

US EPA Method 624 with the Tekmar Lumin and the Agilent 7890B GC/5977A MS



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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 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 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 Mixes. 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-bromochloropropane 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 1 and the GC/MS conditions in Table 2.

Experimental Instrument Conditions

Table 1. 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 2. 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	40 °C, 0.1 min, 13 °C/min to 180 °C, 25 °C/min to 220 °C, 2 min hold, Run Time 14.47 min
Inlet	180 °C, 140:1 Split, Helium Saver 20 mL/min after 2 min
Agilent 5977A Conditions	
Temperature	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 m/z to 260 m/z, 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 and the correlation coefficients (r^2) for the calibration curve points, MDL, accuracy, and precision data are shown in Table 3. 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 to indicate 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 9 hours is graphed in Figure 3. The drift of the surrogate standards and their %RSD for 27 samples tested over approximately 9 hours is depicted in Figure 4.

Table 3. 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)
Bromochloromethane (IS1)	3.8 ¹					
Chloromethane	8.6	0.12	0.9996	0.53	105.1	7.4
Vinyl chloride	5.5	0.13	0.9997	0.48	95.7	8.4
Bromomethane	4.7	0.17	0.9997	0.53	106.9	10.3
Chloroethane	3.6	0.16	0.9992	0.53	106.9	9.6
Trichlorofluoromethane	8.6	0.08	0.9998	0.47	94.9	5.3
1,1-Dichloroethene	4.8	0.13	0.9997	0.49	97.4	8.2
Methylene chloride	4.9	0.17	0.9997	0.83	166.3	6.4
<i>trans</i> -1,2-Dichloroethene	6.0	0.15	0.9998	0.51	102.6	9.4
1,1-Dichloroethane	3.8	0.03	0.9997	0.50	99.4	2.2
Chloroform	3.6	0.10	0.9997	0.50	99.1	6.7
Pentafluorobenzene (Surrogate)	3.8 ¹			29.83	99.4	1.6
1,1,1-Trichloroethane	5.2	0.16	0.9998	0.48	95.4	10.7
Carbon tetrachloride	9.0	0.15	0.9979	0.46	92.9	10.0
Benzene	5.5	0.11	0.9996	0.47	93.7	7.5
1,2-Dichloroethane ²	17.9	0.34	0.9992	0.59	118.0	18.3
1,2-Dichloroethane (62) ²	6.1	0.08	0.9997	0.50	99.1	4.9
Fluorobenzene (Surrogate)	2.9 ¹			30.39	101.3	1.3
Trichloroethene	4.2	0.08	0.9986	0.53	105.4	4.7
1,2-Dichloropropane ²	30.8	0.41	0.9985	0.46	92.0	28.5
1,2-Dichloropropane (63) ²	6.4	0.12	0.9998	0.49	98.9	7.6
2-Bromo-1-chloropropane (IS2)	5.4 ¹			30.00		
Bromodichloromethane ²	10.3	0.26	0.9972	0.54	108.3	15.2
Bromodichloromethane (83) ²	5.9	0.12	0.9991	0.47	94.6	8.3
2-Chloroethylvinyl ether	6.3	0.18	0.9997	0.55	110.9	10.4
<i>cis</i> -1,3-Dichloropropene	9.1	0.17	0.9993	0.45	89.1	12.1
Toluene	4.1	0.12	0.9993	0.48	96.6	8.0
<i>trans</i> -1,3-Dichloropropene	4.8	0.11	0.9997	0.44	88.6	7.8
Tetrachloroethene	5.5	0.17	0.9997	0.49	98.0	10.8
1,1,2-Trichloroethane	7.1	0.06	0.9991	0.51	101.1	3.8
Dibromochloromethane	6.7	0.10	0.9999	0.42	83.7	8.0
Chlorobenzene	5.3	0.06	0.9989	0.49	98.3	4.1
1,4-Dichlorobutane (IS3)	3.5 ¹			30.00		
Ethylbenzene	6.6	0.07	0.9996	0.47	93.7	4.7
Bromoform	13.2	0.07	0.9996	0.42	84.9	5.6
Bromofluorobenzene (Surrogate)	3.1 ¹			29.93	99.8	0.7
1,1,2,2-Tetrachloroethane ²	15.0	0.28	0.9984	0.34	68.3	26.4
1,1,2,2-Tetrachloroethane (83) ²	13.8	0.13	0.9988	0.43	86.9	9.2
1,3-Dichlorobenzene	5.6	0.09	0.9998	0.48	96.9	5.7
1,4-Dichlorobenzene	4.4	0.06	0.9999	0.50	100.0	4.0
1,2-Dichlorobenzene	4.6	0.08	0.9999	0.48	96.9	5.2

