US EPA Method 624 with the Tekmar Lumin P&T Concentrator and the Thermo Scientific™ TRACE™ 1310 GC and ISQ™ LT MS

Application Note

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Abstract

US EPA Method 624 is used primarily by environmental labs for the analysis of volatile organic compounds (VOCs) in wastewater. While this method is effective at concentrating the trace levels of VOCs sometimes found in water, it also tends to transfer significant quantities of water vapor to gas chromatography-mass spectrometry (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 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 624 transfers significant amounts of water vapor to GC-MS systems. This leads to poor chromatography for early eluting gases. This method will be used to show 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 EPA Method 624 Volatiles MegaMix®, and 624 Calibration Mix #1 (gases). A calibration curve was prepared from 0.5 ppb to 200 ppb for all of the compounds. The relative response factor (RF) was calculated for each VOC using one of three internal standards: bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane. Surrogate standards consisted of: pentafluorobenzene, fluorobenzene, and bromofluorobenzene.

Seven 0.5 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	280 °C
Sample Mount Temp	90 °C	MCS 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	2
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	1.00 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	40 °C, 2 min, 10 °C/min to 80 °C, 20 °C/min to 225 °C, 2 min hold, Run Time 15.25 min
Inlet	200 °C, 65:1 Split, P&T Adapter, Gas Saver Flow 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 and the correlation coefficients (r^2) for the calibration curve points, MDL, accuracy and precision data are shown in Table III. Four compounds whose US EPA Method 624 quantitation ion were difficult to consistently detect at the 0.5 ppb levels were also calculated using a different quantitation ion, which is also presented.

A 0.5 ppb standard was analyzed and indicated the initial five 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 27 samples tested over approximately nine hours is graphed in Figure 3. The drift of the surrogate standards and their %RSD for 27 samples tested over approximately nine hours is depicted in Figure 4.

Table III US EPA Method 624 Calibration, Accuracy and Precision Data

Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)		
	Linearity (RF %RSD)	MDL (ppb)	Linearity (r^2)	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
Chloromethane	5.9	0.10	0.9957	0.58	115.6	5.7
Vinyl Chloride	6.5	0.09	0.9982	0.50	100.8	5.6
Bromomethane	4.3	0.11	0.9984	0.61	122.2	5.8
Chloroethane	13.4	0.17	0.9578	0.61	121.6	8.9
Trichlorofluoromethane	5.3	0.14	0.9981	0.51	102.6	8.7
1,1-Dichloroethene	5.2	0.11	0.9985	0.51	101.4	7.0
Methylene Chloride	5.3	0.09	0.9965	0.56	111.2	5.3
trans-1,2-Dichloroethene	5.0	0.15	0.9978	0.56	111.0	8.4
1,1-Dichloroethane	5.4	0.10	0.9975	0.53	106.8	6.0
Bromochloromethane (IS)[1]	8.6					
Chloroform	4.6	0.08	0.9975	0.52	103.4	5.0
Carbon Tetrachloride	6.9	0.10	0.9983	0.48	96.0	6.6
1,1,1-Trichloroethane	6.3	0.08	0.9973	0.51	102.2	5.3
Benzene	5.5	0.09	0.9984	0.53	105.4	5.6
Pentafluorobenzene (Surr)	3.8			29.73	99.1	2.2
1,2-Dichloroethane[2]	8.3	0.20	0.9930	0.41	82.2	15.8
1,2-Dichloroethane (62) [2]	3.7	0.06	0.9984	0.54	108.2	3.4
Fluorobenzene (Surr)	1.7			30.9	102.9	1.7
Trichloroethene	4.4	0.07	0.9976	0.49	98.2	4.8
1,2-Dichloropropane[2]	8.9	0.40	0.9981	0.37	73.2	34.6
1.2-Dichloropropane (63) [2]	3.6	0.09	0.9987	0.53	106.8	5.2
Bromodichloromethane[2]	8.2	0.29	0.9924	0.43	86.2	21.7

