US EPA Method 524.3 with the Teledyne Tekmar Atomx XYZ and the Thermo Scientific™ TRACE™ 1310 GC and ISQ™ LT MS System

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Abstract

US EPA Method 524.3 was used to determine the concentration of volatile organic compounds (VOCs) in drinking water matrices. For this study, a Teledyne Tekmar Atomx XYZ purge and trap (P&T) system and Thermo Scientific TRACE 1310 Gas Chromatograph (GC)/ISQ LT Mass Spectrometer (MS) was used to create a working linear regression (r^2) calibration curve, method detection limits (MDLs), and minimum reporting level (MRL) confirmation for target compounds.

Introduction

The Atomx XYZ is Teledyne Tekmar's second-generation, multi-matrix 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. A reduced footprint of 13 cm (5"), compared to the previous generation, provides more bench space for laboratory tasks.

Sample Preparation

Calibration working standards in concentrations of 10 and 50 ppm were prepared in methanol from the following Restek® standards: 524.3 VOA MegaMix® and 524.3 Gas Calibration Mix. In total, the standards contained 74 compounds.

A nine-point linear regression (r^2) calibration curve was prepared from 0.2 ppb to 40 ppb for all compounds with regression value (r^2) ≥0.995. The 10 ppm calibration working standard was diluted to create 0.2, 0.5, 1, and 2 ppb concentrations. The 50 ppm calibration working standard was diluted to create 5, 10, 20, 30, and 40 ppb concentrations. The relative response factor (RF) 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 together in methanol from Restek standards at a concentration of 12.5 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 12.5 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and accuracy and precision calculations. Seven 20 ppb standards were prepared for the MRL confirmation. All calibration, MDL, accuracy and precision, and MRL 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			
Purge	**Variable**	**Desorb**	**Variable**
Valve Oven Temp	140 ºC	Methanol Needle Rinse	Off
Transfer Line Temp	140 ºC	Methanol Needle Rinse Volume	0.00 mL
Sample Mount Temp	90 ºC	Water Needle Rinse Volume	7.00 mL
Water Heater Temp	90 ºC	Sweep Needle Time	0.25 min
Sample Vial Temp	20 ºC	Desorb Preheat Temp	245 ºC
Soil Valve Temp	100 ºC	GC Start Signal	Begin Desorb
Standby Flow	10 mL/min	Desorb Time	2.00 min
Purge Ready Temp	40 ºC	Drain Flow	300 mL/min
		Desorb Temp	250 ºC
Purge	**Variable**	**Bake**	**Variable**
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Number of Methanol Glass Rinses	0
Prime Sample Fill Volume	3.00 mL	Methanol Glass Rinse Volume	0.00 mL
Sample Volume	5.00 mL	Water Bake Rinses	1
Sweep Sample Time	0.25 min	Water Bake Rinse Volume	7.00 mL
Sweep Sample Flow	100 mL/min	Bake Rinse Sweep Time	0.25 min
Sparge Vessel Heater	Off	Bake Rinse Sweep Flow	100 mL/min
Sparge Vessel Temp	40 ºC	Bake Rinse Drain Time	0.40 min
Pre-purge Time	0.00 min	Bake Time	2.00 min
Pre-purge Flow	0 mL/min	Bake Flow	200 mL/min
Purge Time	5.00 min	Bake Temp	280 ºC
Purge Flow	80 mL/min	Condensate Bake Temp	180 ºC
Purge Temp	20 ºC		
Condensate Purge Temp	20 ºC		
Dry Purge Time	0.00 min	**Trap**	9
Dry Purge Flow	0 mL/min	**Chiller Tray**	On
Dry Purge Temp	20 ºC	**Purge Gas**	Helium

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Table II Thermo Scientific TRACE 1310 GC and ISQ LT MS System Conditions	
Thermo Scientific TRACE 1310 GC	
Column	Rtx®-VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 1 mL/min
Oven Profile	35 ºC, 2 min, 16 ºC/min to 85 ºC, 30 ºC/min to 225 ºC, 1 min hold, Run Time 10.79 min
Inlet	200 ºC, 60:1 Split; Helium Saver 20.0 mL/min after 2.00 min
ISQ LT MS System Conditions	
Temp	Transfer Line 230 ºC; Ion Source 280 ºC
Scan	Range 35 *amu* to 260 *amu*, Time 0.154 min; Solvent Delay 0.10 min
Current	Emission Current 20 µA, Gain 3.00E+005

Results

The linear correlation coefficient of the calibration curve (r^2), MDL, accuracy and precision, and MRL confirmation data are shown in Table III. Figure 1 displays a chromatogram of a 20 ppb standard, indicating excellent peak resolution with minimal water interference for all VOCs.

