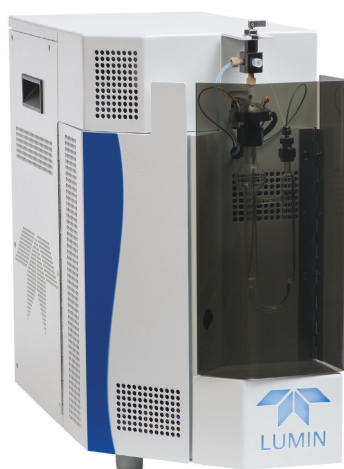


US EPA Method 524.4 with the Tekmar Lumin P&T Concentrator and Agilent 7890B GC and 5977A MSD System



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Abstract

US EPA Method 524.4 is used primarily by environmental labs for the analysis of volatile organic compounds (VOCs) in drinking water. While this method is effective at concentrating the trace levels of VOCs sometimes found in finished drinking water, it also tends to transfer significant quantities of water vapor to the gas chromatography-mass spectrometry (GC-MS) instruments.

Teledyne Tekmar's Lumin purge and trap (P&T) concentrator incorporates a moisture control system (MCS) specifically designed to reduce the amount of water transferred during desorb, in comparison to current purge and trap technologies. This application note will demonstrate the ability of the Lumin to reduce the amount of water transferred to the Agilent GC-MSD system when using this method.

Introduction

Gas chromatography (GC) inlets, columns and mass spectrometers (MS) are sensitive to water. However, to detect toxic VOC compounds, the VOCs must be purged and trapped from water. This places water vapor on the GC-MS system, which contributes to column and inlet issues and frequent MS cleaning to remove the oxidation from the MS source.

While US EPA method 524.4 can place a large amount of water vapor on the GC-MS system, this method allows flexibility in the dry purge and desorb time of the analytical trap to reduce water vapor. By reducing the large volumes of water that inundate the GC-MS system and lead to poor chromatography for early eluting gases, analytical results are improved. It also allows the use of nitrogen for the purge gas, reducing the cost of operation.

Traditionally, purge and trap instruments reduced the amount of water transferred to GC-MS instrument through numerous water management techniques. The Teledyne Tekmar Lumin significantly reduces the amount of water transferred to GC-MS system over current P&T instrumentation through the design of its MCS. Additionally, improvements in analytical trap cooling have further reduced sample cycle times, permitting more samples to be processed within a 12-hour period.

Sample Preparation

Calibration standards were prepared from Restek® 524.3 VOA MegaMix® and 524.3 Gas Calibration Mix standards in deionized water containing the required amount of maleic acid and ascorbic acid. A calibration curve was prepared from 0.2 ppb to 50 ppb for all of the compounds.

The relative response factor (RF) was calculated for each VOC using either 1,4-difluorobenzene, chlorobenzene-d5 or 1,4-dichlorobenzene-d4 as an internal standard. Surrogate standards consisted of: methyl-*t*-butyl ether-d3, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4. A linear calibration curve with 1/X weighting was used for all compounds.

Seven 0.5 ppb and seven 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 and AQUATek 100 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	150 °C	Bake Temp	260 °C
Sample Mount Temp	90 °C	MCS Bake Temp	180 °C
Purge Ready Temp	35 °C	Bake Flow	200 mL/min
MCS Purge Temp	20 °C	AQUATek 100	Variable
Standby Flow	20 mL/min	Sample Loop Time	0.35 min
Purge	Variable	Sample Transfer Time	0.35 min
Purge Time	11.00 min	Rinse Loop Time	0.30 min
Purge Flow	40 mL/min	Sweep Needle Time	0.30 min
Dry Purge Temp	20 °C	Presweep Time	0.25 min
Dry Purge Time	0 min	Water Temp	90 °C
Dry Purge Flow	0 mL/min	Bake Rinse Drain Cycles	3
Desorb	Variable	Bake Rinse Drain Time	0.35 min
Desorb Preheat Temp	245 °C		
Desorb Time	1.00 min	Trap	9
Desorb Temp	250 °C	Chiller Tray	On
Drain Flow	300 mL/min	Purge Gas	Helium

Table 2. Agilent 7890B GC and 5977A MSD System Conditions.

