

US EPA Method 524.4 Using the Teledyne Tekmar Atomx XYZ with Agilent 7890B GC/5977B MS and Hydrogen as an Alternative Carrier Gas

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Tekmar Atomx XYZ, purge and trap, EPA Method 524.4, Agilent 7890 GC/5977B MS, Hydrogen

Abstract

As helium supplies become increasingly scarce and expensive, laboratories have begun seeking alternative carrier gases that are readily available and economical. This application note will evaluate hydrogen as the carrier gas for US EPA Method 524.4 to determine the concentration of volatile organic compounds (VOCs) in drinking water matrices. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) VOC sample preparation system combined with an Agilent 7890B Gas Chromatograph (GC)/5977B Mass Spectrometer (MS) was used to create a working linear (r^2) calibration curve, method detection limits (MDL), a mid-point calibration check with accuracy and precision and minimum reporting level (MRL) confirmation 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 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 50 parts per million (ppm) calibration working standard was prepared in methanol from the following Restek® standards: 524.3 VOA Mega Mix® and 524.3 Gas Calibration Mix. In total, the standards contained 75 compounds.

An eight-point linear (r^2) calibration curve was prepared from 0.2 ppb to 40 parts per billion (ppb) for all compounds with regression value (r^2) ≥ 0.995 . The relative response factor (RRF) was calculated for each compound using three internal standards: 1,4-Difluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Surrogate standards consisted of: Methyl-tert-Butyl Ether-d3, 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 12.5 ppm, after which 5 μ L was then mixed with each 5 mL sample for a resulting concentration of 12.5 ppb.

Seven 1 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Also, seven 10 ppb standards were prepared for the accuracy and precision calculations of the mid-point calibration check. All calibration, MDL, MRL and mid-point calibration check standards were analyzed with the Atomx XYZ conditions in [Table I](#). GC-MS conditions are shown in [Table II](#).



Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Water Method Conditions			
Standby	Variable	Desorb	Variable
Valve Oven Temp	140 °C	Methanol Needle Rinse	Off
Transfer Line Temp	140 °C	Water Needle Rinse Volume	7.00 mL
Sample Mount Temp	90 °C	Sweep Needle Time	0.25 min
Water Heater Temp	90 °C	Desorb Preheat Temp	245 °C
Sample Cup Temp	20 °C	GC Start Signal	Begin Desorb
Soil Valve Temp	50 °C	Desorb Time	2.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40 °C	Desorb Temp	250 °C
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
Spurge Vessel Heater	Off	Bake Time	2.00 min
Purge Time	8.00 min	Bake Flow	200 mL/min
Purge Flow	55 mL/min	Bake Temp	260 °C
Purge Temp	20 °C	MCS Bake Temp	180 °C
MCS Purge Temp	20 °C		
Dry Purge Time	1.00 min	Trap	9
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

Table II Agilent 7890B GC/5977B MS System Conditions	
Agilent 7890B GC Conditions	
Column	Rtx® VMS, 20 m x 0.18 mm, 1µm Film, Column Flow – 0.8 mL/min
Oven Profile	35 °C, 2 min, 10 °C/min to 85 °C, 30 °C/min to 225 °C, 1 min Hold, Run Time 12.67 min
Inlet	200 °C, 80:1 Split, Septum Purge Flow 0.5 mL/min, Carrier Gas - Hydrogen
Agilent 5977B MS Conditions	
Temp	Transfer Line 250 °C; Source 250 °C; Quad 200 °C
Scan	Range 35 <i>m/z</i> to 260 <i>m/z</i> , Solvent Delay 0.50 min, Normal Scanning
Current	Gain Factor 1.00, Extraction Source Tune

Results

The linear correlation coefficient of the calibration curve (r^2), MDL, mid-point calibration check and MRL confirmation data are shown in [Table III](#). [Figure 1](#) displays a 10 ppb standard, indicating excellent peak resolution with minimal water interference for all VOCs.

