

MEE Method HJ639 Using the Teledyne Tekmar Atomx XYZ P&T and Agilent GC/MSD to Determine Volatile Organic Compound Concentration in Water

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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 coupled with the Agilent 7890B GC and 5977B GC/MSD was used to create a working linear calibration curve, method detection limits (MDLs), and a midpoint calibration check for target compounds.

Introduction

The Atomx XYZ is the most advanced Teledyne Tekmar 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. Furthermore, the Agilent 7890B GC is the world's most widely used GC system, featuring accurate temperature controls, precise injection systems, and high-performance electronic pneumatic control (EPC) modules for good retention time and area count repeatability. The Agilent 5977B GC/MSD is the latest in the series of most trusted single quadrupole GC/MS instruments. It is ideal for labs that focus on applications such as environmental, chemical, petrochemical, food, forensic, pharmaceutical, and material testing.

Experimental

Sample preparation

A working 50 parts per million (ppm) calibration standard was prepared in methanol from commercially available 8260B mix, VOA (ketones), and 502.2 calibration mix standards. In total, the standard contained 66 compounds. The calibration standard did not

include 1,1,2-trichloropropane and 1-chloro-2,3-epoxypropane from the MEE HJ639 method compound list, because they were not readily available. Also, *m*- and *p*-xylene were listed as one compound, as they commonly coelute.

The water calibration curve was prepared from 1 to 200 parts per billion (ppb) for all compounds. The relative response factor (RRF) 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 commercially available standards, at a concentration of 25 ppm. After, 5 μ L was mixed with each 5 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 midpoint calibration check, precision, and accuracy. All calibration, MDL, and midpoint calibration check samples were analyzed with the Atomx XYZ conditions in Table 1 and the Agilent GC/MSD conditions in Table 2.

Instrument conditions

Table 1. Teledyne Tekmar Atomx XYZ water method conditions for MEE Method HJ639.

Standby	Variable
Valve Oven Temperature	140 °C
Transfer Line Temperature	140 °C
Sample Mount Temperature	90 °C
Water Heater Temperature	90 °C
Sample Vial Temperature	20 °C
Soil Valve Temperature	50 °C
Standby Flow	10 mL/min
Purge Ready Temperature	40 °C
Purge	Variable
Sample Equilibrate Time	0.00 min
Presweep Time	0.25 min
Prime Sample Fill Volume	3.00 mL
Sample Volume	5.00 mL
Sweep Sample Time	0.25 min
Sweep Sample Flow	100 mL/min
Spurge Vessel Heater	Off
Purge Time	11.00 min
Purge Flow	40 mL/min
Purge Temperature	20 °C
MCS Purge Temperature	20 °C
Dry Purge Time	0.5 min
Dry Purge Flow	100 mL/min
Dry Purge Temperature	20 °C

Desorb	Variable
Water Needle Rinse Volume	7.00 mL
Sweep Needle Time	0.25 min
Desorb Preheat Temperature	245 °C
Desorb Time	2.00 min
Drain Flow	300 mL/min
Standby	Variable
Desorb Temperature	250 °C
Methanol Needle Rinse	Off
GC Start Signal	Begin Desorb
Bake	Variable
Methanol Glass Rinse	Off
Water Bake Rinses	1
Water Bake Rinse Volume	7.00 mL
Bake Rinse Sweep Time	0.25 min
Bake Rinse Sweep Flow	100 mL/min
Bake Rinse Drain Time	0.40 min
Bake Time	2.00 min
Bake Flow	200 mL/min
Bake Temperature	280 °C
MCS Bake Temperature	180 °C
Trap Number	9
Purge Gas	Nitrogen

Table 2. Agilent 7890B GC and 5977B MS system conditions for MEE Method HJ639.

Agilent 7890B GC Conditions	
Column	Agilent DB-VRX – equivalent, 20 m × 0.18 mm, 1 µm film, helium 0.8 mL/min
Oven Profile	35 °C, 3 min 12 °C/min to 85 °C 25 °C/min to 225 °C 2 min hold Run time: 14.767 min
Inlet	220 °C; 80:1 split; septum purge flow: 0.5 mL/min
Agilent 5977B GC/MSD Conditions	
Temperature	Transfer line: 225 °C; source: 250 °C; quad: 200 °C
Scan	Range: 35 to 270 amu; solvent delay: 0.50 minutes; dwell/scan time: 0.15 seconds
Gain	Gain factor: 1.00

Results and discussion

The relative standard deviation (%RSD) of the average of the RRFs for the calibration curve, MDL, precision, and midpoint calibration check accuracy and precision data are shown in Table 3. Figure 1 displays a 10 ppb standard, indicating excellent peak resolution with minimal water inference for all VOCs.

