US EPA Method 524.2 Using the Teledyne Tekmar Atomx XYZ with Agilent 7890B GC/5977B MS and Hydrogen as an Alternative Carrier Gas

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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 the use of hydrogen as the carrier gas for US EPA Method 524.2 to determine the concentration of volatile organic compounds (VOCs) in drinking water. This method is effective at concentrating trace levels of VOCs, however it can also transfer a significant amount of water vapor to the Gas Chromatograph/Mass Spectrometer (GC/MS) due to the four-minute desorb time recommendation. 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 calibration curve, method detection limits (MDLs) and a mid-point calibration check for target compounds. This study will demonstrate the ability of the Atomx XYZ's innovative moisture control system (MCS) to remove water vapor transferred to the GC/MS.

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. The redesigned 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: Drinking Water VOA MegaMix®, Ketone Mix and 502.2 Calibration Mix. In total, the standards contained 83 compounds.

The calibration curves were prepared from 0.2 parts per billion (ppb) to 50 ppb for most compounds. The relative response factor (RRF) was calculated for each compound using one internal standard: Fluorobenzene. Surrogate standards consisted of: 4-Bromofluorobenzene and 1,2-Dichlorobenzene-d4. Internal and surrogate standards were prepared in methanol from Restek standards at a concentration of 25 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and precision for all compounds. Also, seven 10 ppb standards were prepared as a mid-point calibration check to calculate accuracy and precision for all compounds. All calibration, MDL and mid-point calibration check standards were analyzed with the Atomx XYZ conditions in Table I. GC-MS conditions are shown in Table II.

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Experimental Instrument Conditions

Table I Teledyne Tekmar Atomx XYZ Water Method Conditions			
Standby	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	140 ºC	Methanol Needle Rinse	Off
Transfer Line Temp	140 ºC	Water Needle Rinse Volume	7.00 mL
Sample Mount Temp	90 ºC	Sweep Needle Time	0.25 min
Water Heater Temp	90 ºC	Desorb Preheat Temp	245 ºC
Sample Cup Temp	20 ºC	GC Start Signal	Begin Desorb
Soil Valve Temp	50 ºC	Desorb Time	4.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40 ºC	Desorb Temp	250 ºC
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	25.00 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	Trap Bake Temp	260 ºC
Purge Temp	20 ºC	MCS Bake Temp	180 ºC
MCS Purge Temp	20 ºC		
Dry Purge Time	1.00 min	**Trap**	9
Dry Purge Flow	100 mL/min	**Chiller Tray**	Off
Dry Purge Temp	20 ºC	**Purge Gas**	Nitrogen

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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 ºC, 2 min, 10 ºC/min to 85 ºC, 30 ºC/min to 225 ºC, 1 min Hold, Run Time 12.67 min
Inlet	200 ºC, 80:1 Split, Septum Purge Flow 0.5 mL/min, Carrier Gas - Hydrogen
Agilent 5977B MS Conditions	
Temp	Transfer Line 250 ºC; Source 250 ºC; Quad 200 ºC
Scan	Range 35 *m/z* to 260 *m/z*, Solvent Delay 0.50 min, Normal Scanning
Current	Gain Factor 1.00, Extraction Source Tune

Results

The relative standard deviation (%RSD) of the RRFs for the calibration curve, MDL and mid-point calibration check data are shown in Table III. Figure 1 shows a 10 ppb standard, indicating excellent peak resolution with no water inference for all VOCs.

