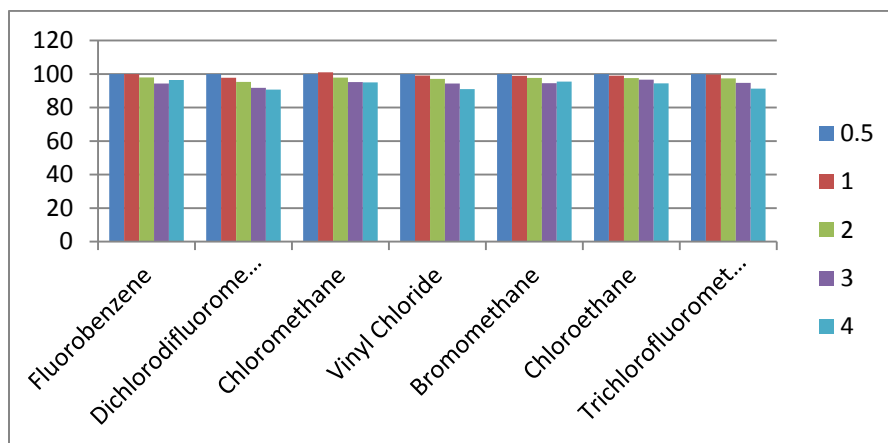
Trap Desorb Time Investigation of Typical 524 Compounds

US EPA Method 524.2 recommends a 4 minute desorb in Section 11.2.2. Significant scientific questions have been raised about the 4 minutes desorb recommendation and its effect on the typical 524 VOC compounds. To investigate the effect trap desorb time has on 95 of the US EPA Method 524 compounds (including internal and surrogate standards) the trap desorb time was varied from 0.5 minutes to 4 minutes. Five 10 ppb standards were tested at each trap desorb time.

The peak areas of each compound's quantitation ion from US EPA method 524 were averaged. These peak areas were then compared as a percent of the 0.5 minute desorb time. All but four of the compounds fell within 20% of the 0.5 minute desorb time.

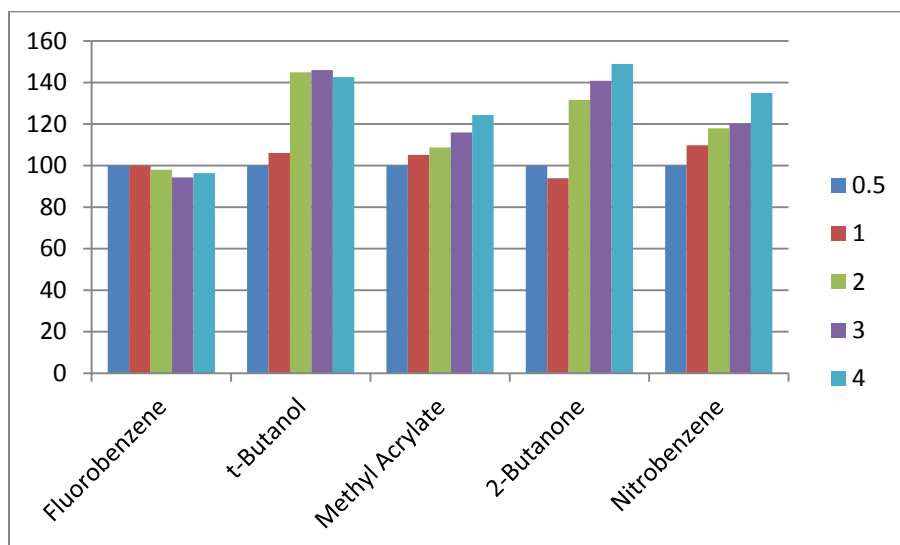
Figure 5 graphically compares this percent for the first six gases. Figure 6 compares the four compounds that had greater than 20% variance from the 0.5 minute desorb time.

Figure 5 Comparison of the Peak Area of the Quantitation Ions for the First Six Gases and Fluorobenzene as a Percent of the 0.5 Minute Trap Desorb Time.*



* - The vertical axis on the left represents %. The legend on the right indicates minutes of trap desorb.

Figure 6 Comparison of the Peak Area of the Quantitation Ions for Four Polar Compounds and Fluorobenzene as a Percent of the 0.5 Minute Trap Desorb Time.*



* - The vertical axis on the left represents %. The legend on the right indicates minutes of trap desorb.

Response Factor (RF) % RSD and MDL Values with Three Different Purge Parameters

The US EPA updated Method 524.2 to 524.3 in 2009 to allow flexibility in several purge and trap parameters. By reducing the P&T cycle time and GC/MS oven cycle time, environmental testing laboratories were able to decrease analysis time and process more samples in a given 12 hour cycle.