Table III Method 524.3 Calibration, Accuracy and Precision and MRL Confirmation Data							
Compound	Calibration		Accuracy and Precision (n=7, 0.5 ppb)[1]			MRL Confirmation (n=7, 20 ppb)[2]	
	Linearity (r^2 ≥0.995)	MDL (ppb)[1]	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Dichlorodifluoromethane	0.997	0.12	0.48	96	8.2	66	116
Chlorodifluoromethane	0.999	0.04	0.50	100	2.3	67	121
Chloromethane	0.999	0.07	0.47	93	4.6	88	111
Vinyl Chloride	0.999	0.03	0.50	99	2.0	66	121
1,3-Butadiene	0.999	0.11	0.49	97	7.1	64	123
Bromomethane	1.000	0.03	0.50	100	2.0	79	116
Trichlorofluoromethane	0.999	0.28	0.45	90	19.5	60	122
Diethyl Ether	0.999	0.06	0.50	100	3.7	88	110
1,1-Dichloroethene	0.995	0.19	0.57	114	10.6	69	122
Iodomethane	0.997	0.15	0.59	118	8.0	68	114
Allyl Chloride	0.997	0.26	0.46	91	18.1	71	118
Carbon Disulfide	0.997	0.16	0.54	107	9.3	80	114
Methylene Chloride	0.995	0.18	0.48	96	11.9	73	117

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	Linearity (r^2 ≥0.995)	MDL (ppb)[1]	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
trans-1,2-Dichloroethene	0.996	0.32	0.58	116	17.3	86	108
Methyl Acetate	0.996	0.13	0.49	97	8.4	82	120
Methyl-tert-Butyl Ether-d3 (SURR)	7.52		13.0	104	5.0	89	109
Methyl-tert-Butyl Ether	0.995	0.20	0.47	94	13.3	87	105
tert-Butyl Alcohol	0.999	0.21	0.51	102	13.4	79	115
Diisopropyl Ether	0.996	0.06	0.46	92	4.0	75	114
1,1-Dichloroethane	0.996	0.11	0.38	77	9.4	75	111
tert-Butyl Ethyl Ether	0.996	0.11	0.47	94	7.2	76	109
cis-1,2-Dichloroethene	0.998	0.20	0.45	89	14.1	74	115
Bromochloromethane	0.998	0.17	0.48	96	11.4	68	120
Chloroform	0.995	0.12	0.41	82	9.7	75	119
Carbon Tetrachloride	0.996	0.20	0.54	109	11.6	70	124
1,1,1-Trichloroehane	0.996	0.21	0.50	100	13.1	80	101
Tetrahydrofuran	0.999	0.11	0.46	91	7.9	67	126
1,1-Dichloropropene	0.996	0.20	0.45	91	13.9	75	106
1-Chlorobutane	0.995	0.09	0.48	97	6.1	70	109
Benzene	0.995	0.11	0.41	83	8.8	79	107
tert-Amyl Methyl Ether	0.996	0.05	0.42	83	4.1	77	108
1,2-Dichloroethane	0.996	0.18	0.45	89	13.0	72	120
Trichloroethene	0.995	0.20	0.45	90	14.4	76	107
1,4-Difluorobenzene (IS)							
tert-Amyl Ethyl Ether	0.996	0.15	0.42	83	11.4	76	108
Dibromomethane	0.997	0.13	0.50	101	8.2	76	113
1,2-Dichloropropane	0.996	0.16	0.42	85	11.7	80	109
Bromodichloromethane	0.996	0.18	0.49	99	11.8	81	104
cis-1,3-Dichloropropene	0.997	0.15	0.49	99	9.6	75	113
Toluene	0.995	0.10	0.47	95	6.4	74	120

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Table III Method 524.3 Calibration, Accuracy and Precision and MRL Confirmation Data							
Compound	Calibration		Accuracy and Precision (n=7, 0.5 ppb)[1]			MRL Confirmation (n=7, 20 ppb)[2]	
	Linearity (r^2 ≥0.995)	MDL (ppb)[1]	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Tetrachloroethene	0.995	0.03	0.37	74	8.1	68	114
trans-1,3-Dichloropropene	0.995	0.11	0.48	95	7.4	77	115
1,1,2-Trichloroethane	0.996	0.12	0.43	87	8.7	71	109
Ethyl Methacrylate	0.996	0.17	0.59	119	9.0	78	116
Dibromochloromethane	0.996	0.24	0.49	97	15.9	83	109
1,3-Dichloropropane	0.997	0.15	0.47	93	10.0	74	115
1,2-Dibromoethane	0.997	0.12	0.43	86	8.8	65	127
Chlorobenzene-d5 (IS)							
Chlorobenzene	0.997	0.15	0.45	91	10.2	73	117
Ethylbenzene	0.995	0.14	0.56	113	8.1	78	118
1,1,1,2-Tetrachloroethane	0.995	0.22	0.54	107	12.9	58	122
m,p-Xylene	0.995	0.11	0.94	94	3.7	75	103
o-Xylene	0.995	0.10	0.45	90	7.3	74	108
Bromoform	0.995	0.32	0.51	103	19.8	66	125
Styrene	0.995	0.20	0.53	106	12.0	78	115
Isopropylbenzene	0.997	0.02	0.43	86	4.5	66	110
4-Bromofluorobenzene (SURR)	5.22		10.8	87	4.7	73	127
Bromobenzene	0.997	0.17	0.47	95	11.2	71	103
n-Propylbenzene	0.995	0.14	0.44	87	10.5	62	110
1,1,2,2-Tetrachloroethane	0.995	0.07	0.42	84	5.0	53	123
2-Chlorotoluene	0.995	0.10	0.44	88	7.6	59	112
1,2,3-Trichloropropane	0.995	0.22	0.43	87	16.0	51	123
1,3,5-Trimethylbenzene	0.997	0.13	0.45	90	9.0	63	103
4-Chlorotoluene	0.995	0.08	0.44	88	5.8	63	110
tert-Butylbenzene	0.995	0.25	0.44	89	17.9	56	109
1,2,4-Trimethylbenzene	0.995	0.18	0.46	92	12.4	66	111
sec-Butylbenzene	0.996	0.05	0.41	81	4.2	66	103