Table III US EPA Method 524.2 Calibration, MDL and Mid-Point Calibration Check Data

Compound	Calibration				Method Detection Limit (n=7, 0.2 ppb)		Mid-Point Recovery (n=7, 10 ppb)	
	Retention Time	Quant Ion	Linearity (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Dichlorodifluoromethane	0.787	85	7.55	1.41	0.09	5.17	5.04	99
Chloromethane	0.878	50	4.97	1.11	0.09	5.77	3.72	96
Vinyl Chloride	0.914	62	4.88	1.38	0.10	6.34	4.27	100
Bromomethane[2]	1.08	94	16.8	0.915	0.10	4.89	3.08	87
Chloroethane	1.15	64	8.76	0.678	0.12	7.00	3.55	99
Trichlorofluoromethane	1.22	101	6.94	1.31	0.10	5.91	3.83	101
Diethyl Ether	1.40	59	5.49	0.462	0.05	3.41	1.67	100
1,1-Dichloroethene	1.51	96	6.69	0.863	0.10	6.28	3.67	98
Iodomethane[1 5]	1.58	142	0.999	0.931	0.16	3.82	2.38	94
Carbon Disulfide	1.81	76	7.72	0.523	0.10	6.49	2.71	99
Allyl Chloride	1.81	76	7.97	0.524	0.09	5.82	2.73	99
Methylene Chloride[2]	1.89	84	9.07	0.914	0.07	3.61	2.03	94
Acetone[2 5]	1.95	43	17.1	0.114	0.21	4.36	7.29	104
trans-1,2-Dichloroethene	2.00	96	4.72	0.962	0.10	6.36	3.06	97
Methyl-t-Butyl Ether	2.11	73	5.05	1.27	0.04	2.41	1.99	104
1,1-Dichloroethane	2.48	63	5.74	1.74	0.05	2.86	2.50	100

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	Retention Time	Quant Ion	Linearity (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Acrylonitrile	2.54	52	10.4	0.085	0.16	9.03	2.98	103
cis-1,2-Dichloroethene	2.92	96	5.03	0.985	0.08	4.90	3.10	99
2,2-Dichloropropane	3.00	77	6.06	1.16	0.09	5.69	5.45	89
Bromochloromethane	3.08	128	5.38	0.316	0.06	3.83	1.87	97
Chloroform	3.17	83	3.92	1.52	0.05	3.00	3.20	102
Carbon Tetrachloride	3.25	117	9.75	0.730	0.11	7.01	3.14	106
1,1,1-Trichloroethane	3.31	97	6.22	1.13	0.09	5.89	3.36	102
Tetrahydrofuran	3.32	71	13.6	0.037	0.11	7.09	3.72	100
Methyl Acrylate	3.32	55	5.32	0.221	0.13	7.48	2.66	107
1,1-Dichloropropene	3.43	75	5.33	1.29	0.10	6.21	3.83	101
2-Butanone	3.49	43	9.28	0.559	0.05	3.10	3.27	101
1-Chlorobutane	3.49	56	5.22	1.79	0.10	6.44	3.51	102
Benzene	3.65	78	5.07	4.09	0.10	6.03	2.85	100
Propionitrile[5]	3.73	54	13.3	0.046	0.17	5.37	3.96	91
Methacrylonitrile	3.73	67	5.97	0.148	0.15	8.77	2.55	97
1,2-Dichloroethane	3.85	62	6.17	0.709	0.06	3.82	1.98	101
Fluorobenzene (IS)	4.05	96						
Trichloroethylene	4.20	95	4.47	1.07	0.08	5.57	3.21	103
Dibromomethane	4.60	93	6.20	0.282	0.12	7.42	1.78	99
1,2-Dichloropropane	4.71	63	6.78	0.909	0.09	6.18	2.60	101
Bromodichloromethane	4.80	83	7.68	0.629	0.10	6.48	1.65	104
Methyl Methacrylate	5.04	69	8.38	0.224	0.09	5.43	2.46	107
cis-1,3-Dichloropropene	5.44	75	11.6	0.853	0.22	14.6	13.9	106
Toluene	5.66	92	7.61	3.05	0.15	10.3	4.74	90
2-Nitropropane[2] [5]	5.93	46	14.9	0.057	0.41	8.48	3.93	96
1,1-Dichloropropanone	5.93	43	4.98	0.063	0.13	7.56	3.58	97
Chloroacetonitrile[3] [5]	6.02	48	14.1	0.010	0.29	10.9	3.29	119
Tetrachloroethene	6.03	166	8.95	1.60	0.07	5.29	4.17	111
trans-1,3-Dichloropropene	6.13	75	13.3	0.551	0.11	8.28	1.79	99

