MEE Method HJ639 Using the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ 7000 MS with an ExtractaBrite Source

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Abstract

Ministry of Ecology and Environment (MEE) Method HJ639 was used to determine the concentration of volatile organic compounds (VOCs) in water. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) and ISQ™ 7000 Mass Spectrometer (MS) with an ExtractaBrite Source was used to create a working linear calibration curve, method detection limits (MDLs) and a mid-point calibration check for target compounds.

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. An innovative moisture control system (MCS) improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column life span. 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: 8260B MegaMix™, VOA (Ketones), and 502.2 Calibration Mix. In total, the standard contained 62 compounds.

The water calibration curve was prepared from 1 parts per billion (ppb) to 200 ppb for all compounds. The relative response factor (RF) was calculated for each compound using one of the three internal standards: Fluorobenzene, Chlorobenzene-d5, and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of: Dibromofluoromethane, Toluene-d8, and 4-Bromofluorobenzene. Internal and surrogate standards were prepared together in methanol from Restek standards at a concentration of 25 parts per million (ppm), after which 10 microliters (µL) was then mixed with each 5 milliliter (mL) sample for a resulting concentration of 50 ppb.

Seven 1 ppb water standards were prepared for MDL and precision calculations. Seven 20 ppb water standards were prepared for the mid-point calibration check, precision and accuracy. All calibration, MDL and mid-point calibration check 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 for HJ639			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	140 ºC	Water Needle Rinse Volume	7.00 mL
Transfer Line Temp	140 ºC	Sweep Needle Time	0.25 min
Sample Mount Temp	90 ºC	Desorb Preheat Temp	245 ºC
Water Heater Temp	90 ºC	Desorb Time	2.00 min
Sample Vial Temp	20 ºC	Drain Flow	300 mL/min
Soil Valve Temp	50 ºC	Desorb Temp	250 ºC
Standby Flow	10 mL/min	Methanol Needle Rinse	Off
Purge Ready Temp	40 ºC	GC Start Signal	Begin Desorb
Purge	**Variable**	**Bake**	**Variable**
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Water Bake Rinses	1
Prime Sample Fill Volume	3.00 mL	Water Bake Rinse Volume	7.00 mL
Sample Volume	5.00 mL	Bake Rinse Sweep Time	0.25 min
Sweep Sample Time	0.25 min	Bake Rinse Sweep Flow	100 mL/min
Sweep Sample Flow	100 mL/min	Bake Rinse Drain Time	0.40 min
Sparge Vessel Heater	Off	Bake Time	2.00 min
Purge Time	11.00 min	Bake Flow	200 mL/min
Purge Flow	40 mL/min	Bake Temp	280 ºC
Purge Temp	20 ºC	MCS Bake Temp	180 ºC
MCS Purge Temp	20 ºC		
Dry Purge Time	0.5 min		
Dry Purge Flow	100 mL/min	**Trap**	#9
Dry Purge Temp	20 ºC	**Purge Gas**	Nitrogen

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Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System Conditions for HJ639	
Thermo Scientific TRACE 1310 GC Conditions	
Column	TraceGOLD TG-VMS, 20 m x 0.18 mm, 1µm Film, Helium – 1 mL/min
Oven Profile	35 ºC, 2 min, 5 ºC/min to 120 ºC, 10 ºC/min to 220 ºC, 2 min Hold, Run Time 33 min
Inlet	220 ºC, 30:1 Split, Purge Flow 0.5 mL/min
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 280 ºC; Ion Source 230 ºC
Scan	Range 35 *amu* to 270 *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 mid-point calibration check accuracy and precision data are shown in Table III. Figure 1 displays a 20 ppb standard, indicating excellent peak resolution with minimal water inference for all VOCs.

Table III HJ639 Water Calibration, Method Detection Limit and Mid-Point Calibration Check Data

