

Application Note

Roger Bardsley, Applications Chemist, Teledyne Tekmar

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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).

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 purge and trap instruments. Additionally, an efficient trap cooling design reduces sample cycle time 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 the GC/MS system used for detection. Because Gas Chromatography (GC) inlets, columns and Mass Spectrometers (MS) are sensitive to water, the transferred water vapor often results in column and inlet issues, as well as frequent MS cleaning to remove oxidation.

Traditionally, purge and trap instruments have reduced the amount of water transferred to GC/MS instruments through a variety of water management techniques, with only moderate success. 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.

The use of US EPA Method 524.2 in particular, places a large amount of water on GC/MS systems due to its recommended 4 minute trap desorb time, inundating the GC/MS system with large volumes of water and resulting in 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 system.

Sample Preparation

Calibration standards were prepared from Restek® standards using 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 shown 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 Instrument 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	Condenser Bake Temp	200 °C
Purge Ready Temp	35 °C	Bake Flow	200 mL/min
Condenser 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	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	Vocarb® 3000 or K
Desorb Temp	250 °C		
Drain Flow	300 mL/min		

Table II PerkinElmer® Clarus® 600 GC / Clarus® SQ8T MS	
PerkinElmer® Clarus® 600 GC Conditions	
Column	Restek® Rtx® VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 0.9 mL/min
Oven Profile	35 °C, 3 min, 14 °C/min to 100 °C, 25 °C/min to 240 °C, 2 min hold
Inlet	160 °C, 100:1 Split, Helium Saver Spilt to 20:1 after 4 min
PerkinElmer® Clarus® SQ8T MS Conditions	
Temp	Transfer Line 200 °C; Source 200 °C; Quad 150 °C
Scan	Range 35 m/z to 260 m/z, Delay 0.5 min

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	9.9	0.14	0.55	110	8.2
Chloromethane	6.5	0.10	0.52	105	6.2
Vinyl Chloride	10.5	0.14	0.50	100	9.0
Bromomethane	14.5	0.16	0.55	111	9.0
Chloroethane	14.6	0.24	0.61	123	12.2
Trichlorofluoromethane	7.5	0.09	0.56	111	5.3
Diethyl Ether	5.9	0.12	0.54	108	6.9
1,1-Dichloroethene	7.4	0.18	0.58	115	9.7
Carbon Disulfide	8.5	0.10	0.54	107	5.7
Iodomethane	7.0	0.10	0.50	100	6.1
Allyl Chloride	6.0	0.16	0.46	92	11.2
Methylene Chloride	0.9958	0.17	0.46	93	11.7
trans-1,2-Dichloroethene	7.9	0.22	0.52	105	13.2
MtBE-d3 (Surogate, 12.5 ppb)	1.5	0.67	12.23	98	1.7
Methyl tert-Butyl Ether (MtBE)	8.2	0.09	0.52	104	5.6
tert-Butyl Alcohol (2.5 ppb)	14.3	0.52	2.46	98	6.7
Diisopropyl Ether (DIPE)	3.9	0.08	0.49	97	5.2
1,1,-Dichloroethane	5.8	0.17	0.54	108	10.0
Acrylonitrile	8.9	0.18	0.55	111	10.5
tert-Butyl Ethyl Ether (ETBE)	4.9	0.07	0.51	102	4.3
cis-1,2,-Dichloroethene	7.2	0.24	0.53	106	14.5
2,2,-Dichloropropane	3.9	0.13	0.47	94	8.8
Bromochloromethane	6.7	0.27	0.52	104	16.4
Chloroform	9.4	0.07	0.53	106	4.1
Carbon Tetrachloride	6.5	0.16	0.58	116	8.9
1,1,1-Trichloroethane	4.6	0.12	0.53	105	7.5
Methyl Acrylate	6.3	0.21	0.50	100	13.5
Tetrahydrofuran	9.6	0.37	0.45	89	26.6
1,1-Dichloropropene	7.7	0.19	0.51	101	12.0
2-Butanone (MEK, 1.25 ppb)	7.5	0.25	1.18	95	6.7
1-Chlorobutane	8.4	0.04	0.53	105	2.4