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Compound	Calibration				Method Detection Limit (n=7, 0.2 ppb)		Mid-Point Recovery (n=7, 10 ppb)	
	Retention Time	Quant Ion	Linearity (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
4-Methyl-2-pentanone	6.13	43	4.80	0.195	0.13	8.60	3.20	94
1,1,2-Trichloroethane	6.29	83	11.3	0.338	0.06	4.51	1.54	100
Ethyl Methacrylate	6.39	69	12.5	0.326	0.08	5.21	1.85	101
Dibromochloromethane	6.45	129	9.35	0.276	0.08	4.90	1.81	98
1,3-Dichloropropane	6.57	76	7.49	0.780	0.12	8.04	1.86	101
1,2-Dibromoethane	6.66	107	10.2	0.326	0.11	7.92	1.91	95
2-Hexanone	7.08	43	6.61	0.158	0.10	6.26	9.67	100
Chlorobenzene	7.27	112	4.72	2.69	0.09	6.18	2.98	97
Ethylbenzene	7.34	91	4.42	5.02	0.09	5.60	3.73	97
1,1,1,2-Tetrachloroethane	7.36	131	14.4	0.456	0.08	6.21	1.91	92
m-,p-Xylene	7.49	106	4.65	2.02	0.20	6.64	3.68	98
o-Xylene	7.86	106	4.84	1.90	0.08	5.40	3.42	97
Bromoform	7.90	173	11.9	0.129	0.02	1.77	1.81	98
Styrene	7.91	104	6.21	2.67	0.08	5.40	2.76	100
Isopropylbenzene	8.13	105	5.50	4.78	0.10	6.81	3.82	101
4-Bromofluorobenzene (SURR)	8.32	95	2.39	1.04		1.09	0.95	97
Bromobenzene	8.37	156	10.7	0.853	0.10	6.89	2.43	97
n-Propylbenzene	8.44	91	9.83	5.81	0.11	7.14	4.07	102
1,1,2,2-Tetrachloroethane	8.51	83	14.7	0.273	0.16	12.0	4.56	86
2-Chlorotoluene	8.52	91	3.84	3.48	0.09	6.08	3.59	100
1,2,3-Trichloropropane	8.58	75	10.3	0.339	0.07	4.75	2.25	100
1,3,5-Trimethylbenzene	8.59	105	7.50	4.42	0.09	5.82	3.81	101
trans-1,4-Dichloro-2-butene	8.63	53	9.49	0.105	0.13	7.94	2.60	85
4-Chlorotoluene	8.64	91	4.29	3.53	0.10	6.54	3.09	100
tert-Butylbenzene	8.80	119	5.21	3.54	0.10	6.17	4.32	97
1,2,4-Trimethylbenzene	8.85	105	6.85	4.32	0.10	6.48	3.54	102
sec-Butylbenzene	8.92	105	9.69	5.22	0.12	7.68	4.34	102
Pentachloroethane	9.03	117	7.18	0.750	0.11	6.82	4.30	99
p-Isopropyltoluene	9.03	119	7.89	4.34	0.12	7.51	3.97	104