Agilent 7890B GC Conditions	
Column	DB-624 UI, 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	150 °C; 35:1 Split; Gas Saver Flow - 20 mL/min after 1 min
Agilent 5977A MSD Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 amu to 260 amu; Threshold 10; Scan Speed n=3; Delay 0.8 min
Current	Gain Factor 14; Trace Ion Detection - On; Tune File – BFB Atune

The correlation coefficient of the calibration curve (r^2), MDL, accuracy and precision data are shown in Table 3.

A 0.2 ppb standard was analyzed to indicate the lowest detectable peak for the initial seven gases unencumbered

by excessive water in Figure 1. Figure 2 displays a 5 ppb standard, indicating excellent peak resolution for all of the VOCs.

Table 3. Method 524.4 Calibration, Accuracy and Precision Data.

Compound	Calibration		MRL Confirmation (0.5 ppb)		Accuracy and Precision (n=7, 0.5 ppb) ³		
	Linearity (r^2)	MDL (ppb)	LPIR (>50 %)	UPIR (<150 %)	Avg. Conc. (ppb)	Accuracy (± 20 %)	Precision (≤ 20 %)
1,4-Difluorobenzene (IS 1)	10.4 ¹						3.0 ²
Dichlorodifluoromethane	1.000	0.10	71.0	121.5	0.48	96	6.6
Chlorodifluoromethane	1.000	0.08	75.6	115.2	0.48	95	5.2
Chloromethane	1.000	0.14	67.1	136.9	0.51	102	8.6
Vinyl chloride	1.000	0.10	71.4	122.3	0.48	97	6.6
1,3-Butadiene	1.000	0.08	78.5	120.9	0.50	100	5.4
Bromomethane	0.998	0.13	67.0	133.0	0.50	100	8.3
Trichlorofluoromethane	0.999	0.13	60.9	126.5	0.47	94	8.8
Diethyl ether	1.000	0.14	65.5	136.3	0.50	101	8.9
1,1-Dichloroethene	1.000						
	0.14	64.9	137.4	0.51	101	9.1	
Carbon disulfide	1.000	0.15	56.6	133.1	0.47	95	10.2
Iodomethane	0.999	0.11	74.9	129.1	0.51	102	6.7
Allyl chloride	1.000	0.17	52.8	139.2	0.48	96	11.3
Methylene chloride (DCM)	1.000	0.17	53.0	140.2	0.48	97	11.4
<i>trans</i> -1,2-Dichloroethene	1.000	0.19	50.7	144.7	0.49	98	12.1
Methyl acetate	0.997	0.12	67.0	126.1	0.48	97	7.7
MtBE-d3 (Surr)	3.1 ¹				12.42	99	2.1 ²
Methyl- <i>t</i> -butyl ether (MtBE)	0.999	0.09	76.1	119.9	0.49	98	5.7
Diisopropyl ether (DIPE)	0.999	0.13	70.4	134.1	0.51	102	7.9
<i>t</i> -Butyl alcohol (TBA) ³	0.997	0.99	79.6	129.7	5.23	105	6.0
1,1-Dichloroethane	1.000	0.10	73.3	121.5	0.49	97	6.2
<i>t</i> -Butyl ethyl ether (ETBE)	1.000	0.12	70.2	132.7	0.51	101	7.8
<i>cis</i> -1,2-Dichloroethene	1.000	0.09	74.0	119.7	0.48	97	5.9
Bromochloromethane	1.000	0.16	50.2	132.0	0.46	91	11.3
Chloroform	1.000	0.13	63.6	128.4	0.48	96	8.5
Carbon tetrachloride	0.999	0.12	72.5	133.8	0.52	103	7.5
Tetrahydrofuran	0.998	0.14	62.6	134.5	0.49	99	9.2
1,1,1-Trichloroethane	1.000	0.08	78.0	119.8	0.49	99	5.3
1,1-Dichloropropene	0.999	0.15	56.3	130.0	0.47	93	10.0
1-Chlorobutane	0.999	0.13	68.6	134.8	0.51	102	8.2
Benzene	1.000	0.09	74.8	121.8	0.49	98	6.0
<i>t</i> -Amyl methyl ether (TAME)	0.999	0.07	83.5	116.5	0.50	100	4.2
1,2-Dichloroethane	1.000	0.11	78.9	132.6	0.53	106	6.4
Trichloroethene	1.000	0.10	73.3	126.2	0.50	100	6.7
<i>t</i> -Amyl ethyl ether (TAEE)	0.999	0.05	86.3	112.0	0.50	99	3.3
Dibromomethane	1.000	0.06	86.1	117.9	0.51	102	3.9
1,2-Dichloropropane	1.000	0.12	61.6	122.4	0.46	92	8.3
Bromodichloromethane	1.000	0.08	83.3	121.8	0.51	103	4.7
<i>cis</i> -1,3-Dichloropropene	0.999	0.09	75.1	119.7	0.49	97	5.8
Chlorobenzene-d5 (IS 2)	5.7 ¹						3.5 ²
Toluene	0.998	0.13	60.1	127.9	0.47	94	9.1

