APPLICATION NOTE: AN2108
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

MEE Method HJ605 Using the Teledyne Tekmar Atomx XYZ and Agilent 7890B GC/5977B MS

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Abstract

Ministry of Ecology and Environment (MEE) Method HJ605 was used to determine the concentration of volatile organic compounds (VOCs) in soil matrices. 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 HJ605 method compound list, because it was not readily available. Also, m&p-xylene are listed as one compound, as they commonly co-elute.

The soil calibration curve was prepared from 2 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 ppm, after which 5 microliters (µL) was then mixed with each 5 milliliter (mL) sample for a resulting concentration of 25 ppb.

Seven 2 ppb soil standards were prepared for MDL and precision calculations. Seven 20 ppb soil standards were prepared for the mid-point calibration check, precision and accuracy. All calibration, MDL and mid-point calibration check samples were analyzed using 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 Soil Method Conditions for MEE HJ605			
Standby	**Variable**	**Purge**	**Variable**
Valve Oven Temp	140 ºC	MCS Purge Temp	20 ºC
Transfer Line Temp	140 ºC	Dry Purge Time	2.00 min
Sample Mount Temp	90 ºC	Dry Purge Flow	100 mL/min
Water Heater Temp	90 ºC	Dry Purge Temp	20 ºC
Sample Vial Temp	40 ºC	**Desorb**	**Variable**
Soil Valve Temp	100 ºC	Methanol Needle Rinse	Off
Standby Flow	10 mL/min	Water Needle Rinse Volume	7.00 mL
Purge Ready Temp	40 ºC	Sweep Needle Time	0.25 min
Purge	**Variable**	Desorb Preheat Temp	245 ºC
Pre-purge Time	0.00 min	GC Start Signal	Begin Desorb
Pre-Purge Flow	0 mL/min	Desorb Time	2.00 min
Pre-heat Mix Speed	Slow	Drain Flow	300 mL/min
Sample Pre-heat Time	0.00 min	Desorb Temp	250 ºC
Pre-sweep Time	0.25 min	**Bake**	**Variable**
Water Volume	10.00 mL	Bake Time	2.00 min
Sweep Water Time	0.25 min	Bake Flow	400 mL/min
Sweep Water Flow	100 mL/min	Bake Temp	280 ºC
Sparge Vessel Heater	Off	MCS Bake Temp	180 ºC
Purge Mix Speed	Medium		
Purge Time	11.00 min		
Purge Flow	40 mL/min	**Trap**	#9
Purge Temp	20 ºC	**Purge Gas**	Nitrogen

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Table II Agilent 7890B GC/5977B MS System Conditions for MEE Method HJ605	
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 MEE Method HJ605 Soil Calibration, Method Detection Limit and Mid-Point Calibration Check Data

Compound	Calibration (2 ppb - 200 ppb)					Method Detection Limit (n=7, 2 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	0.445	5.2	0.64	10.2	9.1	89
Chloromethane	1.19	50	1	0.328	8.2	0.71	10.6	9.5	92
Vinyl Chloride	1.24	62	1	0.329	8.3	0.91	15.0	8.7	97
Bromomethane[1,4]	1.46	94	1	0.271	0.991	1.64	10.4	19.0	109
Chloroethane	1.55	64	1	0.160	18.3	0.89	10.6	5.5	115
Trichlorofluoromethane	1.66	101	1	0.539	12.0	0.35	5.0	2.7	97
1,1-Dichloroethene	2.04	61	1	0.668	7.8	0.29	4.2	2.9	100
Iodomethane[1,4]	2.13	142	1	0.745	0.996	2.28	16.6	19.7	90
Carbon Disulfide	2.44	76	1	0.359	5.4	0.23	3.5	3.1	97
Methylene Chloride[1,4]	2.53	49	1	0.710	0.997	0.99	11.9	3.2	100
Acetone[1,2,5]	2.57	58	1	0.055	0.999	2.50	6.6	8.8	88
trans-1,2-dichloroethene	2.70	61	1	0.717	6.9	0.30	4.4	2.8	100
1,1-Dichloroethane	3.34	63	1	1.12	11.3	0.34	4.9	2.3	102
cis-1,2-Dichloroethene	3.92	61	1	0.702	5.8	0.25	4.1	2.3	101
2,2-Dichloropropane	4.04	77	1	0.879	10.7	0.31	4.6	2.2	92
Bromochloromethane	4.12	130	1	0.441	6.7	0.23	3.6	2.7	97
Chloroform	4.24	83	1	1.03	9.0	0.30	4.4	2.5	94

