Chromatography
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US EPA Method 524.2 with the Tekmar Lumin P&T and the Thermo Scientific™ TRACE™ 1610 GC and ISQ™ 7610 MS System with an HeSaver-H₂Safer™ SSL Injector and an ExtractaBrite Source

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Abstract

As helium supplies become scarcer and more expensive, customers have been seeking alternative carrier gases or ways to conserve helium without sacrificing system performance. US EPA Method 524.2 requires helium to purge volatile organic compounds (VOCs) out of drinking water samples. Therefore, the need for a helium saver Gas Chromatograph (GC) inlet is needed to conserve helium during analysis. This application demonstrates the US EPA Method 524.2 method requirements were met while conserving helium with the Teledyne LABS Lumin Purge and Trap (P&T) concentrator along with the AQUATek LVA autosampler combined with a Thermo Scientific ISQ 7610 Mass Spectrometry (MS) system and coupled with a Thermo Scientific TRACE 1610 GC with a helium saver inlet. This method is effective at concentrating trace levels of VOCs; however, it can also transfer a significant amount of water vapor to the GC/MS due to the four-minute desorb time requirement. This application will demonstrate the ability of the Lumin P&T's innovative moisture control system (MCS) to remove water vapor transferred to the GC/MS. Method requirements include: a working average response factor (RF) calibration curve ≤20% RSD, method detection limits (MDLs), and a mid-point calibration check for target compounds.

Introduction

The US EPA Method 524.2 method specific four minute desorb creates a water peak that can minimize the sensitivity of the analysis, cause compounds to co-elude, shift in retention time, and cause poor peak shape. The Tekmar Lumin P&T has an innovative moisture control system (MCS) that improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. The AQUATek LVA autosampler has an 84-position chiller enabled sample tray and utilizes a fixed volume loop that transfers the liquid sample, internal standards, and surrogate standards to the Lumin P&T concentrator. In addition to other refinements, the AQUATek LVA incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust.

Sample Preparation

A 50 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek® standards: Drinking Water VOA MegaMix™, Ketone Mix, and 502.2 Calibration Mix. In total, the standards contained 83 compounds.

The calibration curves were prepared from 0.2 parts per billion (ppb) to 40 ppb for all compounds. The relative responses were calculated for each compound using one internal standard: Fluorobenzene. Surrogate standards consisted of 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 25 mL sample for a resulting concentration of 10 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and precision for all compounds. Also, seven 10 ppb standards were prepared as a mid-point calibration check to calculate accuracy and precision for all compounds. All calibration, MDL, and mid-point calibration check standards were analyzed with the Lumin P&T and AQUATek LVA conditions in Table I. GC-MS conditions are shown in Table II.

Experimental Instrument Conditions

Table I Tekmar Lumin P&T and AQUATek LVA Water Method Conditions			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	150 °C	Desorb Preheat Temp	245 °C
Transfer Line Temp	150 °C	Desorb Temp	250 °C
Sample Mount Temp	90 °C	Desorb Time	4.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	35 °C	GC Start Signal	Begin Desorb
MCS Purge Temp	20 °C	**Bake**	Variable
Purge	Variable	Bake Time	4.00 min
Purge Temp	20 °C	Bake Temp	270 °C
Purge Time	11.00 min	MCS Bake Temp	180 °C
Purge Flow	40 mL/min	Bake Flow	200 mL/min
Dry Purge Temp	20 °C	**AQUATek LVA**	Variable
Dry Purge Time	1.00 min	Sample Loop Time	1.10 min
Dry Purge Flow	100 mL/min	Sample Transfer Time	1.25 min
Sparge Vessel Heater	Off	Rinse Loop Time	1.10 min
		Sweep Needle Time	0.30 min
		Presweep Time	0.35 min
Trap	9	Water Temp	90 °C
Chiller Tray	On	Bake Rinse Cycles	1
Purge Gas	Helium	Bake Rinse Drain Time	0.60 min

Table II Thermo Scientific TRACE 1610 GC and ISQ 7610 MS System Conditions	
Thermo Scientific TRACE 1610 GC Conditions	
Column	TG-VMS, 30 m x 0.25 mm, 1.4 µm Film, Helium – 1.8 mL/min
Oven Profile	35 °C, 2 min, 15 °C/min to 100 °C, 30 °C/min to 225 °C, 2 min Hold, Run Time 12.5 min
Inlet	200 °C, 30:1 Split, Purge Flow 5.0 mL/min, 0.2 min Helium Delay
Thermo Scientific ISQ 7610 MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 280 °C
Scan	Range 35 *amu* to 260 *amu*, Solvent Delay 1.43 min, Dwell/Scan Time 0.10 sec.
Current	Emission Current 30 µA, Gain 3.00E+005

Results

The relative standard deviation (%RSD) of the response factors for the calibration curve, MDL, and mid-point calibration check data are shown in Table III. Figure 1 shows a 20 ppb standard, indicating excellent peak resolution with no water inference for all VOCs.