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)
Benzene	5.6	0.14	0.57	113	7.8
Propionitrile	8.4	0.24	0.54	108	14.0
Methacrylonitrile	7.4	0.19	0.52	104	11.7
tert-Amyl Methyl Ether (TAME)	4.1	0.06	0.50	100	3.7
1,2-Dichloroethane	5.8	0.14	0.54	107	8.2
Trichloroethene	7.2	0.12	0.48	95	8.3
1,4-Difluorobenzene (Surr, 12.5 ppb)	1.0	0.31	12.45	100	0.8
tert-Amyl Ethyl Ether (TAEF)	4.9	0.07	0.49	98	4.5
Dibromomethane	4.8	0.08	0.55	110	4.4
1,2-Dichloropropane	4.3	0.05	0.52	104	3.2
Bromodichloromethane	6.4	0.09	0.55	109	5.5
Methyl Methacrylate	3.9	0.13	0.50	99	8.0
Chloroacetonitrile	7.5	0.57	4.33	87	4.2
cis-1,3-Dichloropropene	7.6	0.09	0.50	101	5.8
Toluene	6.4	0.08	0.47	95	5.1
1,1-Dichloro-2-propanone (1.25 ppb)	16.1	0.26	1.39	111	5.9
Tetrachloroethene	6.8	0.11	0.54	109	6.4
2-Nitropropane	5.9	0.04	0.47	94	3.0
4-Methyl-2-pentanone (MIBK, 1.25 ppb)	5.9	0.10	1.17	94	2.7
trans-1,3-Dichloropropene	12.5	0.14	0.48	95	9.2
1,1,2-Trichloroethane	5.8	0.08	0.56	113	4.8
Ethyl Methacrylate	10.7	0.13	0.49	97	8.5
Dibromochloromethane	11.2	0.11	0.49	99	7.2
1,3-Dichloropropane	6.2	0.12	0.53	106	7.0
1,2-Dibromoethane (EDB)	6.5	0.07	0.51	102	4.1
2-Hexanone (1.25 ppb)	5.2	0.25	1.16	92	6.8
Chlorobenzene-d5 (Surr)	1.2	0.41	12.58	101	1.0
Chlorobenzene	2.6	0.10	0.51	101	6.4
Ethylbenzene	5.7	0.08	0.48	95	5.3
1,1,1,2-Tetrachloroethane	7.5	0.08	0.50	99	5.2
m-, p-Xylene	10.2	0.10	0.91	91	3.5
o-Xylene	8.3	0.15	0.47	93	10.5
Styrene	10.8	0.14	0.47	94	9.4

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)
Bromoform	13.9	0.08	0.50	99	5.3
Isopropylbenzene	10.0	0.13	0.46	91	9.2
Bromofluorobenzene (Surr, 12.5 ppb)	3.4	0.32	11.88	95	0.9
Bromobenzene	4.9	0.06	0.51	102	4.0
n-Propylbenzene	10.7	0.10	0.45	90	7.0
1,1,2,2-Tetrachloroethane	6.6	0.18	0.52	105	10.9
2-Chlorotoluene	10.8	0.05	0.44	87	3.4
1,3,5-Trimethylbenzene	11.6	0.08	0.45	90	5.4
1,2,3-Trichloropropane	4.4	0.12	0.48	96	8.2
trans-1,4-dichloro-2-butene	6.8	0.18	0.51	102	11.3
4-Chlorotoluene	11.0	0.07	0.45	90	5.0
tert-Butylbenzene	10.5	0.13	0.46	92	8.8
Pentachloroethane	7.8	0.14	0.46	92	9.3
1,2,4-Trimethylbenzene	13.0	0.10	0.44	88	6.9
sec-Butylbenzene	11.6	0.04	0.43	85	3.3
4-Isopropyltoluene	11.8	0.09	0.44	87	6.9
1,3-Dichlorobenzene	7.1	0.07	0.47	93	5.1
1,4-Dichlorobenzene-d4 (Surr, 12.5 ppb)	5.9	0.72	11.99	96	1.9
1,4-Dichlorobenzene	4.6	0.14	0.52	104	8.4
n-Butylbenzene	11.7	0.10	0.44	87	7.2
Hexachloroethane	14.6	0.09	0.52	103	5.4
1,2-Dichlorobenzene-d4 (Surr, 12.5 ppb)	5.1	0.66	12.48	100	1.7
1,2-Dichlorobenzene	6.3	0.18	0.55	109	10.2
1,2-Dibromo-3-chloropropane	6.5	0.13	0.49	98	8.6
Nitrobenzene (2 ppb to 50 ppb, 5ppb MDL) ¹	17.4	3.62	5.37	107	21.4
Hexachlorobutadiene	5.1	0.10	0.48	96	6.9
1,2,4-Trichlorobenzene	8.9	0.17	0.47	95	11.2
Naphthalene	11.5	0.10	0.45	91	6.8
1,2,3-Trichlorobenzene	8.6	0.20	0.50	100	12.7

