US EPA Method 524.2 with the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ TRACE™ 1310 GC and ISQ™ 7000 MS System with an Advanced Electron Ionization (AEI) Source

Amy Nutter, Applications Chemist; Teledyne Tekmar

Abstract

US EPA Method 524.2 was used 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 recommended four-minute desorb time. 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 calibration curve and method detection limits (MDLs) for target compounds. This study will demonstrate the ability of the Atomx XYZ's moisture control system 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. An innovative moisture control system 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: Drinking Water VOA MegaMix™, Ketone Mix, and 502.2 Calibration Mix. In total, the standards contained 82 compounds.

The calibration curve was prepared from 0.2 ppb to 50 ppb for all compounds. The relative response factor (RF) 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.

A quantity of ten, 0.5 ppb standards were prepared to calculate the MDL, accuracy and precision calculations for all compounds. All calibration and MDL standards were analyzed with the Atomx XYZ conditions in Table I. GC-MS conditions are shown in Table II.

Sales/Support: 800-874-2004 • **Main**: 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

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	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	4.00 min
Condensate Ready Temp	45 ºC	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	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	20 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	11.00 min	Bake Temp	260 ºC
Purge Flow	40 mL/min	Condensate Bake Temp	200 ºC
Purge Temp	20 ºC		
Condensate Purge Temp	20 ºC		
Dry Purge Time	2.00 min	**Trap**	9
Dry Purge Flow	100 mL/min	**Chiller Tray**	Off
Dry Purge Temp	20 ºC	**Purge Gas**	Helium

Sales/Support: 800-874-2004 • **Main**: 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

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 ºC, 2 min, 12 ºC/min to 85 ºC, 20 ºC/min to 225 ºC, 2 min Hold, Run Time 15.167 min
Inlet	200 ºC, 50:1 Split
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 300 ºC; Ion Source 280 ºC
Scan	Range 35 *amu* to 260 *amu*, Solvent Delay 0.10 min, Dwell/Scan Time 0.15 sec
Current	Emission Current 25 µA, Gain 3.00E+005

Results

The relative standard deviation (%RSD) of the RFs for the calibration curve, MDL, and accuracy and precision data are shown in Table III. Figure 1 displays a 50 ppb standard, indicating excellent peak resolution with minimal inference for all VOCs.

Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data

Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb)[1]		
	Ret. Time	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (±20%)	Precision (≤20%)
Dichlorodifluoromethane	1.38	7.56	0.09	0.310	0.49	97	6.56
Chloromethane	1.55	12.4	0.10	0.490	0.49	99	7.28
Vinyl Chloride	1.63	3.34	0.09	0.260	0.51	102	6.36
Bromomethane	1.90	19.0	0.09	0.681	0.48	95	7.02
Chloroethane	2.02	10.4	0.05	0.348	0.49	97	3.40
Trichlorofluoromethane	2.15	6.65	0.03	0.769	0.46	93	2.22
Diethyl Ether	2.49	4.25	0.08	0.418	0.49	98	6.03
1,1-Dichloroethene	2.61	6.04	0.09	0.417	0.52	103	6.03
Iodomethane[2]	2.72	0.998	0.06	0.329	0.59	118	3.34
Allyl Chloride	3.03	4.61	0.12	1.03	0.48	96	9.08
Methylene Chloride	3.12	7.63	0.07	0.997	0.53	105	4.68
cis-1,2-Dichloroethene	3.26	4.18	0.11	0.730	0.59	119	6.78
Acetone[2]	3.26	0.996	0.10	0.168	0.58	116	6.44
1,1-Dichloro-2-propanone[2]	3.26	0.998	0.12	0.974	0.52	103	7.94
Methyl-t-Butyl Ether	3.45	3.14	0.07	1.54	0.51	102	5.17
Acrylonitrile	3.78	4.06	0.07	0.954	0.50	100	4.61
1,1-Dichloroethane	3.86	5.99	0.09	0.229	0.52	105	6.02
Propionitrile	3.86	5.99	0.09	0.229	0.52	105	6.02
trans-1,2-Dichloroethene	4.23	3.49	0.10	0.792	0.51	103	6.64
2,2-Dichloropropane	4.30	8.14	0.06	0.660	0.45	90	4.87
Bromochloromethane	4.36	10.2	0.05	0.245	0.52	103	3.76
Chloroform	4.42	4.78	0.07	0.913	0.53	106	4.36
Carbon Tetrachloride	4.51	15.9	0.10	0.508	0.47	94	7.57