Table III US EPA Method 524.2 Calibration, MDL, and Mid-Point Calibration Check Data

Compound	Calibration (0.2-40 ppb)				Method Detection Limit (n=7, 0.5 ppb)		Mid-Point Recovery (n=7, 10 ppb)	
	Retention Time	Quant Ion	Average RF (%RSD)	Average RF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Dichlorodifluoromethane	1.51	85	14.5	0.447	0.06	4.2	6.1	99
Chloromethane	1.71	50	14.3	1.01	0.06	3.9	6.1	87
Vinyl Chloride	1.81	62	8.2	0.509	0.05	3.3	5.7	92
Bromomethane	2.17	94	14.7	0.343	0.08	4.8	3.9	86
Chloroethane	2.32	64	8.7	0.407	0.05	3.5	5.1	81
Trichlorofluoromethane	2.47	101	10.4	0.487	0.05	3.9	4.5	95
Diethyl Ether	2.81	59	7.3	0.218	0.07	4.6	3.6	93
1,1-Dichloroethene	2.99	96	6.7	0.363	0.07	4.7	3.3	92
Carbon Disulfide	3.00	76	7.1	0.934	0.07	4.8	3.7	84
Iodomethane	3.11	142	12.9	0.652	0.03	2.6	2.9	98
Allyl Chloride	3.44	76	4.9	0.272	0.06	3.8	3.7	93
Methylene Chloride	3.54	84	7.2	0.404	0.05	3.3	2.2	90
Acetone[1]	3.60	43	1.0	0.174	0.13	7.4	10.7	98
trans-1,2-Dichloroethene	3.68	96	6.9	0.416	0.07	4.6	2.6	89
Methyl-t-Butyl Ether	3.78	73	4.3	0.657	0.06	3.7	2.3	95
1,1-Dichloroethane	4.20	63	6.7	0.853	0.05	3.1	3.3	92
Acrylonitrile	4.24	52	11.6	0.055	0.16	6.9	4.9	110
cis-1,2-Dichloroethene	4.57	96	5.6	0.428	0.05	3.1	2.9	91
2,2-Dichloropropane	4.64	77	7.4	0.560	0.07	4.4	6.0	94
Bromochloromethane	4.70	128	5.0	0.134	0.05	3.4	1.8	93
Chloroform	4.75	83	6.5	0.688	0.05	3.0	3.4	92
Methyl Acrylate	4.84	55	5.2	0.134	0.08	4.8	3.4	104
Carbon Tetrachloride	4.85	117	5.5	0.461	0.05	3.9	3.5	98
Tetrahydrofuran	4.86	71	11.5	0.021	0.09	4.8	4.5	109
1,1,1-Trichloroethane	4.89	97	5.8	0.537	0.05	3.3	3.7	95
2-Butanone	4.97	43	11.5	0.129	0.09	5.5	9.1	107
1,1-Dichloropropene	4.97	75	6.5	0.509	0.05	3.5	4.4	95
1-Chlorobutane	5.01	56	6.5	0.782	0.05	3.3	4.6	95
Benzene	5.14	78	6.0	1.68	0.04	2.9	3.4	93
Propionitrile	5.17	54	7.5	0.089	0.12	7.1	1.9	102
Methacrylonitrile	5.18	67	5.8	0.071	0.05	3.2	3.5	103
1,2-Dichloroethane	5.28	62	6.6	0.317	0.03	2.2	3.4	95
Fluorobenzene (IS)	5.43	96						
Trichloroethylene	5.54	95	7.4	0.424	0.05	3.5	3.0	92
Dibromomethane	5.84	93	5.1	0.139	0.04	2.4	2.0	95
1,2-Dichloropropane	5.92	63	5.6	0.423	0.03	2.3	3.1	94
Bromodichloromethane	5.96	83	2.1	0.433	0.05	3.1	2.7	96
4-Methyl-2-pentanone	6.08	100	5.4	0.038	0.08	5.1	1.7	101
Methyl Methacrylate	6.08	69	3.5	0.109	0.07	4.9	2.5	102
cis-1,3-Dichloropropene	6.43	75	2.7	0.559	0.04	2.7	3.1	96
Toluene	6.60	92	7.1	1.08	0.06	4.0	2.5	92
Chloroacetonitrile	6.70	48	8.0	0.010	0.19	14.9	9.9	80
2-Nitropropane	6.77	43	7.5	0.110	0.09	5.0	4.3	109
1,1-Dichloropropanone	6.87	43	8.1	0.233	0.08	4.8	5.0	105
Tetrachloroethene	6.87	166	6.1	0.949	0.04	2.8	4.3	92
trans-1,3-Dichloropropene	6.89	75	2.5	0.412	0.05	3.6	2.9	97