Compound	Calibration		MRL Confirmation (0.5 ppb)		Accuracy and Precision (n=7, 0.5 ppb) ³		
	Linearity (r ²)	MDL (ppb)	LPIR (>50 %)	UPIR (<150 %)	Avg. Conc. (ppb)	Accuracy (±20 %)	Precision (≤20 %)
Tetrachloroethene	0.997	0.16	54.1	132.7	0.47	93	10.6
<i>trans</i> -1,3-Dichloropropene	0.998	0.12	66.8	125.7	0.48	96	7.7
Ethyl methacrylate	0.997	0.14	59.1	128.9	0.47	94	9.4
1,1,2-Trichloroethane	0.998	0.14	53.5	122.5	0.44	88	9.9
Dibromochloromethane	0.998	0.12	69.9	129.0	0.50	99	7.5
1,3-Dichloropropane	0.997	0.13	66.2	131.5	0.49	99	8.3
1,2-Dibromoethane (EDB)	0.997	0.09	79.7	127.7	0.52	104	5.8
Chlorobenzene	1.000	0.07	84.4	117.3	0.50	101	4.1
Ethylbenzene	1.000	0.08	77.0	116.7	0.48	97	5.2
1,1,1,2-Tetrachloroethane	0.998	0.07	77.2	112.5	0.47	95	4.7
<i>m</i> -, <i>p</i> -Xylene	1.000	0.26	61.5	126.2	0.94	188	8.7
<i>o</i> -Xylene	1.000	0.16	59.3	138.4	0.49	99	10.1
Styrene	1.000	0.07	81.7	118.8	0.50	100	4.7
Bromoform	0.997	0.07	82.9	117.1	0.50	100	4.3
Isopropylbenzene	0.999	0.12	64.8	123.7	0.47	94	7.9
1,4-Dichlorobenzene-d4 (IS 3)	7.2 ¹						1.1 ²
4-Bromofluorobenzene (Surr)	2.6 ¹				12.85	103	1.4 ²
Bromobenzene	1.000	0.11	72.7	127.9	0.50	100	6.9
<i>n</i> -Propylbenzene	0.999	0.08	76.1	118.8	0.49	97	5.5
1,1,2,2-Tetrachloroethane	0.998	0.13	72.2	138.1	0.53	105	7.9
2-Chlorotoluene	1.000	0.08	76.6	115.4	0.48	96	5.1
1,3,5-Trimethylbenzene	1.000	0.07	81.5	114.5	0.49	98	4.2
1,2,3-Trichloropropane	0.999	0.08	89.5	132.3	0.55	111	4.9
4-Chlorotoluene	1.000	0.08	77.0	116.7	0.48	97	5.2
<i>t</i> -Butylbenzene	0.999	0.12	72.9	134.6	0.52	104	7.5
Pentachloroethane	0.994	0.14	76.6	148.5	0.56	113	8.1
1,2,4-Trimethylbenzene	1.000	0.07	79.2	114.5	0.48	97	4.6
<i>sec</i> -Butylbenzene	1.000	0.07	79.7	116.3	0.49	98	4.7
4-Isopropyltoluene	0.994	0.09	76.7	122.2	0.50	99	5.8
1,3-Dichlorobenzene	1.000	0.08	78.6	116.8	0.49	98	4.9
1,4-Dichlorobenzene	1.000	0.06	88.2	116.3	0.51	102	3.5
<i>n</i> -Butylbenzene	0.998	0.11	72.6	130.3	0.51	101	7.2
Hexachloroethane	1.000	0.19	50.6	146.5	0.49	99	12.3
1,2-Dichlorobenzene	1.000	0.06	86.8	117.2	0.51	102	3.8
1,2-Dichlorobenzene-d4 (Surr)	1.4 ¹				12.64	101	1.6 ²
1,2-Dibromo-3-chloropropane	0.997	0.16	69.1	149.8	0.55	109	9.3
Hexachlorobutadiene	0.999	0.12	70.8	129.7	0.50	100	7.4
1,2,4-Trichlorobenzene	0.997	0.06	86.8	117.2	0.51	102	3.8
Naphthalene	0.997	0.07	87.2	122.5	0.52	105	4.2
1,2,3-Trichlorobenzene	0.998	0.08	79.1	119.7	0.50	99	5.2

