APPLICATION NOTE: AN1902
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

US EPA Method 624 - Atomx XYZ and Agilent 7890B GC/5977A MS

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Abstract

USEPA Method 624 was used to determine the concentration of volatile organic compounds (VOCs) in wastewater samples. The Teledyne Tekmar Atomx XYZ P&T system, along with 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 Atomx XYZ to remove water vapor typically transferred to the GC/MS.

Introduction

The Atomx XYZ is Teledyne Tekmar's second-generation, multi-matrix P&T system and is based on the time-tested Atomx instrument platform. The concentrator's efficient trap cooling design reduces sample cycle time by as much as 14% over the previous model. Combined with its 84-position soil and water autosampler, the result is more samples tested per 12-hour period. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column lifespan. In addition to other refinements, the Atomx XYZ incorporates a precision-machined valve manifold block to reduce potential leak sources and ensure the system is both reliable and robust. A reduced footprint of 13 cm (5"), compared to the previous generation, provides more bench space for laboratory tasks.

Sample Preparation

Two calibration working standards with concentrations of 50 and 100 ppm were prepared in methanol from the following Restek® standards: 8260B MegaMix®, 502.2 Calibration Mix, and 2-Chloroethyl Vinyl Ether. In total, the standards contained 31 compounds.

A water calibration curve was prepared from 0.5 ppb to 200 ppb for all compounds. Concentrations 0.5, 2.0, 5.0, 10 and 20 ppb were made with the 50 ppm calibration working standard. Concentrations of 50, 100 and 200 ppb were made with the 100 ppm calibration working standard.

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, with 5 µL 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, MDL and accuracy and precision samples were analyzed with the Atomx XYZ conditions in Table I. GC/MS conditions are shown in Table II.

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Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Water Method Conditions			
Purge	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	140 ºC	Methanol Needle Rinse	Off
Transfer Line Temp	140 ºC	Methanol Needle Rinse Volume	0.00 mL
Sample Mount Temp	90 ºC	Water Needle Rinse Volume	7.00 mL
Water Heater Temp	90 ºC	Sweep Needle Time	0.25 min
Sample Vial Temp	20 ºC	Dry Purge Temp	20 ºC
Soil Valve Temp	100 ºC	Desorb Preheat Temp	245 ºC
Standby Flow	10 mL/min	GC Start Signal	Begin Desorb
Condensate Ready Temp	45 ºC	Desorb Time	2.00 min
Purge Ready Temp	40 ºC	Drain Flow	300 mL/min
Purge	**Variable**	Desorb Temp	250 ºC
Sample Equilibrate Time	0.00 min	**Bake**	**Variable**
Pre-sweep Time	0.25 min	Methanol Glass Rinse	Off
Prime Sample Fill Volume	3.00 mL	Number of Methanol Glass Rinses	0
Sample Volume	5.00 mL	Methanol Glass Rinse Volume	0.00 mL
Sweep Sample Time	0.25 min	Water Bake Rinses	1
Sweep Sample Flow	100 mL/min	Water Bake Rinse Volume	7.00 mL
Sparge Vessel Heater	Off	Bake Rinse Sweep Time	0.25 min
Sparge Vessel Temp	20 ºC	Bake Rinse Sweep Flow	100 mL/min
Pre-purge Time	0.00 min	Bake Rinse Drain Time	0.40 min
Pre-purge Flow	0 mL/min	Bake Time	2.00 min
Purge Time	11.00 min	Bake Flow	200 mL/min
Purge Flow	40 mL/min	Bake Temp	260 ºC
Purge Temp	20 ºC	Condensate Bake Temp	200 ºC
Condensate Purge Temp	20 ºC		
Dry Purge Time	2.00 min	**Trap**	#9
Dry Purge Flow	100 mL/min	**Purge Gas**	Helium