Table III **US EPA Method 524.2 Calibration, MDL, and Mid-Point Calibration Check Data**								
Ethyl Methacrylate	7.00	69	6.2	0.236	0.06	4.1	3.0	103
1,1,2-Trichloroethane	7.01	83	2.9	0.192	0.04	2.3	1.9	98
Dibromochloromethane	7.12	129	4.8	0.236	0.05	3.6	1.5	100
1,3-Dichloropropane	7.19	76	4.2	0.395	0.03	2.2	2.5	97
1,2-Dibromoethane	7.29	107	2.8	0.195	0.05	3.3	1.6	98
2-Hexanone	7.43	43	9.3	0.196	0.12	7.4	9.2	102
Chlorobenzene	7.63	112	3.5	1.17	0.05	3.7	2.1	95
Ethylbenzene	7.65	91	4.8	2.15	0.05	3.5	3.1	94
1,1,1,2-Tetrachloroethane	7.67	131	4.5	0.349	0.05	3.5	1.8	96
m-,p-Xylene	7.74	106	3.8	0.905	0.09	3.3	2.8	93
o-Xylene	8.01	106	3.1	0.929	0.04	2.9	2.9	92
Styrene	8.05	104	7.4	1.37	0.05	3.6	2.5	95
Bromoform	8.06	173	16.7	0.168	0.04	3.5	0.8	101
Isopropylbenzene	8.21	105	.2	2.43	0.06	4.2	3.9	96
4-Bromofluorobenzene (SURR)	8.38	95	11.0	0.577		1.7	1.3	97
Bromobenzene	8.45	156	8.4	0.648	0.03	2.3	2.4	92
n-Propylbenzene	8.46	91	7.0	3.23	0.05	3.5	3.6	99
1,1,2,2-Tetrachloroethane[1]	8.51	83	1.0	0.232	0.04	2.5	2.0	101
2-Chlorotoluene	8.56	91	4.8	2.20	0.05	3.5	3.4	95
1,3,5-Trimethylbenzene	8.58	105	7.1	2.51	0.05	3.5	3.4	97
1,2,3-Trichloropropane	8.59	75	10.3	0.233	0.05	3.6	3.5	103
trans-1,4-Dichloro-2-butene[1]	8.61	53	1.0	0.072	0.06	4.5	3.5	98
4-Chlorotoluene	8.66	91	7.1	2.10	0.05	3.5	3.3	94
tert-Butylbenzene	8.77	119	8.4	2.35	0.07	4.7	4.4	97
Pentachloroethane	8.79	117	17.8	0.249	0.10	6.6	6.6	99
1,2,4-Trimethylbenzene	8.81	105	6.7	2.62	0.04	3.3	3.4	99
sec-Butylbenzene	8.88	105	8.8	3.28	0.06	4.0	3.5	104
p-Isopropyltoluene	8.96	119	7.5	2.74	0.06	4.1	3.6	103
1,3-Dichlorobenzene	9.01	146	11.3	1.73	0.05	4.0	2.6	95
1,4-Dichlorobenzene	9.06	146	10.2	1.69	0.04	3.1	2.9	96
n-Butylbenzene	9.21	91	7.7	2.67	0.06	4.6	3.7	103
1,2-Dichlorobenzene-d4 (SURR)	9.31	152	15.8	0.820		2.0	3.7	96
Hexachloroethane[1]	9.31	117	0.997	1.68	0.13	8.3	2.1	102
1,2-Dichlorobenzene	9.31	146	8.4	1.47	0.05	3.5	2.6	96
1,2-Dibromo-3-Chloropropane	9.78	75	10.2	0.046	0.07	5.0	2.9	103
Nitrobenzene	10.11	123	12.9	0.005	0.05	3.4	9.7	84
Hexachlorobutadiene	10.14	225	10.1	0.048	0.08	5.6	3.2	103
1,2,4-Trichlorobenzene	10.17	180	7.4	0.595	0.06	4.2	2.0	101
Naphthalene	10.36	128	8.0	0.596	0.06	3.9	1.5	101
1,2,3-Trichlorobenzene	10.46	180	10.1	0.394	0.06	4.4	2.2	102