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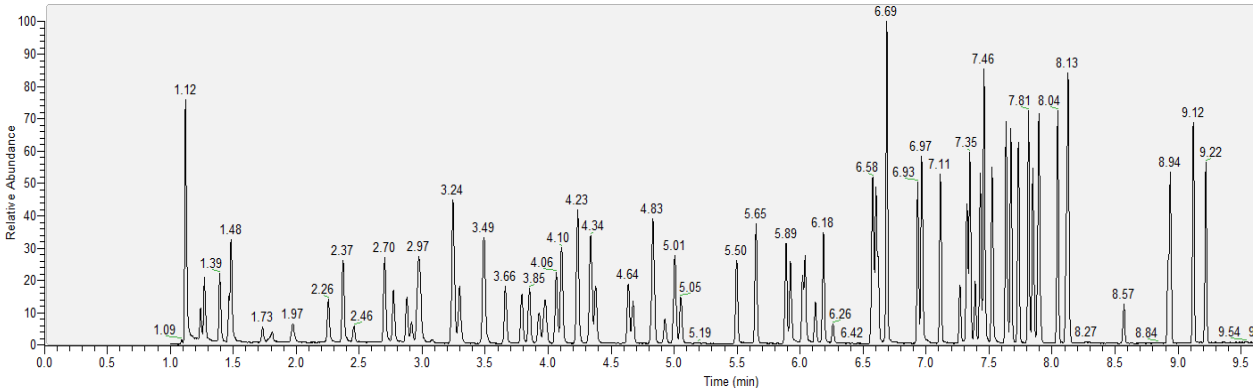
Compound	Calibration		Accuracy and Precision (n=7, 0.5 ppb)[1]			MRL Confirmation (n=7, 20 ppb)[2]	
	Linearity (r^2 ≥0.995)	MDL (ppb)[1]	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
4-Isopropyltoluene	0.995	0.09	0.44	89	6.5	65	107
1,3-Dichlorobenzene	0.997	0.19	0.45	89	13.8	65	113
1,4-Dichlorobenzene	0.997	0.20	0.51	101	12.8	68	107
1,4-Dichlorobenzene-d4 (IS)							
n-Butylbenzene	0.995	0.20	0.52	105	12.2	66	106
Hexachloroethane	0.995	0.24	0.42	85	18.0	63	123
1,2-Dichlorobenzene	0.996	0.10	0.44	88	7.3	61	110
1,2-Dichlorobenzene-d4 (SURR)	8.01		12.3	99	3.2	71	117
1,2-Dibromo-3-Chloropropane	0.995	0.15	0.55	111	8.9	60	114
Hexachlorobutadiene	0.996	0.28	0.37	73	24.7	69	118
1,2,4-Trichlorobenzene	0.995	0.21	0.50	99	13.2	66	121
Napthalene	0.995	0.07	0.44	88	5.1	59	129
1,2,3-Trichlorobenzene	0.996	0.27	0.47	95	18.0	66	121

1. Data from seven 0.5 ppb samples.
2. Data from seven 20 ppb samples.

Figure 1 Total Ion Chromatogram of a 20 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds with No 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 524.3 with detection by a Thermo Scientific TRACE 1310 GC/ISQ LT MS. The linearity of the calibration curve from 0.2 ppb to 40 ppb passed all method requirements with no interference from excessive water. The MDL and accuracy and precision for seven 0.5 ppb standards, as well as the MRL confirmation for seven 20 ppb standards, indicated no interference from excessive water.

The system was capable of analyzing four samples within one hour using the Atomx XYZ and GC/MS conditions shown in Table I and Table II. By making additional, appropriate changes to the GC oven temperature program, the GC/MS cycle time may also be reduced, further increasing laboratory throughput in a 12-hour period.

References

1. Munch, J.W; Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; US EPA Method 524.3 - Revision 1.0, June 2009. [Online] https://www.epa.gov/sites/production/files/2015-06/documents/epa-524.2.pdf (accessed February 25, 2019).