Compound	Calibration (1 ppb – 200 ppb)			Method Detection Limit (n=7, 1 ppb)		Mid-Point Calibration Check (n=7, 20 ppb)	
	Retention Time	Quant Ion	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Dichlorodifluoromethane	1.15	85	8.6	0.24	7.8	4.0	96
Chloromethane	1.28	50	6.1	0.26	8.0	3.5	94
Vinyl Chloride	1.34	62	5.3	0.21	6.9	4.3	99
Bromomethane	1.57	94	18.5	0.15	3.6	3.1	97
Chloroethane	1.66	64	18.9	0.32	7.3	8.7	100
Trichlorofluoromethane	1.76	101	8.6	0.30	8.8	4.5	109
1,1-Dichloroethene	2.19	96	7.8	0.26	7.6	4.9	104
Iodomethane	2.29	142	0.998	0.24	5.6	6.1	106
Carbon Disulfide	2.58	76	6.4	0.32	9.0	4.4	108
Methylene Chloride	2.67	49	6.4	0.19	5.1	3.0	111
Acetone[12]	2.73	58	0.998	1.54	7.9	3.3	125
trans-1,2-Dichloroethene	2.81	61	5.9	0.14	4.1	3.6	110
1,1-Dichloroethane	3.38	63	5.8	0.16	4.5	3.5	114
cis-1,2-Dichloroethene	3.94	61	4.6	0.15	4.5	3.5	113
2,2-Dichloropropane	4.05	77	7.7	0.28	9.2	1.8	115
Bromochloromethane	4.15	128	5.5	0.17	4.6	2.5	115
Chloroform	4.26	83	4.3	0.11	3.0	3.9	116
Carbon Tetrachloride	4.38	117	18.6	0.16	6.8	3.7	110
1,1,1-Trichloroethane	4.46	97	13.7	0.12	4.8	0.7	112
Dibromofluoromethane (SURR)	4.47	111	3.7		2.3	3.6	115

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	Retention Time	Quant Ion	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
1,1-Dichloropropene[1]	4.61	75	0.998	0.21	11.5	5.1	78
2-Butanone[2]	4.63	43	10.6	0.79	8.2	5.2	110
Benzene	4.91	78	8.4	0.11	3.7	3.6	106
1,2-Dichloroethane	5.16	62	3.8	0.16	4.6	2.6	113
Fluorobenzene (IS)	5.46	96					
Trichloroethene	5.69	130	16.4	0.10	3.5	5.7	103
Dibromomethane	6.25	93	3.7	0.30	9.3	2.2	114
1,2-Dichloropropane	6.41	63	19.0	0.23	8.8	2.9	106
Bromodichloromethane	6.56	83	16.1	0.11	4.3	2.4	112
4-Methyl-2-Pentanone[2]	6.91	100	3.9	0.92	11.2	3.3	113
Toluene-d8 (SURR)	7.89	98	6.8		1.4	1.4	114
Toluene	7.98	91	7.2	0.16	4.3	4.1	116
Tetrachloroethene	8.64	166	5.4	0.15	4.1	4.0	115
1,1,2-Trichloroethane	9.05	83	8.7	0.09	2.7	2.1	106
Dibromochloromethane	9.34	129	12.5	0.11	3.7	2.1	109
1,3-Dichloropropane	9.53	76	10.9	0.11	3.6	2.4	106
1,2-Dibromoethane	9.7	107	6.6	0.17	5.1	2.5	107
2-Hexanone[2]	10.44	43	3.7	0.62	6.9	4.9	116
Chlorobenzene-d5 (IS)	10.82	117					
Chlorobenzene	10.85	112	5.2	0.16	4.6	4.3	94
Ethylbenzene	11.03	91	4.7	0.19	6.6	5.2	99
1,1,1,2-Tetrachloroethane	11.05	131	7.2	0.14	5.1	4.4	94
m-,p-Xylene	11.38	106	5.8	0.41	7.3	5.3	101
o-Xylene	12.30	106	6.8	0.25	9.0	5.0	99
Bromoform	12.35	173	19.8	0.07	1.6	2.2	82
Styrene	12.43	104	10.8	0.14	5.5	5.2	103
Isopropylbenzene	13.09	105	8.5	0.21	7.9	6.0	100
4-Bromofluorobenzene (SURR)	13.62	95	3.2		1.7	1.2	97
Bromobenzene	13.77	77	3.7	0.24	8.2	4.0	93
n-Propylbenzene	14.1	91	8.5	0.19	7.4	5.1	97
2-Chlorotoluene	14.32	91	7.1	0.21	7.5	4.4	97
1,1,2,2-Tetrachloroethane[1]	14.33	83	1.0	0.25	9.4	3.0	94
1,3,5-Trimethylbenzene	14.66	105	10.6	0.21	8.1	4.4	98
4-Chlorotoluene	14.74	91	6.1	0.21	7.6	3.8	96
tert-Butylbenzene	15.39	119	9.6	0.20	7.7	4.7	100
1,2,4-Trimethylbenzene	15.60	105	11.1	0.19	7.7	4.4	99
sec-Butylbenzene	15.86	105	9.4	0.21	8.2	5.2	99
1,3-Dichlorobenzene	16.18	146	4.2	0.18	6.2	3.5	97
p-Isopropyltoluene	16.32	119	11.0	0.22	9.1	5.1	101
1,4-Dichlorobenzene-d4 (IS)	16.41	152					