[1]Compound used a quadratic regression calibration

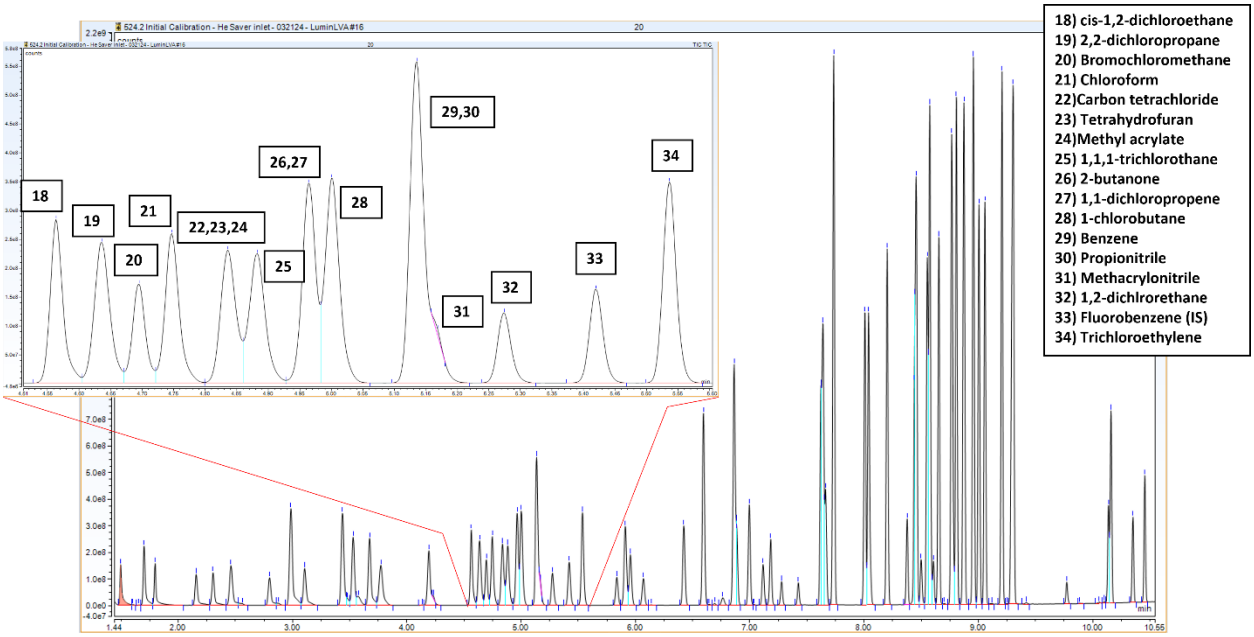

Figure 1 Total Ion Chromatogram of a US EPA 524.2 method 20 ppb VOC standard with an inset indicating consistent peak shapes and separation for all compounds with minimal water interference.

Conclusion

This study demonstrates the capability of the Teledyne LABS Tekmar Lumin P&T along with the AQUATek LVA autosampler to process VOCs in water samples following US EPA Method 524.2 with detection by a Thermo Scientific ISQ 7610 MS system coupled with a Thermo Scientific TRACE 1610 GC. The %RSD of the calibration curve passed all method requirements. Furthermore, the average MDL for all compounds was 0.06 ppb with a 4.1% RSD. Seven 10 ppb mid-point calibration check standards averaged a 97% recovery with a 3.6% RSD. Both MDL and mid-point calibration check showed no interference from excessive water.

By making additional, appropriate changes to the GC oven temperature program, the GC-MS cycle time may also be reduced, increasing laboratory throughput in a 12-hour period.

References

1. U.S. EPA. 1992. “Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry,” Revision 4.1. Cincinnati, OH. [Online] https://www.epa.gov/sites/production/files/2015-06/documents/epa-524.2.pdf (accessed March, 26 2020).