¹ %RSD of all peak areas during approximately 11 hour run, including calibration curve data.

² US EPA Method 624 quantitation ion did not consistently detect the 0.5 ppb standard level. The calibration curve, and precision and accuracy data, calculated using a different quantitation ion is also presented.

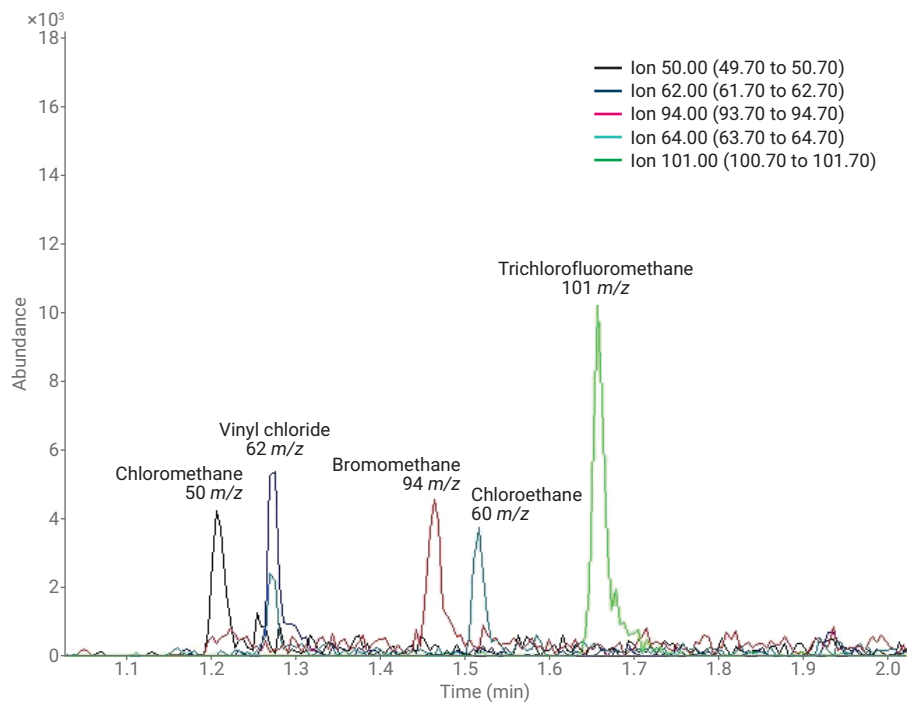


Figure 1. Primary Characteristic Ions for the First Five Gases of a 0.5 ppb Standard Indicating Excellent Detection Limits with Minimal Interference from Water with No Dry Purge of the Sample.