Table III US EPA Method 624 Calibration, Accuracy and Precision Data						
Compound	Calibration			Accuracy and precision (n=7, 0.5 ppb)		
	Linearity (RF %RSD)	MDL (ppb)	Linearity (r^2)	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
Bromodichloromethane (83) [2]	3.5	0.06	0.9985	0.52	103.6	3.6
2-Chloroethyl Vinyl Ether	9.9	0.08	0.9928	0.48	95.4	5.6
cis-1,3-Dichloropropene[2]	5.7	0.05	0.9990	0.48	96.4	3.3
cis-1,3-Dichloropropene (110) [2]	5.3	0.08	0.9969	0.48	95.8	5.4
Toluene	3.7	0.07	0.9984	0.52	104.6	4.0
Tetrachloroethene	2.6	0.08	0.9993	0.47	93.6	5.7
trans-1,3-Dichloropropene[3]	22.1	0.11	0.9987	0.81	162.8	4.1
trans-1,3-Dichloropropene (110)[3]	3.2	0.15	0.9987	0.55	110.8	8.4
2-Bromo-1-chloropropane (IS)[1]	8.2					6.1
1,1,2-Trichloroethane	3.1	0.03	0.9989	0.52	103.6	2.1
Dibromochloromethane	3.4	0.07	0.9988	0.47	94.6	5.0
Chlorobenzene	3.4	0.08	0.9988	0.52	103.8	5.2
Ethylbenzene	8.3	0.06	0.9977	0.46	92.6	3.8
Bromoform	6.5	0.08	0.9952	0.43	86.0	6.0
Bromofluorobenzene (Surr)	4.1			28.4	94.7	1.8
1,4-Dichlorobutane (IS)[1]	8.5					
1,1,2,2-Tetrachloroethane[2]	10.2	0.28	0.9907	0.46	92.0	19.0
1,1,2,2-Tetrachloroethane (83) [2]	3.2	0.04	0.9989	0.45	89.2	2.7
1,3-Dichlorobenzene	6.8	0.07	0.9992	0.50	99.8	4.7
1,4-Dichlorobenzene	8.6	0.10	0.9978	0.48	96.0	6.6
1,2-Dichlorobenzene	6.3	0.07	0.9992	0.47	93.6	4.5

1. %RSD of the peak areas during the calibration curve.
2. While the US EPA Method 624 quantitation ion was detected in all 0.5 ppb standard and samples, a stronger secondary ion characteristic of the compound, as allowed by the method, is also presented.
3. The US EPA 624 mass ion 75 for trans-1,3-dichloropropane had interference from the minor 75 mass ion of the internal standard, 2-bromo-1-chloropropane. The calibration curve, and precision and accuracy data, calculated using a different quantitation ion is presented.