Compound	Calibration (0.2 ppb – 40 ppb)				Method Detection Limits (n=7, 1 ppb)		Mid Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity ($r^2 \geq 0.995$)	Avg. RRF	MDL (ppb)	Precision ($\leq 20\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)	LPIR ($\geq 50\%$)	UPIR ($\leq 150\%$)
Dichlorodifluoromethane	0.788	85	0.998	0.566	0.14	4.8	5.8	106	75	110
Chlorodifluoromethane	0.809	51	1.00	0.896	0.13	4.2	7.1	107	82	116
Chloromethane	0.880	50	0.999	0.424	0.14	4.4	5.6	103	82	116
Vinyl Chloride	0.915	62	0.999	0.587	0.10	3.3	6.7	104	88	114
1,3-Butadiene	0.924	54	0.999	0.606	0.17	5.2	6.7	104	81	123
Bromomethane	1.08	94	0.998	0.614	0.13	4.0	7.3	108	90	124
Trichlorofluoromethane	1.22	101	0.999	0.572	0.10	3.5	6.1	106	75	99
Diethyl Ether	1.40	59	0.999	0.319	0.13	3.8	4.5	106	89	121
Carbon Disulfide ¹	1.51	76	1.00	0.206	0.15	4.7	6.3	100	84	122
1,1-Dichloroethene	1.51	96	1.00	0.288	0.08	2.7	7.0	103	90	111
Iodomethane	1.59	142	0.997	0.238	0.07	1.6	4.5	98	124	141
Allyl Chloride	1.81	76	1.00	0.172	0.16	5.2	6.1	99	79	119
Methylene Chloride	1.89	84	0.999	0.371	0.18	5.8	5.3	105	76	120
trans-1,2-Dichloroethene	2.00	96	0.999	0.269	0.15	5.1	6.1	104	77	115
Methyl-tert-Butyl Ether-d3 (SURR)	2.09	76	1.26	1.05		1.3	1.9	99	94	105
Methyl Acetate	2.10	43	0.999	1.94	0.17	5.3	5.6	107	79	121
Methyl-tert-Butyl Ether	2.11	73	0.999	1.12	0.08	2.9	4.5	107	82	103
tert-Butyl Alcohol	2.23	59	0.999	0.045	0.11	3.1	3.3	104	95	122
Diisopropyl Ether	2.42	45	0.999	1.27	0.13	4.2	5.2	107	84	118
1,1-Dichloroethane	2.47	63	0.999	0.695	0.18	5.7	5.6	106	78	123
tert-Butyl Ethyl Ether	2.71	59	0.999	1.20	0.07	2.5	5.1	106	83	101
cis-1,2-Dichloroethene	2.91	96	1.00	0.380	0.15	4.9	5.5	108	78	117
Bromochloromethane	3.06	128	0.999	0.181	0.17	5.3	5.2	101	81	125
Chloroform	3.14	83	1.00	0.557	0.06	2.1	4.2	104	92	108
Carbon Tetrachloride	3.21	117	1.00	0.221	0.15	4.9	5.8	101	81	119
Tetrahydrofuran	3.28	72	0.999	0.048	0.09	2.9	3.6	94	90	114
1,1,1-Trichloroethane	3.28	97	0.999	0.352	0.12	3.6	4.8	102	89	119
1,1-Dichloropropene	3.38	75	0.999	0.417	0.15	5.0	5.0	105	78	116

