APPLICATION NOTE: AN1904
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

US EPA Method 624 with the Teledyne Tekmar Lumin P&T Concentrator, AQUATek LVA and Agilent 7890B GC/5977A MSD

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Abstract

US EPA Method 624 was used to determine the concentration of volatile organic compounds (VOCs) in wastewater samples. The Teledyne Tekmar Lumin purge and trap (P&T) concentrator along with an AQUATek LVA liquid autosampler and an Agilent 7890B Gas Chromatograph (GC)/5977A Mass Spectrometer (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 VOCs in wastewater samples following US EPA Method 624.

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. 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. By pairing the AQUATek LVA with the Lumin's innovative moisture control system (MCS), water vapor removed is improved by as much as 60%, thereby reducing peak interference and increasing GC column lifespan.

Sample Preparation

A 50 ppm working calibration standard mix was prepared in methanol from the following Restek® standards: 8260B MegaMix®, 502.2 Calibration Mix, and 2-Chloroethyl Vinyl Ether for a total of 31 compounds.

A calibration curve was prepared from 0.5 ppb to 200 ppb for all compounds. The relative response factor (RF) was calculated for each compound using one of the four internal standards: Pentafluorobenzene, 1,4-Difluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of: Dibromofluoromethane, 1,2-Dichloroethane-d4, Toluene-d8 and Bromofluorobenzene. Internal Standards and Surrogates were prepared together in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb standards were prepared for 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/AQUATek LVA Water Method Conditions			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	150 ºC	Desorb Preheat Temp	245 ºC
Transfer Line Temp	150 ºC	Desorb Temp	250 ºC
Sample Mount Temp	90 ºC	Desorb Time	2.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	35 ºC	GC Start Signal	Begin Desorb
MCS Purge Temp	20 ºC		
Purge	**Variable**	**Bake**	**Variable**
Purge Temp	20 ºC	Bake Time	2.00 min
Purge Time	11.00 min	Bake Temp	280 ºC
Purge Flow	40 mL/min	Bake Flow	200 mL/min
Dry Purge Temp	20 ºC	MCS Bake Temp	180 ºC
Dry Purge Time	1.00 min		
Dry Purge Flow	100 mL/min	**AQUATek LVA**	**Variable**
Sample Temp	40 ºC	Sample Loop Time	0.35 min
Pre-Purge Time	0.50 min	Sample Transfer Time	0.35 min
Pre-Purge Flow	40 mL/min	Rinse Loop Time	0.30 min
Preheat Time	1.00 min	Sweep Needle Time	0.30 min
Sample Heater Enable	Off	Presweep Time	0.25 min
Trap	K	Water Temp	90 ºC
Chiller Tray	Off	Bake Rinse Cycles	1
Purge Gas	Helium	Bake Rinse Drain Time	0.35 min

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

Results

The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL and accuracy and precision data are shown in Table III. Figure 1 displays a 50 ppb standard, indicating excellent peak resolution for gas standards VOCs.

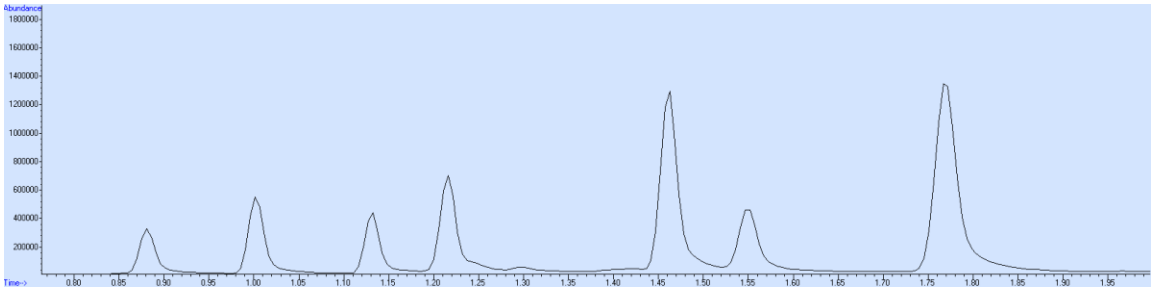
Table III US EPA Method 624 Calibration, Accuracy and Precision Data

