MEE Method HJ639 Using the Teledyne Tekmar Atomx XYZ and Agilent 7890B GC/5977B MS

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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 an Agilent 7890B Gas Chromatograph (GC) and a 5977B Mass Spectrometer (MS) 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 parts per million (ppm) calibration standard was prepared in methanol from Restek® standards: 8260B MegaMix®, VOA (Ketones) and 502.2 Calibration Mix. In total, the standard contained 63 compounds. The calibration standard did not include 1,1,2-Trichloropropane, which is included on the MEE HJ639 method compound list, because it was not readily available. Also, m&p-xylene are listed as one compound, as they commonly co-elute.

The water calibration curve was prepared from 1 part 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 ppm, after which 5 microliters (µL) was then mixed with each 5 milliliter (mL) sample for a resulting concentration of 25 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 MEE Method 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 Agilent 7890B GC/5977B MS System Conditions for MEE Method HJ639	
Agilent 7890B GC Conditions	
Column	Rtx-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	220 ºC, 80:1 Split, Purge Flow 0.5 mL/min
Agilent 5977B MS Conditions	
Temp	Transfer Line 225 ºC Source 250 ºC; Quad 200 ºC
Scan	Range 35 *amu* to 270 *amu*, Solvent Delay 0.50 min, Dwell/Scan Time 0.15 sec
Gain	Gain Factor 1.00

Results

The relative standard deviation (%RSD) of the average 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 10 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	IS	Average RF	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Dichlorodifluoromethane	1.06	85	1	0.493	8.0	0.20	7.5	6.2	96
Chloromethane	1.20	50	1	0.374	19.1	0.35	9.5	13.2	101
Vinyl Chloride	1.24	62	1	0.411	10.2	0.21	7.0	6.1	117
Bromomethane [1,5]	1.46	94	1	0.356	1.0	3.43	19.4	14.9	123
Chloroethane	1.55	64	1	0.217	18.1	0.24	6.1	7.0	123
Trichlorofluoromethane	1.66	101	1	0.568	8.1	0.20	6.9	6.7	101
1,1-Dichloroethene	2.03	61	1	0.441	6.2	0.21	6.6	6.0	111
Iodomethane [1,5,6]	2.13	142	1	0.695	0.998	0.94	4.8	17.9	73
Carbon Disulfide	2.44	76	1	0.261	3.8	0.13	4.1	5.0	107
Methylene Chloride [1,5]	2.53	49	1	0.431	1.0	0.72	4.5	5.6	119
Acetone [1,2,7]	2.57	43	1	0.039	1.0	1.60	4.1	5.4	115
trans-1,2-dichloroethene	2.70	61	1	0.482	4.6	0.20	5.9	5.5	113
1,1-Dichloroethane	3.34	63	1	0.884	11.2	0.21	6.1	5.3	109
cis-1,2-Dichloroethene	3.92	61	1	0.559	5.6	0.15	5.0	4.8	109
2,2-Dichloropropane	4.04	77	1	0.714	12.2	0.21	7.0	7.0	90
Bromochloromethane	4.12	130	1	0.425	7.3	0.12	4.3	5.5	97

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	Retention Time	Quant Ion	IS	Average RF	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Chloroform	4.24	83	1	0.904	10.1	0.17	5.3	5.1	98
Carbon Tetrachloride	4.38	117	1	0.653	5.9	0.18	6.3	6.6	98
Dibromofluoromethane (SURR)	4.42	111	1	0.605	2.4		8.0	1.4	99
1,1,1-trichloroethane	4.44	97	1	0.730	5.1	0.18	6.1	6.4	101
2-Butanone [2,4]	4.56	43	1	0.066	10.2	0.67	6.9	4.6	99
1,1-Dichloropropene	4.58	75	1	0.580	6.6	0.17	7.1	5.6	101
Benzene	4.82	78	1	1.96	5.2	0.14	5.2	5.3	96
1,2-Dichloroethane	5.02	62	1	0.611	8.5	0.10	2.6	4.9	109
Fluorobenzene (IS 1)	5.28	96							
Trichloroethene	5.46	130	1	0.670	4.9	0.16	5.5	5.8	99
Dibromomethane	5.87	174	1	0.338	6.9	0.14	5.1	5.2	89
1,2-Dichloropropane	5.98	63	1	0.457	5.5	0.12	3.6	5.2	109
Bromodichloromethane	6.07	83	1	0.675	9.4	0.15	4.4	4.8	98
4-methyl-2-pentanone [2,4]	6.30	100	1	0.047	18.6	0.41	7.3	4.2	91
Toluene-d8 (SURR)	6.95	98	1	1.87	1.0		0.4	1.0	97
Toluene	7.00	91	1	1.97	6.2	0.12	4.6	6.1	102
Tetrachloroethylene	7.40	166	1	0.908	12.5	0.13	4.9	5.8	96
1,1,2-Trichloroethane	7.58	97	1	0.502	4.0	0.11	3.3	5.2	100
Dibromochloromethane	7.70	129	2	0.307	6.5	0.12	3.6	3.6	103
1,3-Dichloropropane	7.82	76	1	0.830	6.4	0.11	3.5	4.3	99
1,2-Dibromoethane	7.92	107	2	0.270	5.8	0.09	2.8	3.4	102
2-Hexanone [2,4]	8.19	43	2	0.043	6.5	0.26	2.9	3.8	103
Chlorobenzene-d5 (IS 2)	8.39	117							
Chlorobenzene	8.41	112	2	0.760	5.7	0.09	2.9	3.9	105
Ethylbenzene	8.46	91	2	0.972	11.4	0.12	4.4	4.4	114
1,1,1,2-Tetrachloroethane	8.47	131	2	0.282	4.5	0.16	4.9	3.9	98
m,p-Xylene [3]	8.59	91	2	0.784	14.9	0.21	4.2	4.6	122
o-Xylene	8.92	91	2	0.840	14.0	0.10	4.1	4.3	111
Bromoform	8.95	173	2	0.200	15.0	0.10	3.5	3.7	102
Styrene	8.96	104	2	0.683	15.7	0.09	3.9	4.4	113
Isopropylbenzene	9.17	105	2	0.986	15.0	0.12	5.0	4.7	111
4-Bromofluorobenzene (SURR)	9.35	95	2	0.479	4.4		0.7	1.0	104