Table III Thermo Scientific TRACE 1610 GC and ISQ 7610 MS System Conditions

Compound	Calibration (0.2 ppb – 40 ppb)				Method Detection Limits (n=7, 1 ppb)		Mid Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity ($r^2 \geq 0.995$)	Avg. RRF	MDL (ppb)	Precision ($\leq 20\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)	LPIR ($\geq 50\%$)	UPIR ($\leq 150\%$)
1-Chlorobutane	3.44	56	0.999	0.579	0.13	4.2	5.3	106	83	116
Benzene	3.59	78	0.999	1.60	0.18	5.8	4.9	107	77	124
tert-Amyl Methyl Ether	3.75	73	0.999	0.902	0.10	2.9	4.0	102	93	117
1,2-Dichloroethane	3.78	62	0.999	0.489	0.13	4.2	3.8	105	82	115
Trichloroethylene	4.12	95	0.999	0.465	0.10	3.4	4.1	104	82	108
1,4-Difluorobenzene (IS)	4.19	114								
tert-Amyl Ethyl Ether	4.42	59	0.999	0.753	0.10	3.0	4.0	102	94	120
Dibromomethane	4.50	93	0.999	0.192	0.18	5.2	2.4	101	88	133
1,2-Dichloropropane	4.61	63	0.999	0.378	0.06	1.9	4.0	104	100	116
Bromodichloromethane	4.70	83	0.999	0.285	0.10	2.9	3.6	101	100	126
cis-1,3-Dichloropropene	5.34	75	0.999	0.436	0.08	2.3	3.9	99	106	127
Toluene	5.57	92	0.999	0.942	0.09	2.7	4.6	106	93	115
Tetrachloroethylene	5.95	166	0.999	0.493	0.08	2.7	4.9	100	86	107
trans-1,3-Dichloropropene	6.06	75	0.999	0.344	0.08	2.2	3.4	102	104	124
1,1,2-Trichloroethane	6.22	83	0.999	0.245	0.09	2.7	3.7	102	90	112
Ethyl Methacrylate	6.32	69	0.996	0.325	0.14	3.6	3.6	98	108	144
Dibromochloromethane	6.38	129	0.999	0.175	0.17	5.0	4.2	102	85	126
1,3-Dichloropropane	6.50	76	0.999	0.561	0.12	3.7	3.1	105	85	115
1,2-Dibromoethane	6.59	107	0.999	0.213	0.14	3.8	3.5	99	97	131
Chlorobenzene-d5 (IS)	7.21	117								
Chlorobenzene	7.22	112	0.999	1.02	0.06	2.0	4.2	105	88	103
Ethylbenzene	7.30	91	0.999	1.99	0.15	4.7	4.6	106	80	117
1,1,1,2-Tetrachloroethane	7.32	131	0.999	0.188	0.11	3.2	3.7	102	97	125
m,p-Xylene	7.45	106	1.00	0.674	0.08	1.3	4.3	102	96	107
o-Xylene	7.83	106	0.999	0.647	0.09	2.8	4.2	102	93	116
Bromoform	7.87	173	0.997	0.101	0.11	2.9	3.4	98	105	132
Styrene	7.88	104	0.999	0.979	0.07	2.0	3.8	99	104	122
Isopropylbenzene	8.10	105	1.00	1.63	0.09	2.8	4.8	103	88	110
4-Bromofluorobenzene (SURR)	8.30	95	4.01	1.14		2.3	1.2	99	94	112
Bromobenzene	8.35	156	0.999	0.707	0.15	4.7	4.7	104	81	119
n-Propylbenzene	8.42	91	0.998	4.72	0.13	4.0	5.2	111	86	118