Compound	Calibration			Accuracy and Precision (n=7, 0.5 ppb)[1]		
	Linearity RF (≤20%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (70-130%)	Precision (≤20%RSD)
Pentafluorobenzene (IS)						
Chloromethane	10.8	0.13	0.226	0.54	107	7.91
Vinyl Chloride	13.7	0.16	0.363	0.52	103	9.96
Bromomethane[2]	0.995	0.06	0.468	0.63	127	2.77
Chloroethane	9.34	0.17	0.239	0.56	112	9.78
Trichlorofluoromethane	13.6	0.12	0.747	0.49	99	7.73
1,1-Dichloroethene	10.4	0.11	0.410	0.55	110	6.53
Methylene Chloride	9.54	0.06	0.502	0.58	115	3.07
trans-1,2-Dichloroethene	8.95	0.12	0.309	0.51	103	7.65
1,1-Dichloroethane	7.51	0.06	0.373	0.52	103	3.87
Chloroform	6.86	0.08	0.484	0.53	106	4.57
1,1,1-Trichloroethane	13.2	0.11	0.448	0.50	101	7.03
Dibromofluoromethane (SURR)	1.81		0.442	25.1	100	1.52
Carbon Tetrachloride	14.1	0.11	0.470	0.56	112	6.04
1,2-Dichloroethane-d4 (SURR)	3.81		0.310	26.0	104	1.91
Benzene	8.75	0.07	1.03	0.50	100	4.48
1,2-Dichloroethane	9.11	0.09	0.318	0.57	114	4.92
1,4-Diflourobenzene (IS)						
Trichloroethylene	11.8	0.13	0.340	0.54	108	7.74
1,2-Dichloropropane	11.1	0.13	0.169	0.56	112	7.21
Bromodichloromethane	6.10	0.05	0.289	0.47	95	3.15

Table III US EPA Method 624 Calibration, Accuracy and Precision Data						
Compound	Calibration			Accuracy and Precision (n=7, 0.5 ppb)[1]		
	Linearity RF (≤20%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (70-130%)	Precision (≤20%RSD)
2-Chloroethyl Vinyl Ether	9.71	0.10	0.094	0.45	91	7.35
cis-1,3-Dichloropropene	8.30	0.10	0.298	0.46	93	6.61
Toluene-d8 (SURR)	0.880		1.17	24.7	99	0.456
Toluene	11.9	0.09	0.954	0.51	103	5.39
trans-1,3-Dichloropropene	8.33	0.11	0.272	0.48	95	7.27
Tetrachloroethene	14.1	0.09	0.621	0.56	112	4.92
1,1,2-Trichloroethane	2.87	0.11	0.240	0.47	94	7.56
Chlorobenzene-d5 (IS)						
Dibromochloromethane	8.58	0.09	0.280	0.47	95	6.28
Chlorobenzene	9.61	0.13	0.638	0.53	105	7.95
Ethylbenzene	14.7	0.14	0.847	0.48	95	9.25
Bromoform	9.67	0.16	0.253	0.44	89	11.6
Bromofluorobenzene (SURR)	4.04		0.387	23.3	93	0.840
1,4-Dichlorobenzene-d4 (IS)						
1,1,2,2-Tetrachloroethane	4.94	0.11	0.288	0.46	93	7.64
1,3-Dichlorobenzene	11.8	0.11	0.909	0.51	102	6.81
1,4-Dichlorobenzene	9.02	0.15	0.937	0.54	107	8.88
1,2-Dichlorobenzene	8.77	0.12	0.913	0.53	105	7.03

1. Data from seven 0.5 ppb samples.
2. Compounds were linear regressed.

Figure 1 Total Ion Chromatogram of a 50 ppb VOC Gases Standard Indicating Consistent Peak Shapes for all Compounds with No Water Interference.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Lumin P&T concentrator and AQUATek LVA to process wastewater samples for VOCs following US EPA Method 624 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 0.5 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. Appendix A to Part 136 - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater - Method 624: Purgeables; US EPA, Promulgated 1984. [Online] https://www.epa.gov/sites/production/files/2015-10/documents/method_624_1984.pdf (accessed January 29, 2019).

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