US EPA Method 624 using the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) System Coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC)

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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 Atomx XYZ purge and trap (P&T) VOC sample preparation system combined with a Thermo Scientific ISQ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph (GC) was used to create a working calibration curve, method detection limits (MDLs) and initial demonstration of capability (IDC) accuracy and precision for target compounds. This study will demonstrate the ability of the Atomx XYZ's innovative moisture control system (MCS) to remove water vapor transferred to the GC/MS.

Introduction

The Atomx XYZ is Teledyne Tekmar's most advanced 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. The redesigned 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.

Sample Preparation

A working 50 ppm calibration standard was prepared in methanol from Restek® standards: 624 Calibration Mix #1 and Volatiles MegaMix™ and EPA Method 624. In total, the standard contained 31 compounds.

The water calibration curve was prepared from 0.5 ppb to 200 parts per billion (ppb) for all compounds. The relative response factor (RF) was calculated for each compound using one of the three internal standards: Bromochloromethane, 2-Bromo-1-chloropropane and 1,4-Dichlorobutane. Surrogate standards consisted of: Pentafluorobenzene, Fluorobenzene and 4-Bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek® standards at a concentration of 30 parts per million (ppm), after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 30 ppb.

Seven 0.5 ppb standards were prepared for MDLs and precision calculations. Also, seven 5 ppb standards were prepared for the IDC precision and accuracy calculations. All calibration, MDL and IDC samples were analyzed with the Atomx XYZ conditions in Table I and the GC/MS conditions 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	0.00 min	**Trap**	#9
Dry Purge Flow	100 mL/min	**Purge Gas**	Nitrogen

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Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	TG VMS, 20 m x 0.18 mm, 1µm Film, Helium – 0.8 mL/min
Oven Profile	35 ºC, 3 min, 12 ºC/min to 85 ºC, 25 ºC/min to 225 ºC, 2 min Hold, Run Time 14.767 min
Inlet	200 ºC, 50:1 Split, Purge Flow 0.5 mL/min
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 230 ºC; Ion Source 280 ºC
Scan	Range 35 *amu* to 260 *amu*, Solvent Delay 0.50 min, Dwell/Scan Time 0.15 sec.
Current	Emission Current 25 µA, Gain 3.00E+005

Results

The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL, precision and IDC data are shown in Table III. Figure 1 displays a 5 ppb standard, indicating excellent peak resolution with minimal water inference for VOCs standards.

