US EPA Method 524.2 with the Teledyne Tekmar Lumin P&T Concentrator and Agilent 7890B GC / 5977A MS

Application Note

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Abstract

US EPA Method 524.2 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 Chromatograph/Mass Spectrometer (GC/MS) due to the 4 minute desorb time recommendation.

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 transfered to the Agilent GC/MS 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.

The US EPA method that places a large amount of water vapor on the GC/MS system is US EPA method 524.2. This method recommends approximately 4 minutes of desorb time from the analytical trap, which inundates the GC/MS system with large volumes of water, and leads to poor chromatography for early eluting gases.

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 the 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® standards from Drinking Water VOA MegaMix, Oxygenates, Ketones and 502.2 Mix. 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 50 ppb for all of the compounds except the ketones and t-butanol. The ketones range was from 1.25 ppb to 125 ppb. The t-butanol range was from 2.5 ppb to 250 ppb. The relative Response Factor (RF) using fluorobenzene as the internal standard was calculated for each VOC.

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 and AQUATek 100 conditions in Table I and the GC/MS conditions in Table II.

The Relative Standard Deviation (RSD) of the Response Factor (RF), MDL, accuracy, and precision data are shown in Table III. A 0.2 ppb standard was analyzed to indicate the lowest detectable peak for the initial six gases unencumbered by excessive water in Figure 1. Figure 2 displays a 5 ppb standard, indicating excellent peak resolution for all of the VOCs, including the first six gases.

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	150 °C	Bake Temp	280 °C
Sample Mount Temp	90 °C	MCS Bake Temp	200 °C
Purge Ready Temp	35 °C	Bake Flow	200 mL/min
MCS Purge Temp	20 °C	**AQUATek 100**	**Variable**
Standby Flow	10 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	1.00 min	Water Temp	90 °C
Dry Purge Flow	100 mL/min	Bake Rinse Drain Cycles	1
Desorb	**Variable**	Bake Rinse Drain Time	0.35 min
Desorb Preheat Temp	245 °C		
Desorb Time	4.00 min	**Trap**	K
Desorb Temp	250 °C		
Drain Flow	300 mL/min		

Table II Agilent 7890B GC / 5977A MS

Agilent 7890B Conditions	
Column	DB-624 UI, 20 m x 0.18 mm, 1 m Film, Helium – 0.8 mL/min
Oven Profile	35 °C, 4 min, 15 °C/min to 70 °C, 25 °C/min to 225 °C, 2 min hold
Inlet	150 °C, 100:1 Split, helium saver 20 mL/min after 4 min
Agilent 5977A Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 m/z to 260 m/z, Delay 0.8 min
Gain	Gain Factor 14

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Results

Table III Method 524.2 Calibration, Accuracy and Precision Data

Compound	Calibration		Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
Dichlorodifluoromethane	8.0	0.12	0.48	95	8.0
Chloromethane	16.2	0.17	0.69	137	8.0
Vinyl Chloride	3.7	0.15	0.53	105	9.3
Bromomethane	11.7	0.29	0.82	165	11.2
Chloroethane	5.4	0.14	0.56	111	8.2
Trichlorofluoromethane	6.4	0.11	0.50	101	7.0
Diethyl ether	3.8	0.14	0.53	106	8.5
1,1-Dichloroethene	7.6	0.16	0.54	108	9.2
Carbon Disulfide	4.0	0.17	0.55	109	10.0
Iodomethane	12.4	0.08	0.67	133	3.6
Allyl Chloride	4.4	0.15	0.57	115	8.1
Methylene Chloride	8.4	0.18	0.53	107	10.7
Acetone (1.25 ppb)	5.2	1.39	2.58	207	17.1
trans-1,2-Dichloroethene	4.0	0.10	0.53	107	6.1
MTBE-d3 (Surrogate, 12.5 ppb)	2.2		12.69	101	1.3
MTBE	3.5	0.13	0.50	100	8.0
t-Butyl Alcohol (2.5 ppb)	3.9	0.68	2.56	102	8.4
Diisopropyl Ether (DIPE)	5.2	0.08	0.53	105	5.1
1,1-Dichloroethane	3.4	0.16	0.51	102	9.9
Acrylonitrile	7.9	0.22	0.62	124	11.4
t-Butyl Ethyl Ether (ETBE)	2.9	0.10	0.49	99	6.3
cis-1,2-Dichloroethene	4.5	0.17	0.54	108	10.1
2,2-Dichloropropane	5.8	0.08	0.49	98	5.3
Bromochloromethane	6.0	0.23	0.55	109	13.3
Chloroform	4.7	0.03	0.51	101	1.9
Carbon Tetrachloride	4.6	0.13	0.47	94	8.6
Methyl Acrylate	5.8	0.18	0.59	118	9.9
Tetrahydrofuran	15.3	0.44	0.62	124	22.6
1,1,1-Trichloroethane	5.3	0.11	0.52	104	6.8
1,1-Dichloropropane	7.1	0.19	0.51	102	12.1
2-Butanone (MEK, 1.25 ppb)	8.3	0.49	1.41	113	11.1
1-Chlorobutane	5.8	0.15	0.50	99	9.9
Benzene	4.4	0.16	0.49	98	10.6
Propionitrile (1 ppb to 50 ppb)[1]	6.2				