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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%)
Carbon Tetrachloride	4.38	117	1	0.841	5.7	0.27	4.2	2.6	93
Dibromofluoromethane (SURR)	4.42	111	1	0.562	5.4		6.2	2.6	103
1,1,1-trichloroethane	4.44	97	1	0.921	3.7	0.25	3.9	2.6	95
2-Butanone[2,4]	4.56	43	1	0.101	6.2	1.17	6.5	5.4	89
1,1-Dichloropropene	4.58	75	1	0.758	2.1	0.26	4.4	2.3	95
Benzene	4.82	78	1	2.37	3.5	0.26	4.3	2.4	91
1,2-Dichloroethane	5.02	62	1	0.655	8.8	0.29	4.2	2.5	101
Fluorobenzene (IS 1)	5.28	96							
Trichloroethene	5.46	130	1	0.785	2.8	0.31	5.1	2.4	92
Dibromomethane	5.86	174	1	0.331	8.5	0.22	3.7	2.4	89
1,2-Dichloropropane	5.97	63	1	0.534	5.6	0.30	4.7	2.2	101
Bromodichloromethane	6.07	83	1	0.701	8.5	0.29	3.8	2.4	94
4-methyl-2-pentanone[2,4]	6.30	100	1	0.045	19.8	0.46	3.9	1.9	85
Toluene-d8 (SURR)	6.95	98	1	1.75	2.2		0.6	0.6	100
Toluene	7.00	91	1	2.38	9.2	0.24	4.4	2.2	94
Tetrachloroethylene	7.40	166	1	1.04	11.7	0.37	6.8	3.4	88
1,1,2-Trichloroethane	7.58	97	1	0.488	3.4	0.33	5.4	2.5	96
Dibromochloromethane	7.74	129	2	0.316	6.9	0.31	4.9	1.6	96
1,3-Dichloropropane	7.82	76	1	0.793	4.1	0.25	3.9	2.5	97
1,2-Dibromoethane	7.92	107	2	0.278	3.8	0.26	4.4	1.5	93
2-Hexanone[2,4]	8.18	43	2	0.058	9.3	1.32	8.1	2.4	87
Chlorobenzene-d5 (IS 2)	8.39	117							
Chlorobenzene	8.41	112	2	0.941	2.8	0.26	4.3	1.9	96
Ethylbenzene	8.46	91	2	1.26	12.8	0.22	4.5	1.9	99
1,1,1,2-Tetrachloroethane	8.47	131	2	0.338	4.4	0.28	4.6	1.8	90
m,p-Xylene[3]	8.59	91	2	1.02	15.0	0.45	4.8	1.6	105
o-Xylene	8.91	91	2	1.06	16.0	0.20	4.4	1.7	96
Bromoform	8.95	173	2	0.203	11.7	0.20	3.8	1.6	94
Styrene	8.96	104	2	0.826	17.0	0.25	5.9	1.6	98
Isopropylbenzene	9.17	105	2	1.29	15.9	0.21	4.7	1.9	98
4-Bromofluorobenzene (SURR)	9.35	95	2	0.455	3.5		0.8	0.9	103
Bromobenzene	9.41	77	2	0.592	6.8	0.30	4.6	1.8	93
n-Propylbenzene	9.47	91	2	1.46	17.3	0.24	5.4	2.2	98
1,1,2,2-Tetrachloroethane	9.51	83	3	0.580	18.0	0.42	5.0	4.6	97
2-Chlorotoluene	9.56	91	3	2.07	7.2	0.33	5.7	2.8	100
1,2,3-Trichloropropane [1,4]	9.59	75	3	0.676	0.997	1.03	15.0	4.4	106
1,3,5-Trimethylbenzene	9.63	105	3	2.63	8.1	0.27	5.0	3.2	102
4-Chlorotoluene	9.68	91	3	2.19	8.0	0.30	5.3	2.9	98