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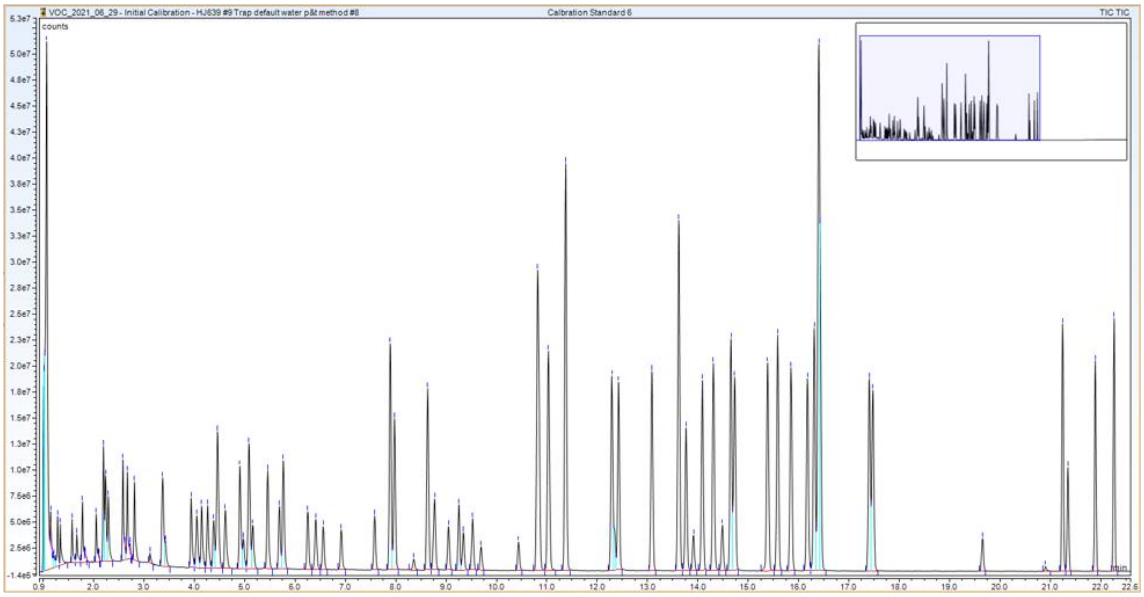
Compound	Calibration (1 ppb – 200 ppb)			Method Detection Limit (n=7, 1 ppb)		Mid-Point Calibration Check (n=7, 20 ppb)	
	Retention Time	Quant Ion	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
1,4-Dichlorobenzene	16.44	146	1.5	0.19	6.1	3.4	95
n-Butylbenzene	17.41	91	8.9	0.21	8.2	5.5	99
1,2-Dichlorobenzene	17.48	146	3.4	0.19	6.5	3.2	97
1,2-Dibromo-3-Chloropropane	19.65	157	6.4	0.29	10.1	3.3	98
1,2,4-Trichlorobenzene	21.25	180	5.6	0.23	7.5	3.4	99
Hexachlorobutadiene	21.35	225	3.2	0.22	7.2	4.3	95
Naphthalene	21.9	128	9.8	0.17	6.3	3.2	105
1,2,3-Trichlorobenzene	22.27	180	6.4	0.23	7.8	3.3	99

1. Linear calibration
2. Calibration range from 2.5-500 ppb

Figure 1 Total Ion Chromatogram (TIC) of MEE Method HJ639 20 ppb VOC Standard.



Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in water samples following MEE Method HJ639 with detection by a Thermo Scientific TRACE 1310 GC and ISQ 7000 MS with an ExtractaBrite Source. The %RSD of the calibration curve passed all method requirements. Furthermore, MDL and precision for seven 1 ppb standards showed minimal interference from excessive water. For most compounds, MDL analysis resulted in values of <0.25 ppb. The mid-point calibration check for seven 20 ppb water standards displayed less than 9% RSD for all compounds and an average recovery of 104% for the compounds of interest.

By making additional, appropriate changes to the P&T method and GC oven temperature program, the sample cycle time and moisture conveyed to the GC column may be reduced, increasing laboratory throughput in a 12-hour period and improving sensitivity.