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

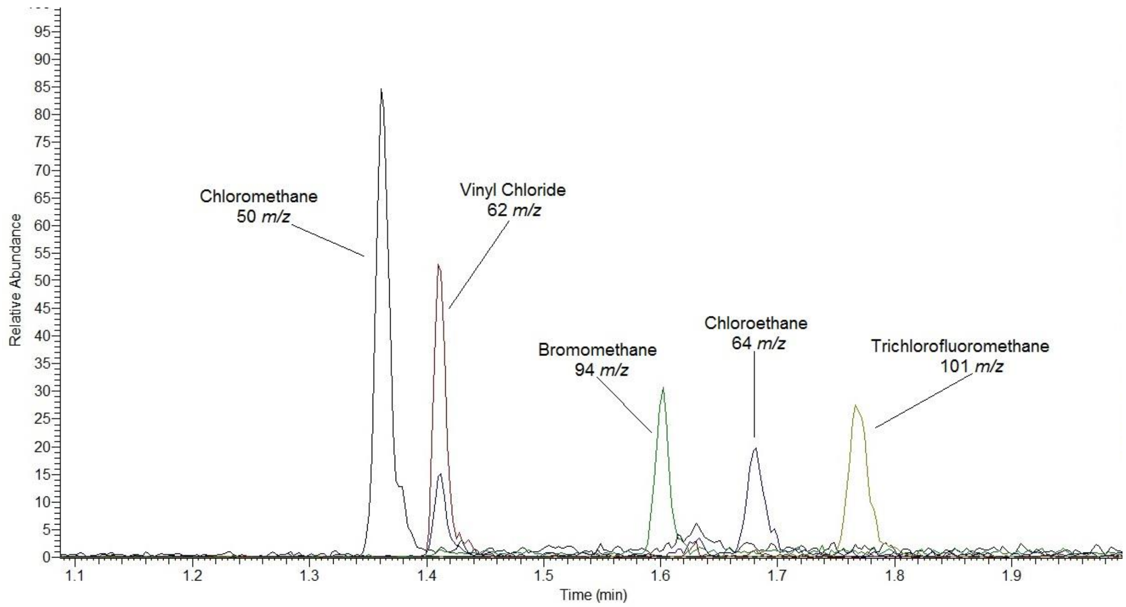


Figure 2 Total Ion Chromatogram of a 30 ppb VOC Standard indicating Consistent Peak Shapes for all Compounds with No Water Interference.

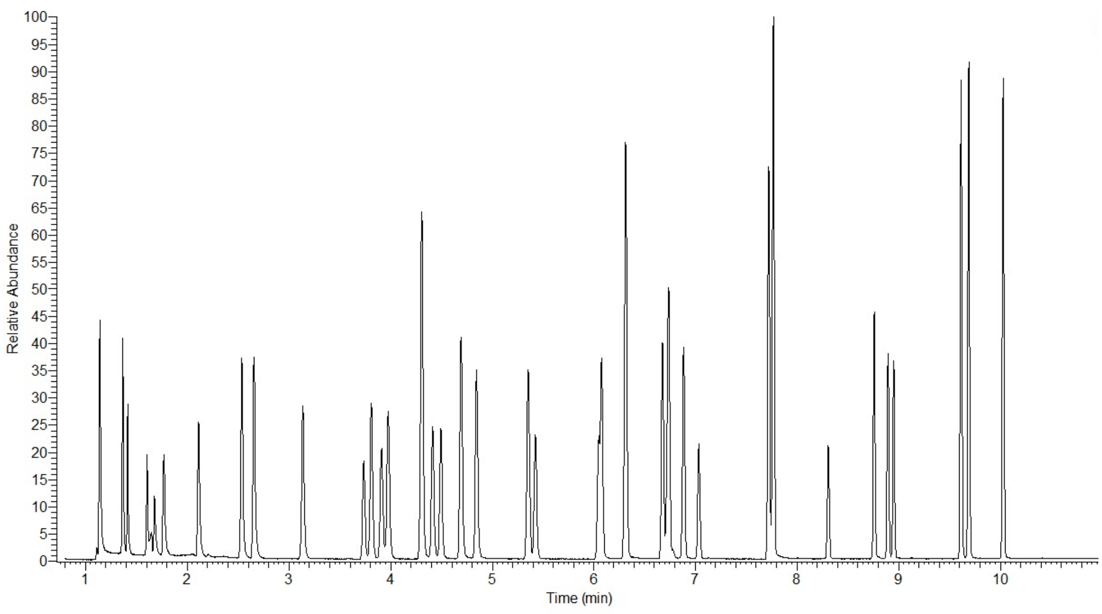


Figure 3 Graph of the Internal Standard Peak Areas and their Respective %RSD from 29 Samples During Approximately 10 Hours of Testing.