The effect of varying purge times and flow rates to reduce P&T cycle times was investigated. No dry purge time was used based on the evaluation of the results from [Lumin Moisture Control System \(MCS\) Vs. Stratum Condensate Trap & Dry Purge](#). Two purge parameter sets that exemplified the US EPA Method 524.3 upper and lower recommended limits for purge times and flow were chosen for this study. Data produced using these “High Volume” and “Low Volume” purge parameters sets was compared to data when using the typical 524.2 P&T method parameters. A calibration curve from 0.5 ppb to 50 ppb was used for all three data sets.

The calibration standard included compounds from Restek® Drinking Water VOA MegaMix, Oxygenates, Ketones and 502.2 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 5 times the concentration of other compounds in the mix.

Seven of each 0.5 ppb and 5 ppb standards were prepared to calculate the Method Detection Limit (MDL). The Relative Response Factor (RF) for each VOC was calculated using fluorobenzene, the recommended internal standard for US EPA Method 524.2, for all three data sets. The Lumin PTC method parameters were varied as shown in [Table III](#). GC/MS conditions are shown in [Table IV](#). The Relative Standard Deviation (RSD) of the RF and MDL for the three different purge volumes are shown in [Table V](#).

Experimental Instrument Conditions

Table III Lumin and AQUATek 100 Conditions			
Purge Parameter	Low Volume	524.2	High Volume
Total Purge Volume	360 mL	440 mL	520 mL
Purge Time	4.5 min	11 min	5.2 min
Purge Flow	80 mL/min	40 mL/min	100 mL/min
Total Purge Time	4.5 min	11 min	5.2 min
Dry Purge Time	0 min	0 min	0 min
Desorb Time	1 min	4 min	1 min
Total Time	5.5 min	15 min	6.2 min

Table IV Agilent 7890A GC / 5975C MS Conditions	
Agilent 7890A Conditions	
Column	Restek® Rtx® VMS -VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 0.8 mL/min
Oven Profile	35 °C, 2 min, 10 °C/min to 85 °C, 25 °C/min to 220 °C, 2 min hold
Inlet	150 °C, 100:1 Split, Helium Saver 20 mL/min after 4 min
Agilent 5975C Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 to 300, Delay 0.6 min, Gain Factor 4

Results

Table V Method 524.2						
Compound	Linearity Response Factor (% RSD)			Method Detection Limit (MDL) (ppb)		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
Dichlorodifluoromethane	9.9	4.5	7.7	0.09	0.04	0.06
Chloromethane	18.2	10.9	12.0	0.08	0.09	0.08
Vinyl Chloride	3.8	3.6	6.3	0.11	0.13	0.07
Bromomethane	11.7	6.7	10.2	0.12	0.15	0.10
Chloroethane	5.2	3.1	4.5	0.14	0.17	0.17
Trichlorofluoromethane	6.0	4.8	3.0	0.07	0.08	0.06
Diethyl Ether	6.7	7.3	5.6	0.13	0.12	0.15
1,1-Dichloroethene	10.8	4.7	5.5	0.20	0.13	0.08
Carbon disulfide	6.5	4.0	6.2	0.08	0.09	0.04
Iodomethane	5.7	11.3	5.9	0.08	0.09	0.11
Allyl chloride	3.4	4.5	6.1	0.12	0.12	0.21
Methylene Chloride ¹	1.0000	0.9993	0.9998	0.25	0.28	0.17
Acetone ^{1,2}	0.9990	0.9997	0.9995	1.31	0.73	0.74
trans-1,2-Dichloroethene	4.3	5.4	2.5	0.08	0.10	0.10
MTBE-d3 (Surr) ³	3.9	1.6	2.5	0.28	0.53	0.65
Methyl tert Butyl Ether	4.9	5.5	3.3	0.05	0.05	0.09
t-Butanol ⁴	14.3	5.7	9.2	1.17	0.75	1.09
Diisopropyl ether	5.9	6.2	6.9	0.12	0.11	0.12
1,1-Dichloroethane	6.8	4.8	3.3	0.11	0.12	0.10
Acrylonitrile	15.4	13.3	7.4	0.18	0.28	0.21
t-Butyl Ethyl Ether (ETBE)	7.2	7.4	8.0	0.07	0.07	0.09
cis-1,2-Dichloroethene	2.3	2.8	4.1	0.11	0.09	0.08
2,2-Dichloropropane	3.4	3.5	6.1	0.08	0.12	0.08
Bromochloromethane	8.8	2.5	6.0	0.22	0.14	0.11
Chloroform	7.7	2.1	5.1	0.09	0.06	0.05
Carbon Tetrachloride	4.4	2.6	5.5	0.06	0.11	0.09
Methyl Acrylate	19.5	5.7	14.1	0.28	0.09	0.19
Tetrahydrofuran	8.6	8.8	17.7	0.57	0.74	0.28

