

US EPA Method 524.3 with the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ 7000 MS with an Advanced Electron Ionization (AEI) Source

Amy Nutter, Applications Chemist; Teledyne Tekmar

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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. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) system along with a Thermo Scientific TRACE 1310 GC/ISQ 7000 MS with an advanced electron ionization (AEI) source was used to create a working linear regression (r^2) calibration curve, method detection limits (MDLs) and midpoint accuracy 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 25 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 73 compounds.

A nine-point linear regression (r^2) calibration curve was prepared from 0.2 ppb to 50 ppb for all compounds with regression value (r^2) ≥ 0.995 . 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 in methanol from Restek standards at a concentration of 25 ppm, after which 5 μ L was then mixed with each 5 mL sample for a resulting concentration of 25 ppb.

A quantity of ten, 0.5 ppb standards were prepared to calculate the MDL and accuracy and precision calculations. An additional ten 20 ppb standards were prepared for the midpoint accuracy check. All calibration, MDL, accuracy and precision, and midpoint accuracy 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	Methanol Needle Rinse Volume	0.00 mL
Sample Mount Temp	90 °C	Water Needle Rinse Volume	7.00 mL
Water Heater Temp	90 °C	Sweep Needle Time	0.25 min
Sample Vial Temp	20 °C	Desorb Preheat Temp	245 °C
Soil Valve Temp	100 °C	GC Start Signal	Begin Desorb
Standby Flow	10 mL/min	Desorb Time	1.00 min
Purge Ready Temp	40 °C	Drain Flow	300 mL/min
Purge	Variable	Desorb Temp	250 °C
Sample Equilibrate Time	0.00 min	Bake	Variable
Pre-sweep Time	0.25 min	Methanol Glass Rinse	Off
Prime Sample Fill Volume	3.00 mL	Number of Methanol Glass Rinses	0
Sample Volume	5.00 mL	Methanol Glass Rinse Volume	0.00 mL
Sweep Sample Time	0.25 min	Water Bake Rinses	1
Sweep Sample Flow	100 mL/min	Water Bake Rinse Volume	7.00 mL
Spurge Vessel Heater	Off	Bake Rinse Sweep Time	0.25 min
Spurge Vessel Temp	40 °C	Bake Rinse Sweep Flow	100 mL/min
Pre-purge Time	0.00 min	Bake Rinse Drain Time	0.40 min
Pre-purge Flow	0 mL/min	Bake Time	2.00 min
Purge Time	5.00 min	Bake Flow	200 mL/min
Purge Flow	80 mL/min	Bake Temp	280 °C
Purge Temp	20 °C	Condensate Bake Temp	180 °C
Condensate Purge Temp	20 °C		
Dry Purge Time	2.00 min	Trap	9
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20 °C	Purge Gas	Helium

Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	Rtx® VMS, 20 m x 0.18 mm, 1µm Film, Helium – 0.8 mL/min
Oven Profile	35 °C, 2 min, 12°C/min to 85 °C, 20°C/min to 225 °C, 2 min Hold, Run Time 15.167 min
Inlet	200 °C, 50:1 Split
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 300 °C; Ion Source 280 °C
Scan	Range 35 <i>amu</i> to 260 <i>amu</i> , Solvent Delay 0.10 min, Dwell/Scan Time 0.15 sec
Current	Emission Current 25 µA, Gain 3.00E+005

Results

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

Table III Method 524.3 Calibration, Accuracy and Precision Data									
Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb) ¹			Midpoint Accuracy Check (n=10, 20 ppb) ²	
	Ret. Time	Linearity ($r^2 \geq 0.995$)	Avg. RF	MDL (ppb) ¹	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Dichlorodifluoromethane	1.33	0.999	0.561	0.10	0.52	103	6.85	75	105
Chlorodifluoromethane	1.36	0.997	0.791	0.08	0.55	110	5.47	82	126
Chloromethane	1.46	0.999	0.725	0.09	0.57	114	5.83	76	112
Vinyl Chloride	1.52	0.999	0.532	0.06	0.45	89	4.97	71	111
1,3-Butadiene	1.53	1.00	0.830	0.06	0.47	94	4.85	72	104
Bromomethane	1.74	0.998	0.349	0.12	0.55	111	7.53	66	111
Trichlorofluoromethane	1.92	0.996	0.769	0.09	0.56	112	5.72	85	116
Diethyl Ether	2.24	0.997	0.244	0.20	0.44	88	16.1	92	113
1,1-Dichloroethene	2.33	0.998	0.064	0.05	0.57	115	3.13	78	118
Iodomethane	2.43	0.999	0.266	0.07	0.41	81	5.91	58	99
Allyl Chloride	2.71	0.999	0.095	0.07	0.50	99	5.26	78	116
Carbon Disulfide	2.71	0.999	0.095	0.07	0.50	99	5.26	78	116
Methylene Chloride	2.79	0.999	0.460	0.06	0.57	114	3.55	91	119

