

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

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Page | 1

Abstract

US EPA Method 524.2 was used to determine the concentration of volatile organic compounds (VOCs) in drinking water. The Teledyne Tekmar Lumin purge and trap (P&T) concentrator, along with an AQUATEk LVA (liquid vial autosampler) and Agilent 7890B GC/5977A MS was used to create a working linear calibration curve and method detection limits (MDLs) for target compounds. This study will demonstrate the ability of the Lumin P&T concentrator with AQUATEk LVA to process drinking water samples for VOC analysis according to US EPA Method 524.2.

Introduction

The AQUATEk LVA is Teledyne Tekmar's most advanced water-only P&T autosampler and is based on the proven Atomx XYZ platform. The AQUATEk LVA includes whisper-quiet XYZ automation, two standard addition vessels and an optional pH meter. Combined with its 84-position chiller enabled sample tray, the result is simple and reliable sample preparation and handling. While US EPA Method 524.2 is effective at concentrating trace levels of VOCs, it can also transfer a significant amount of water vapor to the Gas Chromatograph/Mass Spectrometer (GC/MS) due to the four-minute desorb time recommendation. By pairing the AQUATEk LVA with the Lumin PTC's innovative moisture control system (MCS), water vapor removal is improved by as much as 60%, thereby reducing peak interference and increasing GC column life span. 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 25 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 standard contained 83 compounds.

A calibration curve was prepared from 0.2 ppb to 50 ppb for all compounds. The relative response factor (RF) was 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 5 mL sample for a resulting concentration of 25 ppb. Seven 0.2 ppb standards were prepared to calculate the MDL and accuracy and precision calculations. All calibration and MDL standards were analyzed with the Lumin P&T concentrator and AQUATEk LVA conditions in [Table I](#). GC-MS conditions are shown in [Table II](#).

Experimental Instrument Conditions

Table I Teledyne Tekmar Lumin P&T Concentrator 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	40 °C	GC Start Signal	Begin Desorb
MCS Purge Temp	20 °C		
Purge	Variable	Bake	Variable
Purge Temp	20 °C	Bake Time	2.00 min
Purge Time	11.00 min	Bake Temp	280 °C
Purge Flow	40 mL/min	Bake Flow	200 mL/min
Dry Purge Temp	20 °C	MCS Bake Temp	180 °C
Dry Purge Time	1.00 min		
Dry Purge Flow	100 mL/min		
Sample Temp	40 °C	AQUATEk LVA	Variable
Pre-Purge Time	0.50 min	Sample Loop Time	0.35 min
Pre-Purge Flow	40 mL/min	Sample Transfer Time	0.35 min
Preheat Time	1.00 min	Rinse Loop Time	0.30 min
Sample Heater Enable	Off	Sweep Needle Time	0.30 min
	K	Presweep Time	0.25 min
Chiller Tray	Off	Water Temp	90 °C
Purge Gas	Helium	Bake Rinse Cycles	1
		Bake Rinse Drain Time	0.35 min

Table II Agilent 7890B GC and 5977A MSD System Conditions	
Agilent 7890B GC Conditions	
Column	Rtx®-VMS, 20m x 0.18 mm, 1µm Film, Helium – 1 mL/min
Oven Profile	35 °C, 4 min, 15 °C/min to 85 °C, 30 °C/min to 225 °C, 2 min hold, Run Time 14.00 min
Inlet	180 °C, 120:1 Split, 19.752 psi
Agilent 5977A MSD Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 <i>m/z</i> to 260 <i>m/z</i> , Solvent Delay 0.50 min, Normal Scanning
Gain	Gain Factor 10.00, Autotune

Results

The relative standard deviation (%RSD) of the response factors (RF) for the calibration curves, MDL, and accuracy and precision data are shown in [Table III](#). [Figure 1](#) displays a 30 ppb standard, indicating excellent peak resolution with minimal water interference for all VOCs, including the first six gases.

Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data						
Compound	Calibration			Accuracy and Precision (n=7, 0.2 ppb)1		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (±20%)	Precision (≤20%)
Fluorobenzene (IS)						
Dichlorodifluoromethane	6.99	0.06	0.071	0.23	113	8.03
Chloromethane	10.3	0.08	0.107	0.23	117	11.0
Vinyl Chloride	8.46	0.06	0.202	0.22	112	8.08
Bromomethane	6.43	0.10	0.276	0.23	114	13.5
Chloroethane	5.58	0.09	0.157	0.24	120	12.5
Trichlorofluoromethane	15.6	0.07	0.483	0.21	103	10.4
Diethyl Ether	12.9	0.08	0.072	0.20	98	13.7
1,1-Dichloroethene	14.7	0.10	0.064	0.22	112	14.1
Acetone2	0.998	0.10	0.079	0.22	111	14.6
Carbon Disulfide	7.08	0.09	0.046	0.22	109	13.5
Iodomethane2	0.995	0.12	0.083	0.22	109	17.6
Allyl Chloride	7.83	0.12	0.046	0.21	107	17.8
Methylene chloride	8.29	0.09	0.119	0.23	113	13.0
Acrylonitrile	9.10	0.08	0.052	0.22	111	11.2
trans-1,2-Dichloroethene	8.03	0.09	0.210	0.23	116	12.8
Methyl tert-butyl ether	2.69	0.07	0.532	0.22	108	9.96
1,1-Dichloroethane	5.19	0.08	0.213	0.23	117	10.4
Methyl Methacrylate	12.4	0.11	0.063	0.22	109	15.9
2,2-Dichloropropane	5.07	0.12	0.245	0.19	96	19.8
Propionitrile	18.9	0.10	0.033	0.21	104	15.5

Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data

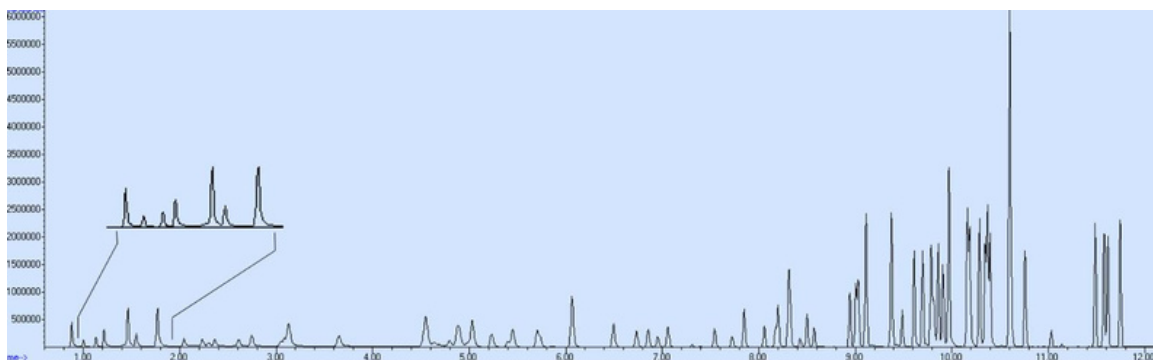
Compound	Calibration			Accuracy and Precision (n=7, 0.2 ppb) ¹		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (±20%)	Precision (≤20%)
cis-1,2-Dichloroethene	11.5	0.09	0.075	0.22	109	12.5
2-Butanone	16.5	0.08	0.092	0.22	112	11.8
Methyl Acrylate	14.3	0.09	0.097	0.23	114	13.0
Methacrylonitrile	7.33	0.09	0.108	0.22	108	12.8
Bromochloromethane	4.25	0.11	0.132	0.21	105	16.5
Chloroform	4.59	0.07	0.419	0.23	115	9.39
Carbon Tetrachloride	6.07	0.08	0.129	0.18	91	13.3
Tetrahydrofuran	11.0	0.08	0.026	0.19	94	13.5
1,1,1-Trichloroethane	5.83	0.06	0.168	0.22	111	9.19
1,1-Dichloropropene	8.91	0.10	0.062	0.22	108	15.3
1-Chlorobutane	7.85	0.09	0.083	0.20	99	14.3
Benzene	5.41	0.05	0.267	0.24	119	6.60
1,2-Dichloroethane	5.44	0.08	0.112	0.23	114	11.3
Trichloroethene	16.2	0.12	0.143	0.23	114	17.4
Dibromomethane	4.61	0.07	0.080	0.20	99	12.0
1,2-Dichloropropane	8.44	0.09	0.105	0.22	112	12.3
2-Nitropropane	13.5	0.13	0.024	0.21	106	20.0
Bromodichloromethane	10.7	0.06	0.173	0.17	84	10.8
Chloroacetonitrile ²	0.995	0.13	0.003	0.22	111	19.0
cis-1,3-Dichloropropene	5.66	0.08	0.115	0.22	109	11.3
1,1-Dichloro-2-propanone	6.70	0.09	0.084	0.19	97	14.8
4-Methyl-2-Pentanone	8.08	0.13	0.084	0.22	109	18.4
Toluene	6.23	0.08	0.223	0.19	97	13.2
Tetrachloroethene	12.6	0.09	0.384	0.23	114	12.7
trans-1,3-Dichloropropene	6.53	0.05	0.142	0.18	91	8.18
Ethyl Methacrylate	6.80	0.08	0.134	0.20	101	13.3
1,1,2-Trichloroethane	7.91	0.07	0.127	0.22	109	10.5
2-Hexanone	10.4	0.04	0.062	0.18	91	7.55
Dibromochloromethane	13.0	0.08	0.197	0.18	91	13.7
1,3-Dichloropropane	5.57	0.05	0.219	0.23	116	6.42
1,2-Dibromoethane	5.74	0.07	0.140	0.20	100	11.9
Chlorobenzene	4.75	0.08	0.399	0.22	109	11.0
Ethylbenzene	9.18	0.04	0.827	0.19	94	6.44
1,1,1,2-Tetrachloroethane	3.07	0.04	0.220	0.20	98	7.14
m-, p-Xylene	11.8	0.07	0.228	0.37	92	6.03
o-Xylene	8.77	0.06	0.248	0.20	99	10.0
Styrene	9.60	0.04	0.459	0.17	85	6.79
Bromoform	12.5	0.09	0.196	0.19	94	15.6
Isopropylbenzene	11.6	0.05	0.721	0.18	91	8.67
4-Bromofluorobenzene (SURR)	6.81		0.329	22.9	92	1.52
Bromobenzene	6.94		0.283	0.20	98	13.5
n-Propylbenzene	11.7		0.813	0.18	89	6.28
		0.08				
		0.03				

Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data

Compound	Calibration			Accuracy and Precision (n=7, 0.2 ppb) ¹		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (±20%)	Precision (≤20%)
1,1,2,2-Tetrachloroethane	12.5	0.07	0.169	0.18	91	12.9
2-Chlorotoluene	11.8	0.04	0.812	0.18	90	7.17
1,3,5-Trimethylbenzene	12.8	0.02	0.645	0.17	85	3.40
1,2,3-Trichloropropane	7.32	0.05	0.268	0.22	109	7.20
trans-1,4-Dichloro-2-butene	7.61	0.12	0.033	0.20	101	19.2
4-Chlorotoluene	9.84	0.02	0.617	0.18	88	4.48
t-Butylbenzene	11.9	0.04	0.813	0.16	82	6.90
Pentachloroethane	12.7	0.08	0.150	0.20	99	12.7
1,2,4-Trimethylbenzene	12.6	0.06	0.696	0.16	81	11.6
sec-Butylbenzene	12.6	0.02	0.997	0.17	84	4.52
4-Isopropyltoluene	12.9	0.03	0.889	0.17	84	6.66
1,3-Dichlorobenzene	10.7	0.05	0.574	0.19	94	8.34
1,4-Dichlorobenzene	7.65	0.05	0.640	0.18	89	8.81
n-Butylbenzene	9.32	0.04	0.806	0.20	100	5.77
Hexachloroethane	12.2	0.08	0.178	0.18	91	13.7
1,2-Dichlorobenzene-d4 (SURR)	6.54		0.645	22.7	91	0.699
1,2-Dichlorobenzene	4.95		0.655	0.20	99	8.13
1,2-Dibromo-3-chloropropane	13.6	0.05	0.033	0.22	111	12.1
Nitrobenzene ²	0.999	0.08	0.006	0.21	106	14.3
Hexachlorobutadiene	12.4	0.10	0.302	0.20	99	10.0
1,2,4-Trichlorobenzene	9.63	0.06	0.502	0.20	98	6.50
Napthalene	13.1	0.04	0.945	0.20	99	7.92
1,2,3-Trichlorobenzene	11.0	0.05	0.508	0.18	92	5.30
		0.03				

1. Data from seven 0.2 ppb samples.
2. Compounds were linear regressed.

Figure 1 Total Ion Chromatogram of a 30 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 using a Four-Minute Desorb.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Lumin P&T concentrator with AQUATek LVA to process drinking water samples for 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. Furthermore, MDL and accuracy and precision for seven 0.2 ppb standards 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. 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