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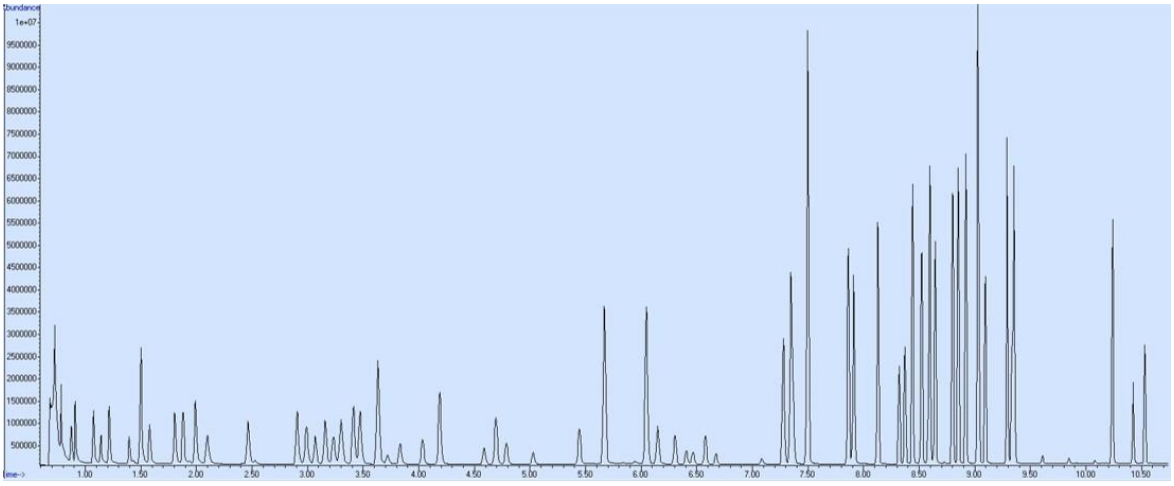
Compound	Calibration				Method Detection Limit (n=7, 0.2 ppb)		Mid-Point Recovery (n=7, 10 ppb)	
	Retention Time	Quant Ion	Linearity (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
1,3-Dichlorobenzene	9.03	146	7.05	1.93	0.09	6.42	2.78	106
1,4-Dichlorobenzene	9.09	146	7.27	1.83	0.09	6.35	2.97	100
n-Butylbenzene	9.29	91	8.00	4.26	0.12	7.51	4.40	103
Hexachloroethane[4]	9.33	117	17.4	0.347	0.08	5.52	3.09	96
1,2-Dichlorobenzene-d4 (SURR)	9.35	152	4.84	0.958		1.51	1.53	102
1,2-Dichlorobenzene	9.36	146	4.87	1.65	0.09	6.02	2.71	101
1,2-Dibromo-3-Chloropropane	9.85	75	10.3	0.036	0.05	3.16	4.03	95
Nitrobenzene[3 5]	10.18	51	17.2	0.012	0.17	5.32	7.32	100
Hexachlorobutadiene	10.24	225	14.3	0.445	0.15	10.7	3.97	97
1,2,4-Trichlorobenzene	10.24	180	6.36	1.08	0.10	7.18	2.27	103
Naphthalene	10.43	128	6.09	1.58	0.08	5.09	1.84	98
1,2,3-Trichlorobenzene	10.53	180	6.64	0.858	0.11	7.98	2.18	103

1. Compound used a linear regression calibration
2. Calibration range 0.5-50 ppb
3. Calibration range 2-50 ppb
4. Calibration range 1-50 ppb
5. MDL calculated using n=7, 1 ppb

Figure 1 Total Ion Chromatogram of a US EPA 524.2 Water Method 10 ppb VOC Standard Indicating Consistent Peak Shapes and Separation for all Compounds with Minimal Water Interference.



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Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in drinking water samples following US EPA Method 524.2 with detection by an Agilent 7890B GC/5977B MS. The %RSD of the calibration curve passed all method requirements. Furthermore, the average MDL for all compounds was 0.11 ppb with a 6.3% RSD. Seven 10 ppb mid-point calibration check standards averaged a 99% recovery with a 3.4% RSD. Both MDL and mid-point calibration check showed no interference from excessive water.

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. U.S. EPA. 1992. “Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry,” Revision 4.1. Cincinnati, OH. [Online] https://www.epa.gov/sites/production/files/2015-06/documents/epa-524.2.pdf (accessed April 29, 2022).