Table III US EPA Method 8260 Water Calibration, Accuracy and Precision Data

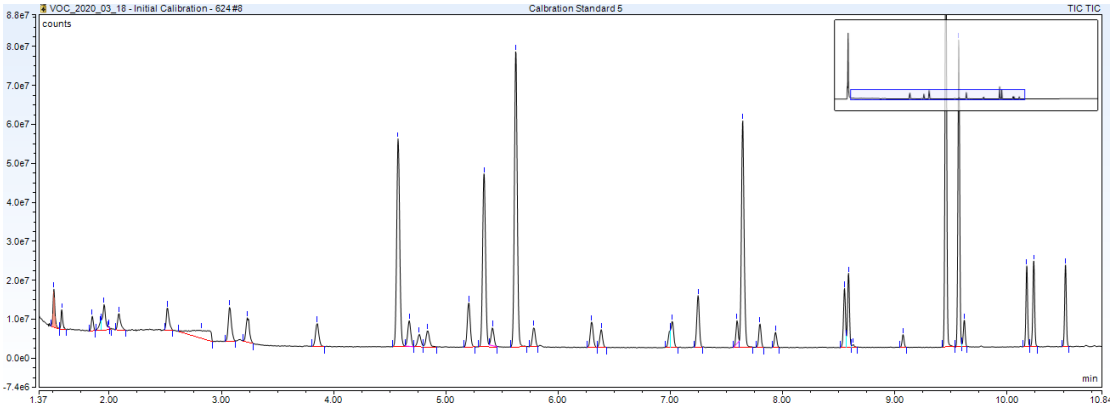
Compound	Calibration			Method Detection Limit (n=7, 0.5 ppb)			Initial Demonstration of Capability (n=7, 5 ppb)	
	Retention Time	Linearity RF (≤20% RSD)	Average RF	MDL (ppb)	Average Concentration (ppb)	Precision (≤20%)	Accuracy	Precision (≤20% RSD)
Chloromethane	1.51	17.8	1.36	0.31	0.54	18.4	83	13.2
Vinyl Chloride	1.58	5.61	0.672	0.12	0.43	8.91	91	12.9
Bromomethane	1.85	16.7	0.349	0.17	0.69	7.61	101	11.3
Chloroethane[1]	1.96	16.2	0.382	0.28	0.68	12.9	119	12.5
Trichlorofluoromethane	2.09	5.76	0.610	0.15	0.44	10.9	90	13.4
1,1-Dichloroethene	2.52	6.09	0.396	0.11	0.44	8.01	94	14.0
Methylene Chloride	3.07	14.5	0.576	0.09	0.56	5.03	95	13.1
trans-1,2-Dichloroethene	3.22	5.83	0.449	0.12	0.50	7.26	97	13.8
1,1-Dichloroethane	3.84	5.41	1.09	0.09	0.45	6.13	95	12.9
Bromochloromethane (IS)	4.57							
Chloroform	4.67	6.42	0.793	0.08	0.44	5.97	96	12.8
Carbon Tetrachloride	4.76	13.7	1.66	0.09	0.38	7.71	101	14.3
1,1,1-Trichloroethane	4.83	8.67	2.17	0.11	0.41	8.25	100	13.8
Benzene	5.20	6.55	7.24	0.09	0.44	6.73	94	12.8
Pentafluorobenzene (SURR)	5.34	8.64	3.78		30.0	2.19	99	2.49
1,2-Dichloroethane	5.41	13.9	0.241	0.29	0.60	15.4	105	11.9
Fluorobenzene (SURR)	5.62	1.75	7.39		29.8	0.994	100	0.726
Trichloroethene	5.78	10.2	1.36	0.12	0.44	8.49	100	14.6
1,2-Dichloropropane[3]	6.29	10.1	0.233	0.32	0.94	10.7	94	16.1
Bromodichloromethane	6.38	9.20	0.154	0.18	0.42	13.7	100	12.8
2-Chloroethyl Vinyl Ether	6.99	3.90	0.234	0.17	0.46	11.8	91	13.9
trans-1,3-Dichloropropene	7.02	10.4	2.73	0.10	0.40	7.75	88	14.0

Table III US EPA Method 8260 Water Calibration, Accuracy and Precision Data

Compound	Calibration			Method Detection Limit (n=7, 0.5 ppb)			Initial Demonstration of Capability (n=7, 5 ppb)	
	Retention Time	Linearity RF (≤20% RSD)	Average RF	MDL (ppb)	Average Concentration (ppb)	Precision (≤20%)	Accuracy	Precision (≤20% RSD)
Toluene	7.24	7.18	3.81	0.12	0.45	8.42	94	13.4
Tetrachloroethene	7.59	6.07	0.315	0.13	0.44	9.67	87	13.3
2-Bromo-1-chloropropane (IS)	7.64							
cis-1,3-Dichloropropene[2,3]	7.65	17.7	0.721	0.22	1.2	5.72	81	11.8
1,1,2-Trichloroethane	7.80	9.54	0.345	0.07	0.43	4.94	91	14.0
Dibromochloromethane	7.93	12.2	0.276	0.09	0.41	6.71	87	13.6
Chlorobenzene	8.55	8.35	1.09	0.10	0.45	6.99	88	12.3
Ethylbenzene	8.58	6.55	0.613	0.12	0.42	9.14	84	13.9
Bromoform	9.07	7.80	0.259	0.07	0.41	5.28	83	14.4
4-Bromofluorobenzene (SURR)	9.45	4.37	0.772		28.5	2.19	95	2.18
1,4-Dichlorobutane (IS)	9.57							
1,1,2,2-Tetrachloroethane	9.61	9.60	0.038	0.18	0.47	11.9	88	14.3
1,3-Dichlorobenzene	10.17	10.9	1.20	0.14	0.50	9.01	87	13.3
1,4-Dichlorobenzene	10.24	10.7	1.24	0.13	0.51	8.10	86	12.8
1,2-Dichlorobenzene	10.52	10.0	1.17	0.13	0.48	8.47	89	13.3

1. Calibration curve 2-200 ppb.
2. Calibration curve 1-200 ppb.
3. MDL with 1 ppb.

Figure 1 Total Ion Chromatogram of a Water Method 5 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds with Minimal Water Interference.



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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 a Thermo Scientific ISQ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph (GC). The %RSD of the calibration curve passed all method requirements with no interference from excessive water. Furthermore, MDL, precision and IDC for seven 0.5 ppb and seven 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 March 26, 2020).