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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	IS	Average RF	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Bromobenzene	9.42	77	2	0.514	8.6	0.11	3.1	3.7	105
n-Propylbenzene	9.47	91	2	1.11	14.3	0.14	5.6	4.9	115
1,1,2,2-Tetrachloroethane	9.51	83	3	0.514	19.4	0.36	8.9	3.5	90
2-Chlorotoluene	9.56	91	3	1.51	11.5	0.17	5.2	4.1	112
1,2,3-Trichloropropane [1,5]	9.59	75	3	0.601	0.998	1.22	7.3	4.9	122
1,3,5-Trimethylbenzene	9.63	105	3	1.89	13.7	0.15	5.3	4.5	114
4-Chlorotoluene	9.68	91	3	1.60	12.3	0.18	5.7	4.0	113
tert-Butylbenzene	9.85	119	3	1.62	10.7	0.18	6.2	4.0	103
1,2,4-Trimethylbenzene	9.89	105	3	1.82	14.6	0.14	5.2	4.0	114
sec-Butylbenzene	9.97	105	3	2.22	13.0	0.16	5.9	4.3	112
p-Isopropyltoluene	10.08	119	3	1.78	14.0	0.16	6.2	4.1	110
1,3-Dichlorobenzene	10.10	146	3	1.20	8.9	0.22	6.3	4.4	91
1,4-Dichlorobenzene-d4 (IS 3)	10.15	152							
1,4-Dichlorobenzene	10.16	146	3	1.19	7.9	0.20	5.6	3.3	97
n-Butylbenzene	10.37	91	3	1.37	16.4	0.19	7.2	4.2	106
1,2-Dichlorobenzene	10.44	146	3	1.16	10.3	0.18	4.9	4.0	91
1,2-Dibromo-3-chloropropane	10.97	157	3	0.130	13.7	0.24	6.5	4.4	92
Hexachlorobutadiene	11.44	180	3	0.622	18.5	0.15	6.0	3.8	98
1,2,4-Trichlorobenzene	11.44	225	3	0.340	11.9	0.14	4.4	4.9	87
Naphthalene	11.65	128	3	1.36	19.9	0.19	6.6	4.0	99
1,2,3-Trichlorobenzene	11.77	180	3	0.611	19.7	0.11	4.3	3.5	100

1. Compound calibrated by linear regression
2. Calibration curve 2.5 ppb – 500 ppb
3. Calibration curve 2 ppb – 400 ppb
4. MDL calculated using 2.5 ppb
5. MDL calculated using 5 ppb
6. MDL calculated using 10 ppb
7. MDL calculated using 25 ppb

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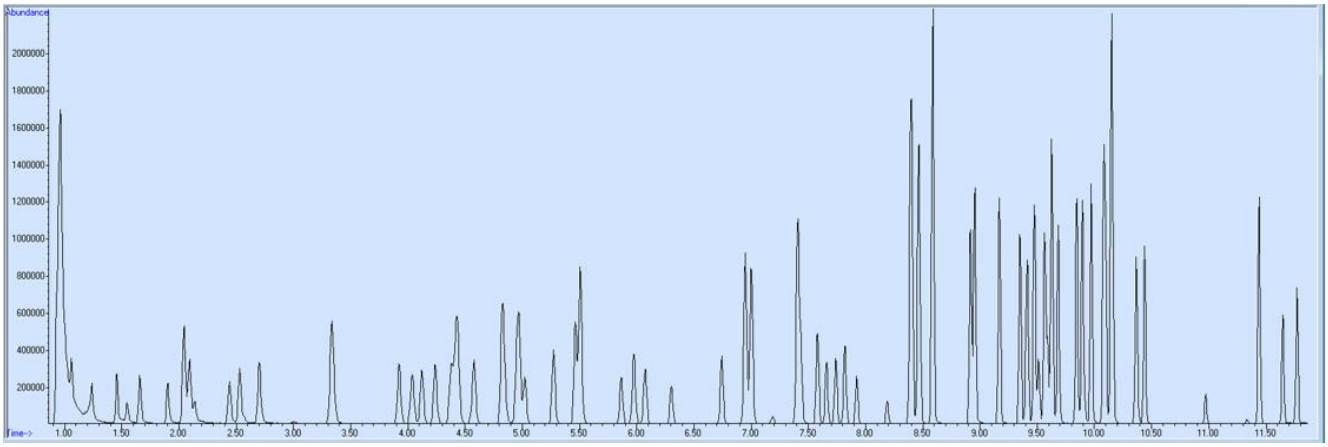
Figure 1 Total Ion Chromatogram (TIC) of MEE Method HJ639 10 ppb VOC Standard Indicating Excellent Peak Resolution with Minimal Water Inference for all VOCs.



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 an Agilent 7890B GC and 5977B MS. 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 an average of 5% RSD 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 also be reduced, increasing laboratory throughput in a 12-hour period and improving sensitivity.

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