Table III Thermo Scientific TRACE 1610 GC and ISQ 7610 MS System Conditions

Compound	Calibration (0.2 ppb – 40 ppb)				Method Detection Limits (n=7, 1 ppb)		Mid Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity ($r^2 \geq 0.995$)	Avg. RRF	MDL (ppb)	Precision ($\leq 20\%$)	Precision ($\leq 20\%$)	Accuracy ($\pm 30\%$)	LPIR ($\geq 50\%$)	UPIR ($\leq 150\%$)
1,1,2,2-Tetrachloroethane	8.50	83	0.995	0.438	0.12	4.6	3.8	102	114	143
2-Chlorotoluene	8.51	91	0.999	2.61	0.14	4.6	5.3	110	77	111
1,2,3-Trichloropropane	8.56	75	0.998	0.684	0.18	5.9	3.7	106	74	119
1,3,5-Trimethylbenzene	8.58	105	0.999	3.38	0.16	5.8	5.2	109	69	110
4-Chlorotoluene	8.63	91	0.999	2.65	0.12	4.0	4.8	108	82	113
tert-Butylbenzene	8.79	119	0.997	2.53	0.11	4.0	5.2	114	73	100
Pentachloroethane	8.79	167	0.999	0.063	0.17	5.4	6.1	102	78	120
1,2,4-Trimethylbenzene	8.84	105	0.999	3.25	0.12	4.2	4.7	109	77	107
sec-Butylbenzene	8.91	105	0.999	3.83	0.12	4.7	5.4	110	66	97
p-Isopropyltoluene	9.02	119	0.998	3.08	0.06	2.3	5.1	110	74	89
1,3-Dichlorobenzene	9.02	146	0.999	1.44	0.07	2.1	4.5	104	95	112
1,4-Dichlorobenzene-d4 (IS)	9.08	152								
1,4-Dichlorobenzene	9.09	146	0.999	1.44	0.08	2.5	4.6	105	88	107
n-Butylbenzene	9.28	91	0.998	3.44	0.15	4.9	4.9	111	80	118
Hexachloroethane	9.33	166	0.999	0.335	0.16	5.4	6.1	104	76	117
1,2-Dichlorobenzene-d4 (SURR)	9.34	152	1.72	0.999		1.5	1.3	99	92	103
1,2-Dichlorobenzene	9.35	146	0.999	1.40	0.07	2.5	4.2	106	86	104
1,2-Dibromo-3-Chloropropane	9.84	75	0.995	0.111	0.16	4.7	2.6	102	86	126
Hexachlorobutadiene	10.24	225	0.999	0.266	0.17	5.0	3.8	102	89	133
1,2,4-Trichlorobenzene	10.24	180	0.999	0.861	0.08	2.2	3.4	99	106	126
Naphthalene	10.42	128	0.998	2.66	0.12	4.3	3.8	108	76	107
1,2,3-Trichlorobenzene	10.53	180	0.998	0.817	0.06	1.7	3.5	99	107	123

1. Calibration range from 0.5-40 ppb

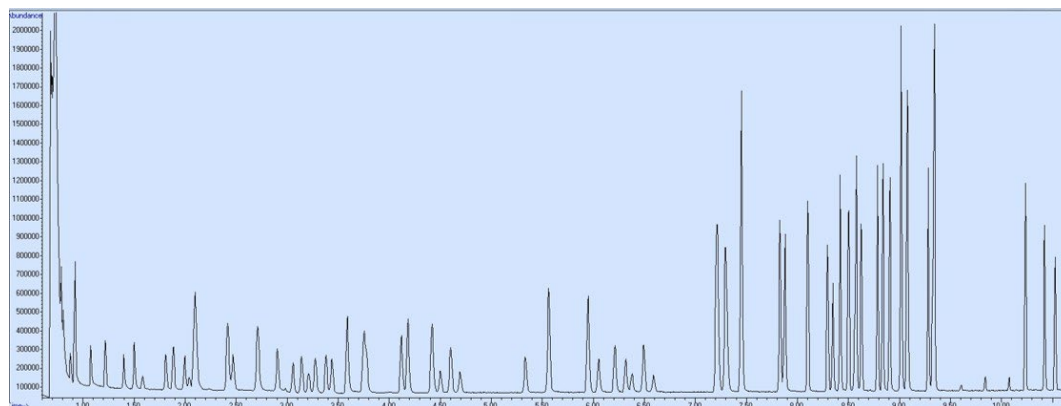


Figure 1 Total Ion Chromatogram (TIC) of a US EPA 524.4 Water Method 10 ppb VOC Standard Indicating Consistent Peak Shapes and Separation with Minimal Water Interference.

Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in drinking water samples following the US EPA Method 524.4 with detection by an Agilent 7890B GC/5977B MS. The linearity of the calibration curve from 0.2 ppb to 40 ppb passed all method requirements with no interference from excessive water. Furthermore, the average MDL for all compounds was 0.12 ppb with a 3.7% RSD. Seven 10 ppb mid-point calibration check standards averaged a 104% recovery with a 4.6% RSD. Both MDL, MRL and mid-point calibration check showed no interference from excessive water.

The Atomx XYZ and GC-MS conditions displayed in [Table I](#) and [Table II](#) allow for up to three samples to run, within one hour. 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. US EPA. 2013. "Method 524.4: "Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas," Cincinnati, OH. [Online] <https://nepis.epa.gov/Exe/ZyPDF.cgi/P100J7EE.PDF?Dockkey=P100J7EE.PDF> (accessed April 29, 2022).