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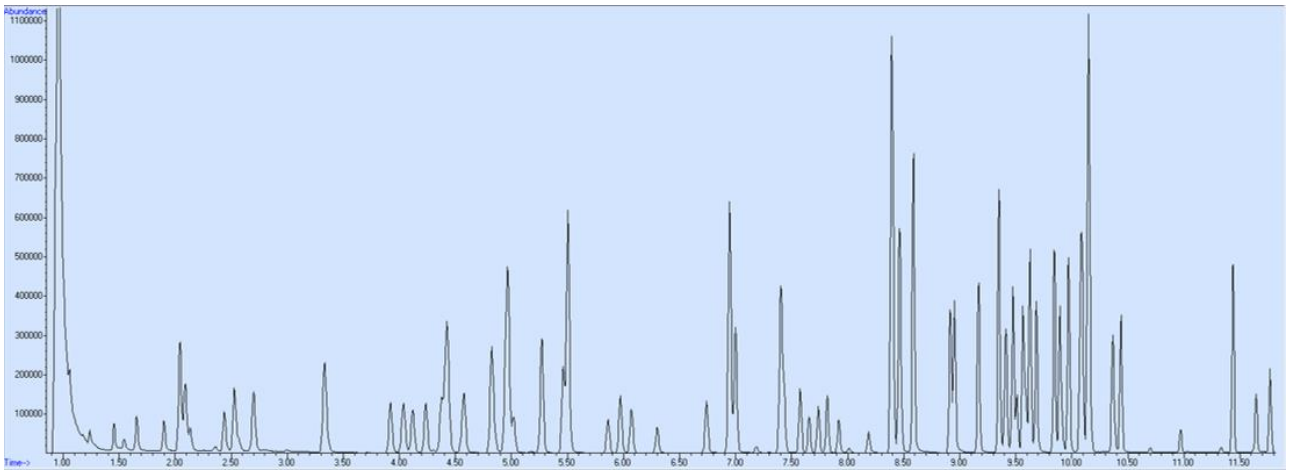
Compound	Calibration (2 ppb - 200 ppb)					Method Detection Limit (n=7, 2 ppb)		Mid-Point Calibration Check (n=7, 20 ppb)	
	Retention Time	Quant Ion	IS	Average RF	Linearity RF (≤20% RSD r^2≥0.99)	MDL	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
tert-Butylbenzene	9.85	119	3	2.29	5.3	0.24	4.4	3.5	99
1,2,4-Trimethylbenzene	9.89	105	3	2.41	13.0	0.30	6.2	2.8	103
sec-Butylbenzene	9.97	105	3	3.29	9.0	0.28	5.1	3.2	103
p-Isopropyltoluene	10.08	119	3	2.53	10.4	0.31	6.3	3.3	101
1,3-Dichlorobenzene	10.09	146	3	1.59	9.3	0.36	5.4	3.1	82
1,4-Dichlorobenzene-d4 (IS 3)	10.15	152							
1,4-Dichlorobenzene	10.16	146	3	1.52	7.1	0.55	8.2	2.7	84
n-Butylbenzene[1]	10.37	91	3	1.88	0.996	0.89	9.4	3.5	81
1,2-Dichlorobenzene	10.44	146	3	1.41	9.3	0.30	4.3	3.4	85
1,2-Dibromo-3-chloropropane	10.97	157	3	0.150	11.2	0.30	4.5	4.3	90
Hexachlorobutadiene	11.44	180	3	0.707	19.5	0.50	10.9	3.7	86
1,2,4-Trichlorobenzene	11.44	225	3	0.569	10.1	0.35	5.3	4.5	83
Naphthalene	11.65	128	3	1.31	17.5	0.48	9.3	4.7	89
1,2,3-Trichlorobenzene	11.77	180	3	0.693	19.1	0.35	7.3	4.6	87

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 5 ppb
5. MDL calculated using 25 ppb

Figure 1 Total Ion Chromatogram (TIC) of MEE Method HJ605 10 ppb VOC Standard Indicating Excellent Peak Resolution with Minimal Water Inference for all VOCs.



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Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in soil samples following MEE Method HJ605 with detection by an Agilent 7890B GC and 5977B MS. The %RSDs of the calibration curve passed all method requirements. Furthermore, MDL and precision for seven 2 ppb standards showed minimal interference from excessive water. The average MDL analysis was 0.48 ppb with a 5.8% RSD. The mid-point calibration check for seven 20 ppb water standards displayed an average of less than 4% RSD and an average recovery of 95% 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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