¹ %RSD of the peak areas for the internal standard or the calculated amount for the surrogate standards from the calibration curve samples.

² %RSD of the peak areas for the internal standard or the calculated amount for the surrogate standards from the seven MDL samples.

³ Data from seven 5 ppb samples.

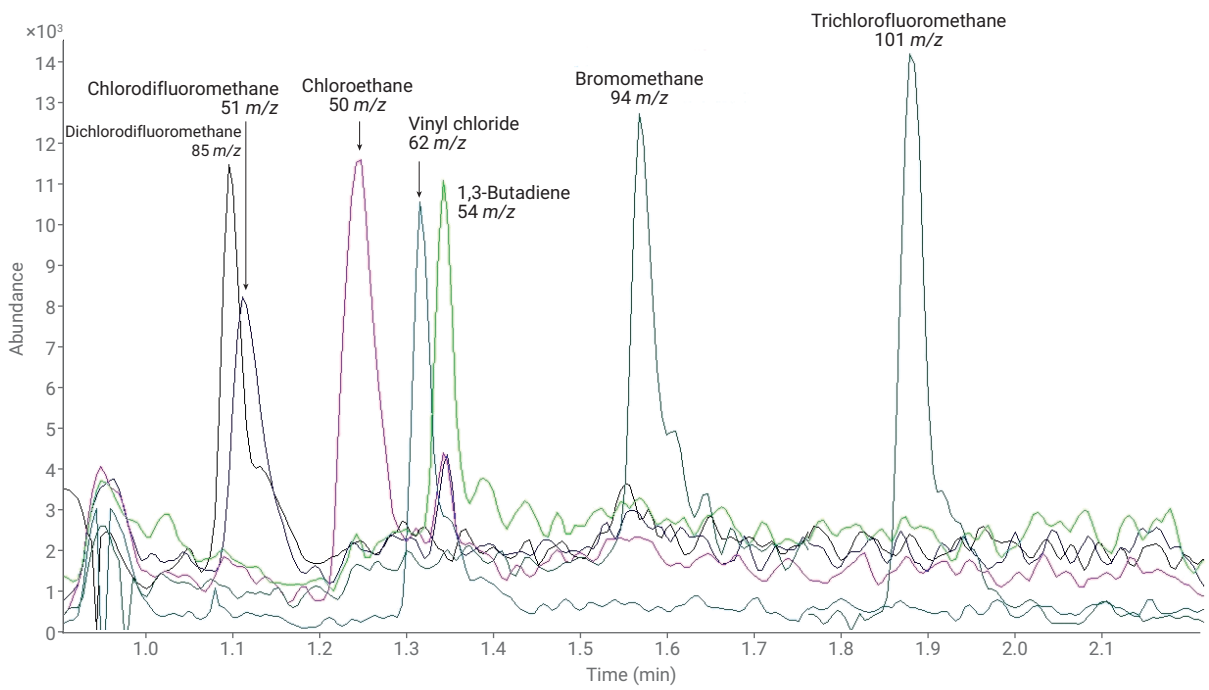


Figure 1. Primary Characteristic Ions for the First Seven Gases of a 0.2 ppb Standard Indicating Excellent Detection Limits with Minimal Interference from Water.