Table V Method 524.2						
Compound	Linearity Response Factor (% RSD)			Method Detection Limit (MDL) (ppb)		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
1,1,1-Trichloroethane	3.1	5.0	2.0	0.08	0.06	0.08
1,1-Dichloropropene	8.4	6.8	8.9	0.08	0.09	0.10
2-Butanone ²	10.1	4.1	14.3	0.48	0.54	0.36
1-Chlorobutane	6.6	4.9	6.8	0.07	0.10	0.09
Benzene	2.5	3.8	4.0	0.04	0.05	0.06
Propionitrile ⁵	16.4	8.5	7.8	1.04	0.93	1.10
Methacrylonitrile	7.9	4.3	7.3	0.18	0.22	0.16
t-Amyl Methyl Ether (TAME)	8.8	6.8	10.5	0.08	0.12	0.07
1,2-Dichloroethane	8.3	5.2	2.7	0.10	0.07	0.05
Trichloroethylene	7.3	8.0	9.9	0.09	0.17	0.08
1,4-Difluorobenzene (Surr) ³	0.8	2.0	2.3			
t-Amyl Ethyl Ether (TAEE)	8.3	6.1	9.2	0.07	0.05	0.11
Dibromomethane	7.7	7.8	8.8	0.12	0.15	0.19
1,2-Dichloropropane	2.8	5.0	3.7	0.14	0.12	0.08
Bromodichloromethane	2.1	3.5	3.2	0.08	0.13	0.07
Methylmethacrylate	12.1	5.6	11.3	0.19	0.18	0.12
cis-1,3-Dichloropropene	8.3	4.6	8.1	0.17	0.13	0.12
Toluene	14.4	4.9	9.9	0.09	0.07	0.09
Chloroacetonitrile ⁶	13.1	0.6	9.4	1.62	2.61	1.08
2-Nitropropane	18.7	8.4	12.4	0.75	0.62	0.38
1,1-Dichloro-2-propanone ²	6.4	5.3	8.6	0.61	0.26	0.33
Tetrachloroethylene	5.5	6.7	2.1	0.06	0.07	0.10
Methyl Isobutyl Ketone ²	12.0	5.6	12.8	0.46	0.24	0.33
trans-1,3-Dichloropropene	14.0	5.6	12.4	0.11	0.14	0.07
1,1,2-Trichloroethane	7.2	6.5	4.3	0.13	0.20	0.12
Ethyl Methacrylate	20.1	9.2	15.0	0.10	0.22	0.13
Dibromochloromethane	6.5	5.1	3.2	0.08	0.07	0.11
1,3-Dichloropropane	6.6	4.6	3.3	0.11	0.10	0.11
1,2-Dibromoethane	3.9	6.8	2.3	0.10	0.10	0.05
2-Hexanone ²	14.3	11.3	14.8	0.35	0.57	0.17
Chlorobenzene-d5 (524.3 IS) ³	1.7	5.5	1.8			

Table V Method 524.2						
Compound	Linearity Response Factor (% RSD)			Method Detection Limit (MDL) (ppb)		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
Chlorobenzene	5.5	6.1	6.1	0.04	0.11	0.05
Ethylbenzene	16.4	8.9	13.1	0.06	0.17	0.08
1,1,1,2-Tetrachloroethane	3.3	5.8	2.8	0.07	0.16	0.10
m-, p-Xylene	18.8	13.3	17.3	0.08	0.31	0.09
o-Xylene	16.0	10.2	13.9	0.10	0.16	0.10
Styrene	23.3	13.9	21.4	0.04	0.13	0.09
Bromoform	2.7	6.5	5.2	0.13	0.14	0.08
Isopropylbenzene	18.5	11.7	16.3	0.05	0.15	0.02
Bromofluorobenzene (Surr) ³	7.2	5.2	6.1			
Bromobenzene	4.6	5.9	3.9	0.07	0.13	0.05
n-Propylbenzene	18.5	11.7	15.3	0.04	0.13	0.06
1,1,2,2-Tetrachloroethane	3.9	4.8	2.2	0.07	0.07	0.05
2-Chlorotoluene	15.5	11.6	11.4	0.06	0.18	0.05
1,2,3-Trichloropropane	3.9	5.7	3.1	0.15	0.17	0.06
1,3,5-Trimethylbenzene	24.3	14.0	20.3	0.04	0.11	0.02
trans-1,4-Dichloro-2-butene	12.5	11.7	5.6	0.27	0.20	0.10
4-Chlorotoluene	18.9	12.7	15.1	0.04	0.12	0.03
tert-Butylbenzene	17.2	11.3	13.9	0.04	0.12	0.04
Pentachloroethane	2.8	3.1	1.4	0.08	0.17	0.08
1,2,4-Trimethylbenzene	25.6	15.1	23.1	0.05	0.14	0.05
sec-Butylbenzene	22.9	14.1	19.4	0.04	0.12	0.05
4-Isopropyltoluene	25.9	15.0	23.0	0.05	0.11	0.06
1,3-Dichlorobenzene	8.6	8.1	7.7	0.07	0.10	0.06
1,4-Dichlorobenzene-d4 (524.3 IS) ³	8.1	6.5	6.5			
1,4-Dichlorobenzene	8.5	8.3	8.6	0.05	0.11	0.04
n-Butylbenzene	22.5	14.9	20.0	0.04	0.07	0.06
Hexachloroethane ⁷	0.9991	0.9988	0.9998	0.26	0.38	0.25
1,2-Dichlorobenzene-d4 (Surr) ³	3.9	6.6	3.3			
1,2-Dichlorobenzene	5.1	6.7	6.0	0.06	0.06	0.08
1,2-Dibromo-3-chloropropane	6.6	5.5	4.4	0.19	0.08	0.12
Nitrobenzene ⁸	20.2	16.6	16.5	1.32	1.63	1.92