Table III Method 524.2 Calibration, Accuracy and Precision Data					
Compound	Calibration		Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
Methacrylonitrile	7.0	0.40	0.61	121	20.9
t-Amyl Methyl Ether (TAME)	3.2	0.05	0.52	104	3.2
1,2-Dichloroethane	2.6	0.16	0.50	100	10.5
Fluorobenzene (IS, 12.5 ppb)	2.8				1.1
Trichloroethene	3.1	0.13	0.51	101	7.9
1,4-Difluorobenzene (Surr, 12.5 ppb)	2.5		12.51	100	1.8
t-Amyl Ethyl Ether (TAEE)	2.9	0.10	0.49	99	6.3
Dibromomethane	8.9	0.18	0.52	104	11.2
1,2-Dichloropropane	2.7	0.14	0.55	111	8.3
Bromodichloromethane	7.1	0.10	0.46	92	6.6
Methyl Methacrylate	8.6	0.12	0.51	102	7.4
cis-1,3-Dichloropropene	5.7	0.14	0.46	92	9.6
Toluene	4.1	0.08	0.48	96	5.4
2-Nitropropane	7.6	0.32	0.47	95	21.7
Tetrachloroethene	10.1	0.29	0.58	115	16.2
1,1-Dichloropropanone (63 m/z, 1.25 ppb)[2]	0.9987	2.07	1.53	123	43.0
4-Methyl-2-pentanone (58 m/z, 1.25 ppb)[2]	16.4	0.30	1.23	98	7.8
trans-1,3-Dichloropropene	7.1	0.10	0.48	97	6.3
1,1,2-Trichloroethane	5.1	0.11	0.50	101	6.8
Ethyl Methacrylate	10.4	0.17	0.48	97	11.3
Dibromochloromethane	7.1	0.11	0.46	92	7.4
1,3-Dichloropropane	2.5	0.16	0.50	99	10.2
1,2-Dibromoethane (EDB)	5.3	0.15	0.51	102	9.3
2-Hexanone (1.25 ppb)	16.6	0.51	1.27	101	12.8
Chlorobenzene-d5 (Surr, 12.5 ppb)	3.4		12.1	97	2.2
Chlorobenzene	2.5	0.11	0.50	99	6.9
Ethylbenzene	4.4	0.10	0.48	96	6.5
1,1,1,2-Tetrachloroethane	5.7	0.07	0.45	90	5.0
m-, p-Xylene	4.6	0.09	0.94	94	3.1
o-Xylene	5.1	0.12	0.48	96	8.2
Styrene	5.9	0.12	0.50	99	7.5
Bromoform	10.1	0.06	0.46	93	3.9
Isopropylbenzene	6.0	0.07	0.46	91	5.2
4-Bromofluorobenzene (Surr, 12.5 ppb)	4.2		12.2	97	1.8
Bromobenzene	3.5	0.08	0.50	100	5.2

Table III Method 524.2 Calibration, Accuracy and Precision Data

Compound	Calibration		Accuracy and precision (n=7, 0.5 ppb)		
	Linearity RF (%RSD)	MDL (ppb)	Avg. Conc. (ppb)	Accuracy (%)	Precision (%RSD)
n-Propylbenzene	5.7	0.06	0.48	96	4.3
1,1,2,2-Tetrachloroethane	7.9	0.17	0.52	104	10.6
2-Chlorotoluene	5.1	0.09	0.48	96	5.6
1,3,5-Trimethylbenzene	6.3	0.11	0.47	93	7.5
1,2,3-Trichloropropane	4.9	0.12	0.52	103	7.4
trans-1,4-Dichloro-2-butene	8.2	0.34	0.54	108	20.2
4-Chlorotoluene	7.0	0.05	0.49	97	3.5
t-Butylbenzene	8.3	0.15	0.47	95	9.7
Pentachloroethane	13.2	0.36	0.37	75	30.2
1,2,4-Trimethylbenzene	4.4	0.12	0.45	89	8.8
sec-Butylbenzene	7.0	0.12	0.47	93	8.0
4-Isopropyltoluene	5.7	0.03	0.45	90	1.8
1,3-Dichlorobenzene	6.0	0.11	0.47	93	7.5
1,4-Dichlorobenzene-d4 (Surr, 12.5 ppb)	4.1		12.3	98	0.5
1,4-Dichlorobenzene	5.1	0.08	0.51	103	4.9
n-Butylbenzene	5.2	0.13	0.47	94	8.5
Hexachloroethane	6.8	0.13	0.49	98	8.6
1,2-Dichlorobenzene-d4 (Surr, 12.5 ppb)	4.1		12.1	96	2.4
1,2-Dichlorobenzene	4.7	0.07	0.50	100	4.4
Nitrobenzene (2 ppb to 50 ppb)[1]	1.7				
1,2-Dibromo-3-chloropropane	12.1	0.42	0.67	133	20.0
Hexachlorobutadiene	7.1	0.17	0.52	104	10.6
1,2,4-Trichlorobenzene	9.1	0.12	0.49	97	7.8
Napthalene	13.7	0.08	0.49	98	5.3
1,2,3-Trichlorobenzene	10.3	0.13	0.50	100	8.2