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Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb) ¹			Midpoint Accuracy Check (n=10, 20 ppb) ²	
	Ret. Time	Linearity (r ² ≥ 0.995)	Avg. RF	MDL (ppb) ¹	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
cis-1,2-Dichloroethene	2.92	0.999	0.123	0.10	0.55	110	6.75	84	114
Methyl Acetate	3.01	0.998	0.286	0.27	0.54	109	15.5	95	117
Methyl-tert-Butyl Ether-d3 (SURR)	3.10	2.58	1.08		26	105	1.55	123	139
Methyl-tert-Butyl Ether	3.11	0.999	0.893	0.04	0.53	106	2.58	87	119
tert-Butyl Alcohol	3.28	0.999	0.040	0.15	0.57	115	9.55	93	27
Diisopropyl Ether	3.40	0.999	1.72	0.04	0.49	99	3.02	82	117
1,1-Dichloroethane	3.41	0.999	0.505	0.06	0.50	101	3.92	83	121
tert-Butyl Ethyl Ether	3.69	1.00	1.08	0.04	0.48	97	2.79	84	116
trans-1,2-Dichloroethene	3.84	0.999	0.386	0.07	0.51	101	4.82	83	122
Bromochloromethane	4.00	1.00	0.106	0.07	0.46	92	5.30	88	120
Chloroform	4.07	0.999	0.547	0.05	0.52	105	3.34	85	121
Carbon Tetrachloride	4.17	1.00	0.319	0.09	0.44	87	7.41	75	113
1,1,1-Trichloroethane	4.22	0.999	0.404	0.06	0.50	99	3.98	79	118
1,1-Dichloropropene	4.33	1.00	0.255	0.07	0.47	95	5.10	74	114
Tetrahydrofuran	4.34	0.999	0.137	0.08	0.47	93	6.35	94	113
1-Chlorobutane	4.38	0.999	0.411	0.08	0.48	95	5.99	74	117
Benzene	4.53	0.999	0.821	0.06	0.50	99	4.42	82	118
1,2-Dichloroethane	4.71	0.999	0.485	0.05	0.50	101	3.30	89	120
tert-Amyl Methyl Ether	4.74	1.00	0.874	0.03	0.48	95	2.20	84	116
Trichloroethylene	5.03	0.998	0.333	0.07	0.56	113	4.10	91	125
1,4-Difluorobenzene (IS)	5.08								
tert-Amyl Ethyl Ether	5.32	1.00	0.876	0.03	0.46	92	2.18	79	114
Dibromomethane	5.39	0.999	0.199	0.04	0.48	96	2.83	87	120
1,2-Dichloropropane	5.48	0.999	0.329	0.05	0.50	100	3.67	85	119
Bromodichloromethane	5.55	0.999	0.454	0.06	0.55	111	3.85	82	121
trans-1,3-Dichloropropene	6.13	0.999	0.448	0.04	0.44	89	3.34	77	112

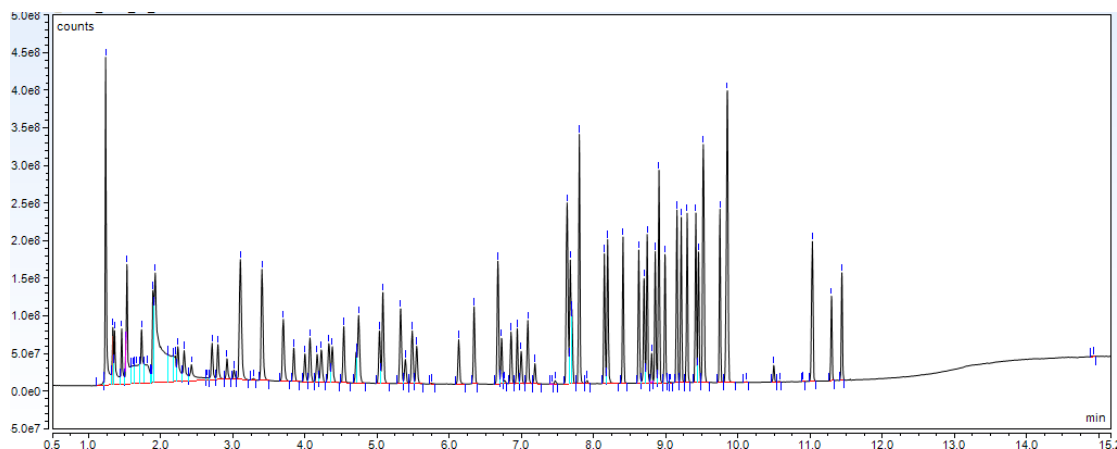
Table III Method 524.3 Calibration, Accuracy and Precision Data

Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb) ¹			Midpoint Accuracy Check (n=10, 20 ppb) ²	
	Ret. Time	Linearity (r ² ≥ 0.995)	Avg. RF	MDL (ppb) ¹	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Toluene	6.34	0.999	1.16	0.05	0.46	93	4.10	75	116
Tetrachloroethylene	6.67	0.996	0.695	0.06	0.55	109	3.60	86	115
cis-1,3-Dichloropropene	6.72	1.00	0.381	0.12	0.48	96	9.17	81	115
1,1,2-Trichloroethane	6.85	0.998	0.296	0.06	0.45	91	4.32	77	118
Ethyl Methacrylate	6.94	0.998	0.445	0.04	0.41	83	3.43	74	115
Dibromochloromethane	6.99	0.998	0.326	0.10	0.52	104	6.96	76	119
1,3-Dichloropropane	7.09	0.999	0.534	0.05	0.47	94	3.78	79	116
1,2-Dibromoethane	7.18	0.999	0.295	0.07	0.49	97	4.80	82	118
Chlorobenzene-d5 (IS)	7.62								
Chlorobenzene	7.64	0.999	0.850	0.06	0.50	100	4.14	77	119
Ethylbenzene	7.67	0.999	1.58	0.07	0.45	91	5.32	70	121
1,1,1,2-Tetrachloroethane	7.70	0.999	0.320	0.04	0.43	86	3.68	75	117
m,p-Xylene	7.80	0.999	0.606	0.11	0.86	86	4.39	137	114
o-Xylene	8.15	0.999	0.602	0.06	0.45	90	4.57	74	119
Bromoform	8.19	0.997	0.282	0.12	0.50	100	8.76	76	116
Styrene	8.19	0.997	0.965	0.05	0.45	90	4.18	75	112
Isopropylbenzene	8.40	0.999	1.63	0.07	0.43	87	5.50	71	116
4-Bromofluorobenzene (SURR)	8.62	6.45	0.600		25	98	1.28	113	122
Bromobenzene	8.70	0.999	0.852	0.04	0.50	100	2.68	78	115
n-Propylbenzene	8.74	0.998	1.93	0.07	0.47	94	5.08	72	116
1,1,2,2-Tetrachloroethane	8.80	0.997	0.259	0.14	0.44	87	11.2	77	118
2-Chlorotoluene	8.85	0.998	1.17	0.06	0.49	98	4.28	75	119
1,2,3-Trichloropropane	8.90	0.997	0.396	0.05	0.51	102	3.55	84	121
1,3,5-Trimethylbenzene	8.90	0.999	1.43	0.06	0.45	89	4.63	70	118
4-Chlorotoluene	8.99	0.998	1.22	0.07	0.49	99	4.81	75	119
tert-Butylbenzene	9.15	0.999	1.17	0.07	0.46	92	5.31	70	117

Table III Method 524.3 Calibration, Accuracy and Precision Data

Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb) ¹			Midpoint Accuracy Check (n=10, 20 ppb) ²	
	Ret. Time	Linearity (r ² ≥ 0.995)	Avg. RF	MDL (ppb) ¹	Avg. Conc. (ppb)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
1,2,4-Trimethylbenzene	9.21	0.999	1.46	0.05	0.45	89	4.30	72	119
sec-Butylbenzene	9.29	0.998	1.76	0.07	0.45	91	5.41	69	117
p-Isopropyltoluene	9.41	0.998	1.37	0.06	0.46	92	5.02	68	121
1,3-Dichlorobenzene	9.45	0.996	0.853	0.07	0.55	111	4.22	83	123
1,2-Dichlorobenzene-d4 (SURR)	9.51	1.56	1.00		24	95	1.60	117	126
1,4-Dichlorobenzene	9.52	0.995	0.851	0.06	0.57	115	3.47	83	124
n-Butylbenzene	9.75	0.997	1.57	0.07	0.47	93	5.51	72	115
1,4-Dichlorobenzene-d4 (IS)	9.85								
1,2-Dichlorobenzene	9.85	0.995	0.833	0.07	0.58	116	4.04	88	125
1,2-Dibromo-3-Chloropropane	10.49	0.996	0.066	0.13	0.52	103	9.21	102	132
Hexachlorobutadiene	10.90	0.999	0.000	0.25	0.50	100	17.4	85	128
1,2,4-Trichlorobenzene	11.03	0.995	0.465	0.08	0.58	116	4.92	93	125
Napthalene	11.29	0.997	0.874	0.08	0.50	100	5.91	95	123
1,2,3-Trichlorobenzene	11.44	0.995	0.423	0.07	0.59	118	4.36	99	128

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

Figure 1 Total Ion Chromatogram of a 20 ppb VOC Standard Indicating Consistent Peak Shapes for all Compounds 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 US EPA Method 524.3 with detection by a Thermo Scientific TRACE 1310 GC/ISQ 7000 MS with an AEI source. The linearity of the calibration curve from 0.2 ppb to 50 ppb passed all method requirements with no interference from excessive water. The MDL and accuracy and precision for ten 0.5 ppb standards, and mid-point accuracy check for ten 20 ppb standards, also indicated minimal interference from excessive water.

Furthermore, 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. 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.