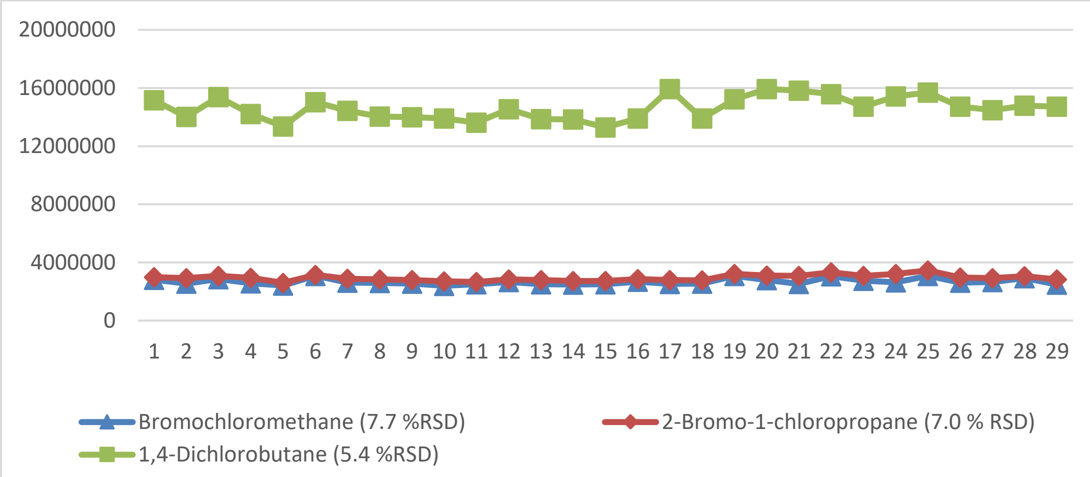
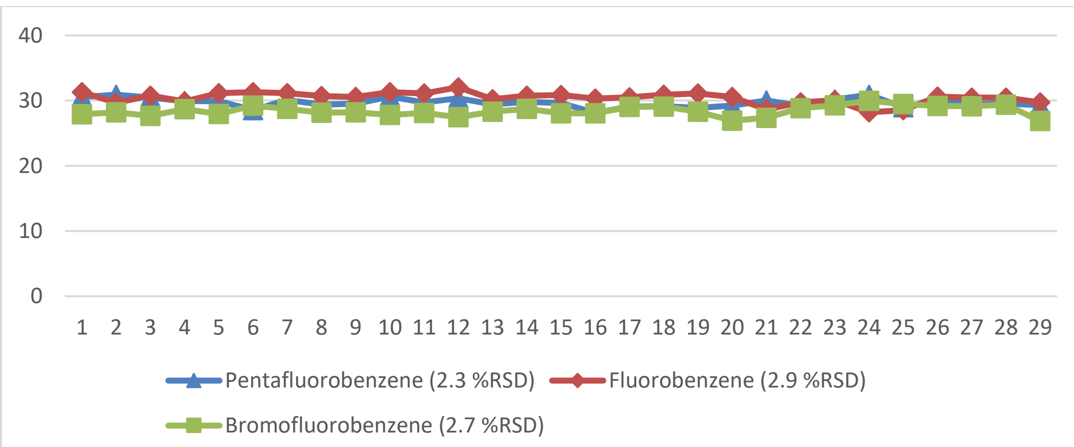


Figure 4 Graph of the Calculated Surrogate Standards 30 ppb Concentration and their Respective %RSD from 29 Samples During Approximately 10 Hours of Testing.



Conclusion

The Teledyne Tekmar Lumin purge and trap concentrator and AQUATek 100 was used to process water samples containing VOCs following US EPA Method 624 with detection by a Thermo Scientific TRACE 1310 GC and ISQ LT 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 indicated no interference from excessive water.

This data indicates that US EPA Method 624 can be performed with the Lumin and AQUATek 100 using no dry purge time to reduce the purge and trap cycle time. By reducing sample time, more samples can be analyzed in a 12-hour period, and laboratory throughput optimized.

References

1. *Appendix A to Part 136 - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater - Method 624: Purgeables;* US EPA, Promulgated 1984. [Online] https://www.epa.gov/sites/production/files/2015-10/documents/method_624_1984.pdf (accessed March 23, 2017).