1. Compound is a poor purger. Data is presented for calibration curve data and the detectable range. MDL samples were not detectable.
2. Co-eluting peaks. Different ions used due to interference on this column between 1,1-dichloropropanone and 4-methyl-2-pentanone.

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

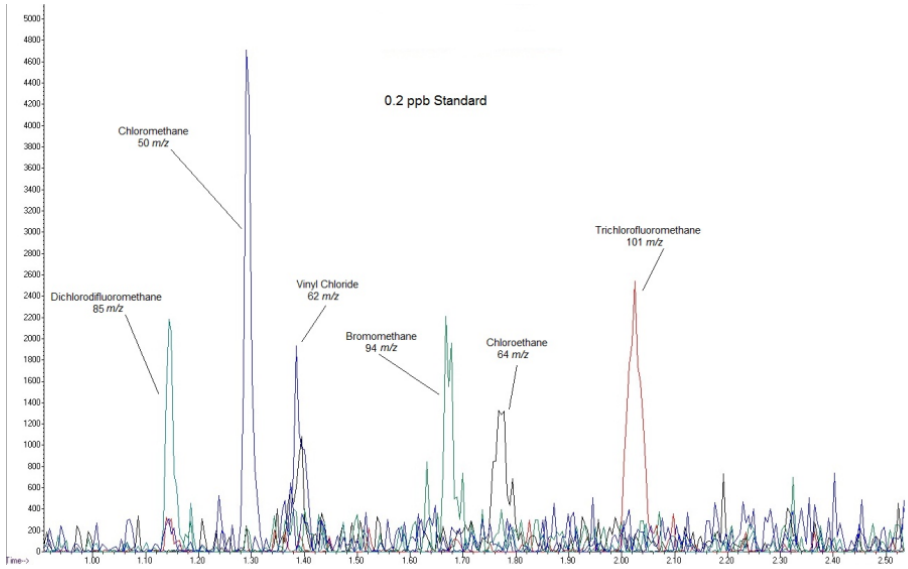
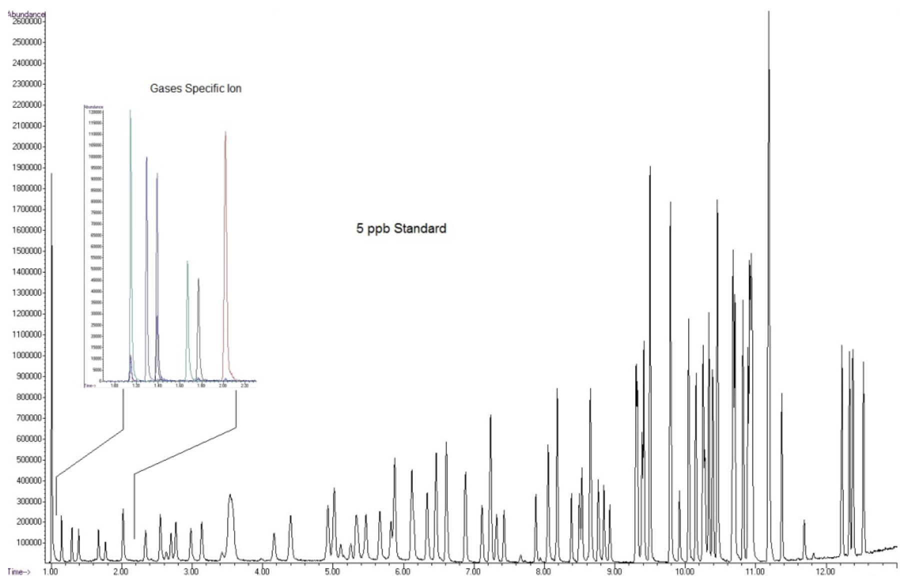


Figure 2 Total Ion Chromatogram of a 5 ppb VOC Standard with an Inset of the Primary Characteristic Ions for the First Six gases Indicating Consistent Peak Shapes for all Compounds with No Water Interference.



Conclusion

The Teledyne Tekmar Lumin Purge and Trap Concentrator and AQUATek 100 was used to process water samples containing VOCs following US EPA Method 524.2 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.

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, 1995