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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 MS Conditions	
Temp	Transfer Line 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 the gas standard's 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	7.95	0.23	0.326	0.57	115	12.7
Vinyl Chloride	5.49	0.10	0.493	0.51	103	6.24
Bromomethane[2]	9.08	0.23	0.535	0.57	114	12.6
Chloroethane	4.44	0.28	0.309	0.58	116	15.3
Trichlorofluoromethane	4.93	0.13	0.859	0.44	89	9.27
1,1-Dichloroethene	5.13	0.19	0.557	0.53	106	11.3
Methylene Chloride	4.76	0.10	0.555	0.58	117	5.17
trans-1,2-Dichloroethene	5.40	0.10	0.518	0.56	113	5.36
1,1-Dichloroethane	4.27	0.16	0.532	0.50	101	10.0
Chloroform	5.76	0.14	0.659	0.54	107	7.41
1,1,1-Trichloroethane	7.44	0.21	0.586	0.54	109	13.0
Dibromofluoromethane (SURR)	3.28		0.438	24	94	1.96
Carbon Tetrachloride	9.16	0.17	0.544	0.40	79	12.5
1,2-Dichloroethane-d4 (SURR)	1.76		0.380	25	99	4.69
Benzene	4.54	0.11	1.39	0.55	110	7.27
1,2-Dichloroethane	5.06	0.11	0.392	0.55	110	5.45
1,4-Diflourobenzene (IS)						
Trichloroethylene	5.97	0.14	0.334	0.53	106	7.55
1,2-Dichloropropane	3.77	0.26	0.213	0.52	105	15.4
Bromodichloromethane	8.50	0.19	0.336	0.48	96	12.5
2-Chloroethyl Vinyl Ether	7.29	0.27	0.141	0.56	112	14.3
cis-1,3-Dichloropropene	9.66	0.12	0.379	0.47	93	8.51

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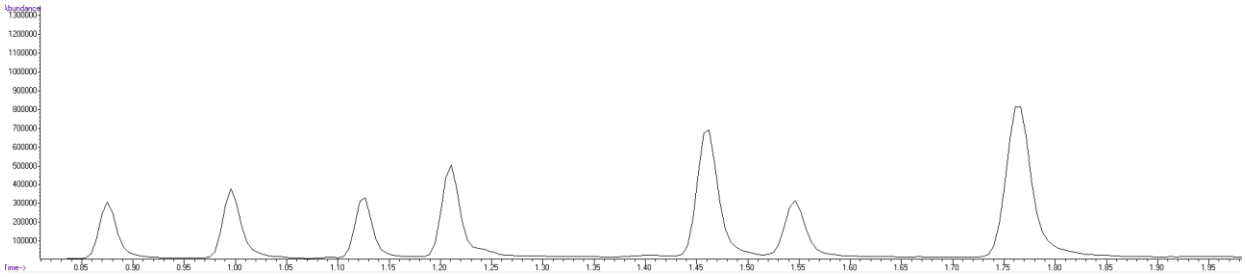
	Linearity RF (≤20%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (70-130%)	Precision (≤20%RSD)
Toluene-d8 (SURR)	1.40		1.10	24	96	1.38
Toluene	5.59	0.08	1.18	0.52	105	5.77
trans-1,3-Dichloropropene	12.0	0.21	0.336	0.49	98	13.7
Tetrachloroethene	13.7	0.21	0.409	0.61	122	11.0
1,1,2-Trichloroethane	9.68	0.13	0.254	0.49	98	8.16
Chlorobenzene-d5 (IS)						
Dibromochloromethane	9.22	0.09	0.353	0.50	100	6.00
Chlorobenzene	4.48	0.14	0.898	0.55	110	8.18
Ethylbenzene	7.36	0.11	1.45	0.54	107	6.48
Bromoform	10.5	0.19	0.247	0.48	96	12.3
Bromofluorobenzene (SURR)	3.22		0.381	25	100	3.64
1,4-Dichlorobenzene-d4 (IS)						
1,1,2,2-Tetrachloroethane	7.35	0.10	0.644	0.51	101	5.88
1,3-Dichlorobenzene	6.38	0.08	1.52	0.55	110	3.64
1,4-Dichlorobenzene	5.08	0.07	1.57	0.52	105	3.85
1,2-Dichlorobenzene	7.79	0.12	1.50	0.54	108	7.04

1. Data from seven 0.5 ppb samples.

Figure 1 Total Ion Chromatogram of the Water Method 50 ppb VOC Gas Standards Indicating Consistent Peak Shapes for all Compounds with No Water Interference.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in wastewater samples 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 precision and accuracy 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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