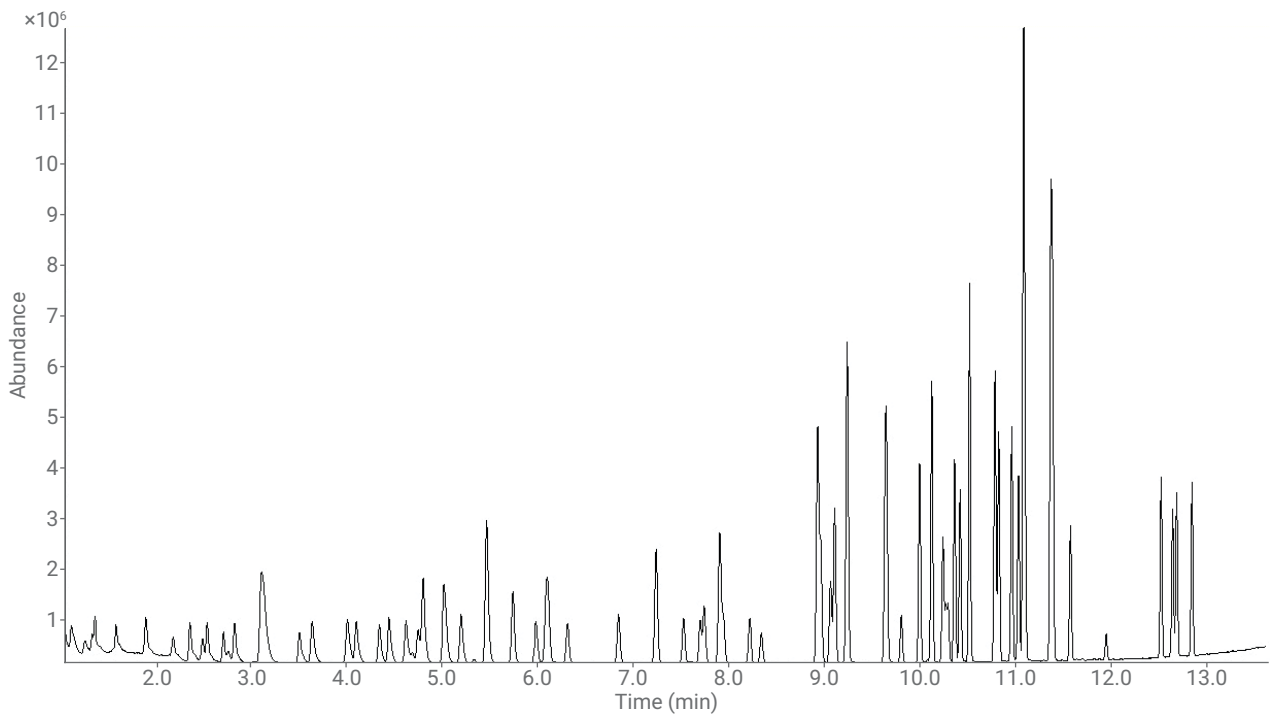


Figure 2. Total Ion Chromatogram of a 5 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds with No Water Interference.

Conclusion

The Teledyne Tekmar Lumin purge and trap concentrator and AQUATek 100 were used to process water samples containing VOCs following US EPA Method 524.4 with detection by an Agilent 7890B GC and 5977A MSD system. The linearity of the calibration curve from 0.2 ppb to 50 ppb 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.

References

1. Munch, J. W. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; *US EPA Method 524.3 - Revision 1.0*, June **2009**.

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