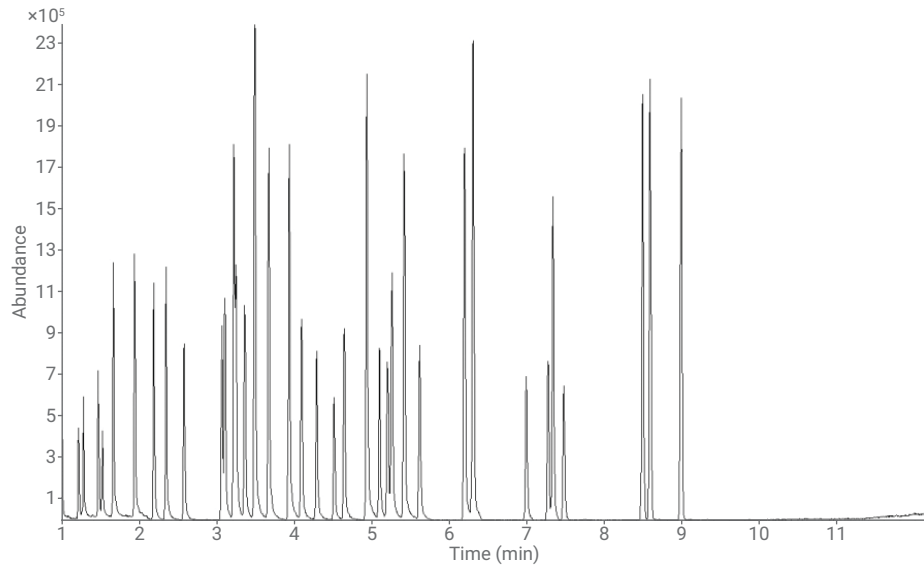


Figure 2. Total Ion Chromatogram of a 30 ppb VOC Standard indicating Consistent Peak Shapes for all Compounds with No Water Interference.

Conclusions

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 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 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 sample can be analyzed in a 12-hour period, and laboratory throughput optimized.

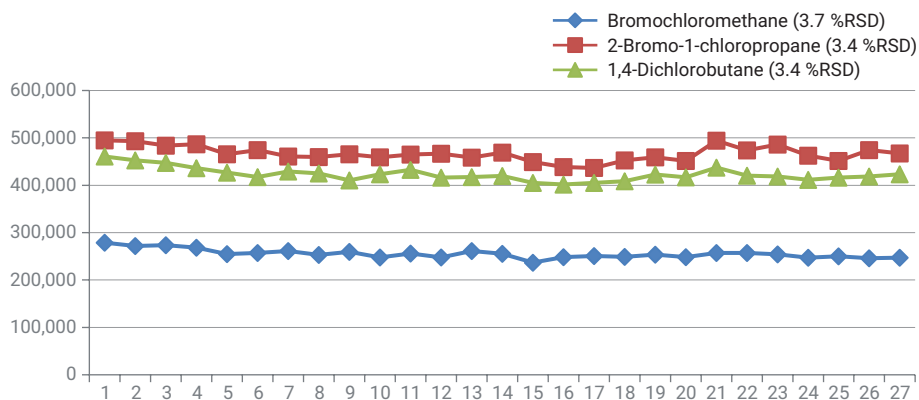


Figure 3. Graph of the Internal Standard Peak Areas and their Respective %RSD from 27 Samples During Approximately 9 Hours of Testing.

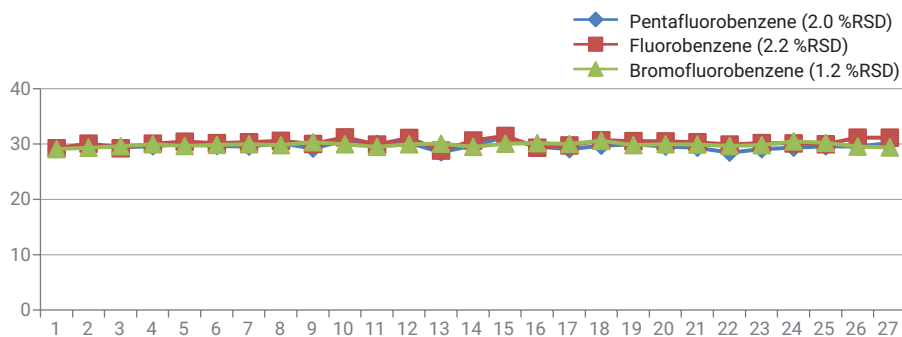


Figure 4. Graph of the Calculated Surrogate Standards 30 ppb Concentration and their Respective %RSD from 30 Samples During Approximately 9 Hours of Testing.

Reference

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 October 10, 2016).

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