- Compound is a poor purger. Data is presented for calibration curve data and the detectable range. MDL samples were not detectable.

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.

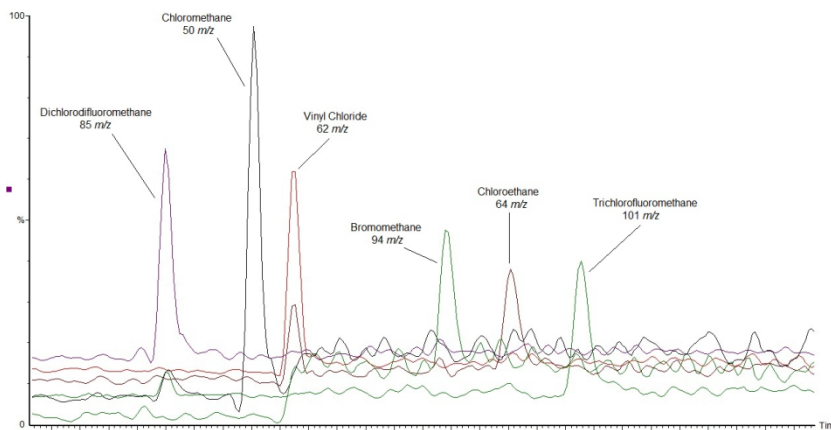
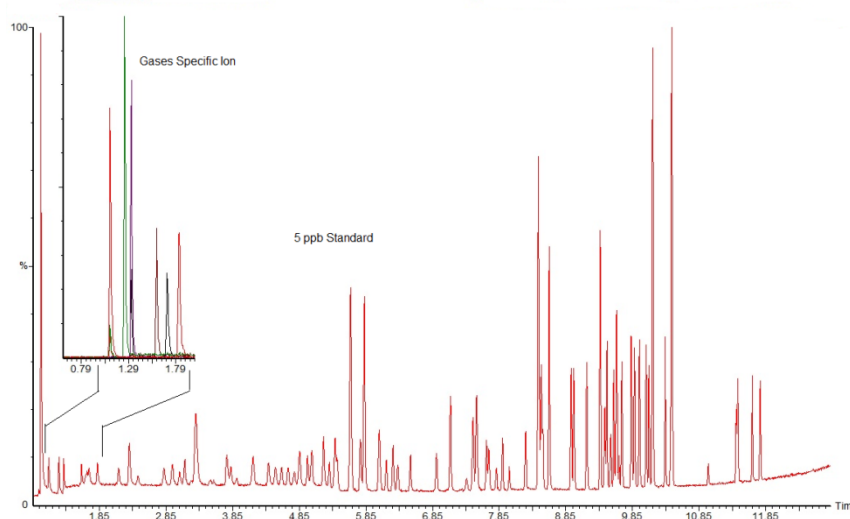


Figure 2 Total Ion Chromatogram of a 5 ppb VOC Standard with an Inset of the Primary Characteristic Ions for the First Six gases indicating Consistent Peak Shapes for all Compounds with No Water Interference.



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 a PerkinElmer® Clarus® 600GC/Clarus® SQ8T 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; U.S. Environmental Protection Agency - National Exposure Research Laboratory Office of Research and Development: Cincinnati, Oh, 1995