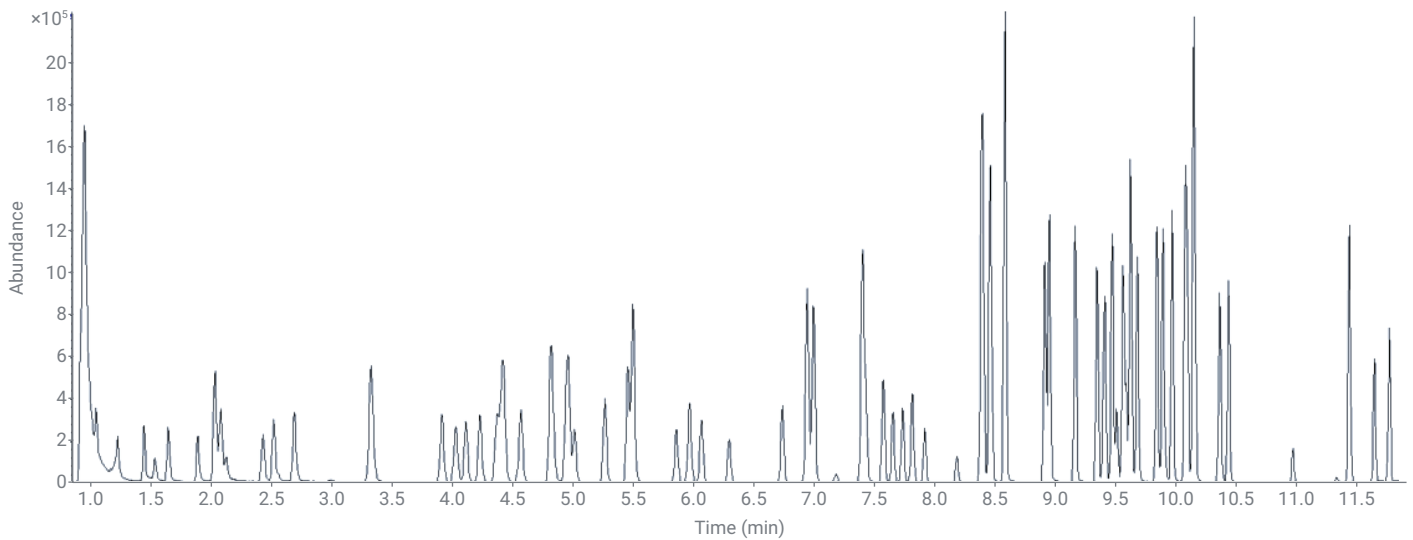


Figure 1. Total ion chromatogram of MEE Method HJ639 10 ppb VOC standard.

Table 3. HJ639 water calibration, method detection limit and midpoint calibration check data.

Compound	Calibration (1 to 200 ppb)					Method Detection Limit (n = 7, 1 ppb)		Midpoint Calibration Check (n = 7, 20 ppb)	
	Retention Time (min)	Quant Ion	IS	Average RRF	RRF (≤20% RSD R ² ≥0.99)	MDL (ppb)	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
<i>trans</i> -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

Compound	Calibration (1 to 200 ppb)					Method Detection Limit (n = 7, 1 ppb)		Midpoint Calibration Check (n = 7, 20 ppb)	
	Retention Time (min)	Quant Ion	IS	Average RRF	RRF ($\leq 20\%$ RSD $R^2 \geq 0.99$)	MDL (ppb)	Precision ($\leq 20\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)
2-Chloro-1,3-Butadiene	3.37	53	1	0.736	6.2	0.17	5.8	5.1	104
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
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
cis-1,3-Dichloropropene	6.74	75	1	0.754	5.1	0.14	5.0	4.8	99
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
trans-1,3-Dichloropropene	7.44	75	1	0.705	6.1	0.11	3.7	4.7	100
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
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
1,1,1,2-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

Compound	Calibration (1 to 200 ppb)					Method Detection Limit (n = 7, 1 ppb)		Midpoint Calibration Check (n = 7, 20 ppb)	
	Retention Time (min)	Quant Ion	IS	Average RRF	RRF ($\leq 20\%$ RSD $R^2 \geq 0.99$)	MDL (ppb)	Precision ($\leq 20\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)
<i>tert</i> -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
<i>sec</i> -Butylbenzene	9.97	105	3	2.22	13.0	0.16	5.9	4.3	112
<i>p</i> -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
<i>n</i> -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 to 500 ppb

³ Calibration curve 2 to 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

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 an Agilent 5977B GC/MSD. 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 midpoint 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. This can increase laboratory throughput in a 12-hour period and improve sensitivity.

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