Table V Method 524.2						
Compound	Linearity Response Factor (% RSD)			Method Detection Limit (MDL) (ppb)		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
1,2,4-Trichlorobenzene	10.1	8.5	8.6	0.07	0.05	0.08
Hexachlorobutadiene	5.2	6.8	3.8	0.13	0.12	0.15
Naphthalene	19.3	13.3	16.7	0.06	0.04	0.09
1,2,3-Trichlorobenzene	11.9	13.0	10.5	0.11	0.08	0.09

1. Laboratory Background, Linear Curve used
2. Ketone Mix Compound, Calibration Curve from 1.25 ppb to 125 ppb
3. Surrogate/Internal Standard at 12.5 ppb
4. Calibration Curve from 2.5 ppb to 250 ppb
5. Peak not detected below 1 ppb for 360 mL Purge Curve, MDL calculated from 5 ppb standard
6. Peak not detected below 5 ppb for 360 mL curve, or 2 ppb for 440 mL and 520 mL curve, MDL calculated from 5 ppb standard
7. Quantitation Ion from 524.2 used. Interference from 1,2-Dichlorobenzene-d4 ion. Linearity used.
8. Peak not detected below 2 ppb for all three Calibration Curves, MDL calculated from 5 ppb standard.

Conclusion

The Lumin MCS reduced the amount of water vapor transferred to the GC/MS system, removing up to 50% more water than the Stratum condensate trap without the need for a dry purge step. By eliminating the dry purge, the P&T cycle time was reduced by a minimum of 1 minute.

The calibration data for Response Factor % RSD for a calibration curve from 0.5 ppb to 50 ppb indicated similar values for all compounds studied when varying the purge and trap parameters. The MDL for all compounds was also similar. By varying the US EPA Method 524.2 purge flow rate and volume, the purge portion of the P&T cycle time was cut in half. As a result, more samples can be processed during a typical calibration cycle without analytical short-comings.

The Lumin MCS data indicated that a 4 minute trap desorb time transferred more water vapor to the GC/MS instrument than a 0.5 minute desorb time. Similar amounts of 90 of the 94 typical compounds were transferred to the GC/MS instrument with a 0.5 minute trap desorb time versus a 4 minute trap desorb time. This indicates that for the analytical laboratory interested in these 90 compounds, a 0.5 trap desorb time is adequate and will result in further time savings.

All of these conclusions evidence the advantages of the Teledyne Tekmar Lumin Purge and Trap Concentrator for the high volume Volatile Organic Analysis (VOA) laboratory.

References

1. Munch, J.W. US EPA Method 524.2 – Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; Revision 4.1; U.S. Environmental Protection Agency – National Exposure Research Laboratory Office of Research and Development: Cincinnati, OH, 1995.
2. Prakash, B.; Zaffiro, A.D.; Zimmerman, M; Munch, D.J.; Pepich, B.V. US EPA Method 524.3 - Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; Version 1.0; U.S. Environmental Protection Agency – Technical Support Center Office of Ground Water and Drinking Water: Cincinnati, OH, 2009.
3. Munch, D.J.; Wendelken, S.C. PhD. US EPA Method 524.4 - Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas; Revision 4.1; U.S. Environmental Protection Agency – Office of Water: Cincinnati, OH, 2013.