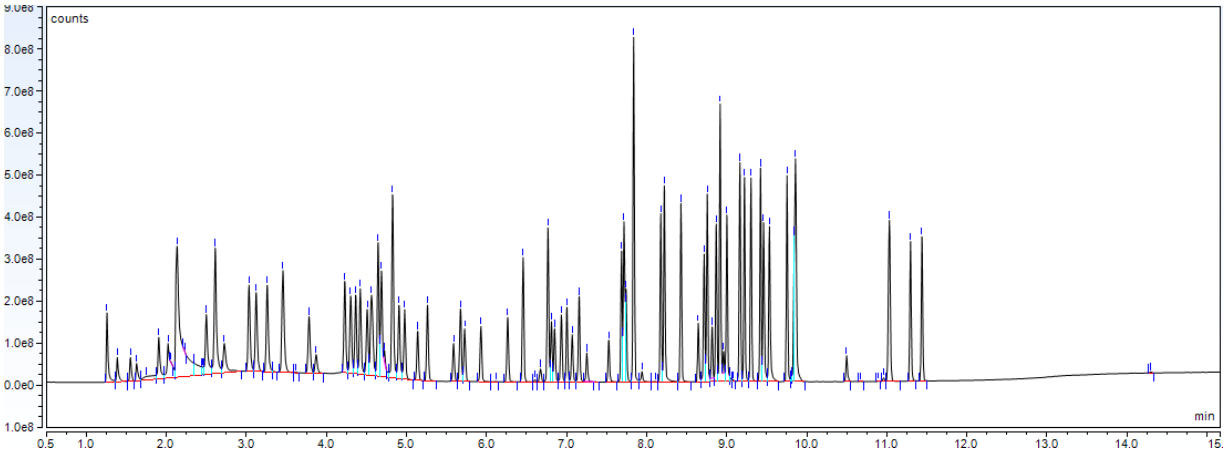
Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data							
Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb)[1]		
	Ret. Time	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (±20%)	Precision (≤20%)
1,1,1-Trichloroethane	4.56	5.62	0.07	0.673	0.48	96	4.87
Methyl Acrylate	4.58	13.4	0.08	0.423	0.45	91	6.31
1,1-Dichloropropene	4.64	4.83	0.11	0.710	0.50	99	7.69
1-Chlorobutane	4.68	17.1	0.05	0.987	0.46	93	3.78
Tetrahydrofuran	4.68	9.30	0.12	0.191	0.51	101	8.47
2-Butanone	4.72	7.12	0.12	0.081	0.57	114	7.44
Benzene	4.82	16.1	0.19	2.46	0.54	108	12.8
Methacrylonitrile	4.90	16.9	0.09	0.982	0.53	106	6.23
1,2-Dichloroethane	4.97	4.69	0.06	0.687	0.51	103	4.10
Fluorobenzene (IS)	5.14						
Trichloroethylene	5.26	14.2	0.09	0.379	0.54	109	5.67
Dibromomethane	5.59	6.92	0.09	0.203	0.47	94	6.84
1,2-Dichloropropane	5.67	3.60	0.07	0.314	0.48	96	5.55
Bromodichloromethane	5.72	19.5	0.11	0.34	0.46	91	8.59
Methyl Methacrylate	5.93	8.29	0.04	0.435	0.46	91	2.89
cis-1,3-Dichloropropene	6.26	8.87	0.09	0.337	0.47	93	7.04
Toluene	6.46	5.50	0.08	1.10	0.48	96	6.16
Chloroacetonitrile	6.61	17.0	0.18	0.006	0.50	101	12.7
2-Nitropropane	6.67	10.6	0.14	0.137	0.51	102	9.43
Tetrachloroethene	6.67	7.50	0.11	0.621	0.55	110	7.06
trans-1,3-Dichloropropene	6.77	14.5	0.09	0.274	0.47	94	6.42
4-Methyl-2-pentanone	6.85	14.8	0.09	0.575	0.47	94	6.86
1,1,2-Trichloroethane	6.93	5.77	0.07	0.226	0.47	94	4.90
Ethyl Methacrylate	7.00	7.96	0.10	0.335	0.47	94	7.34
Dibromochloromethane	7.07	15.8	0.10	0.238	0.45	90	7.51
1,3-Dichloropropane	7.16	4.41	0.08	0.443	048	96	6.06
1,2-Dibromoethane	7.25	5.32	0.09	0.263	0.49	97	6.8
2-Hexanone	7.53	9.83	0.13	0.388	0.49	98	9.37
Chlorobenzene	7.69	4.29	0.13	0.689	0.51	101	9.07
Ethylbenzene	7.72	5.86	0.09	1.21	0.46	92	6.75
1,1,1,2-Tetrachloroethane	7.74	6.82	0.05	0.232	0.46	91	4.12
m- , p-Xylene	7.84	7.95	0.24	0.458	0.90	90	9.63
o-Xylene	8.18	5.71	0.07	0.449	0.47	95	4.95
Bromoform	8.22	16.4	0.13	0.207	0.50	100	9.38
Styrene	8.22	7.74	0.11	0.678	0.46	92	8.66
Isopropylbenzene	8.43	6.21	0.09	1.15	0.46	93	6.99
4-Bromofluorobenzene (SURR)	8.64	3.02		0.453	24	97	3.45
Bromobenzene	8.72	7.39	0.15	0.670	0.51	102	10.4
n-Propylbenzene	8.76	5.88	0.14	1.54	0.48	96	10.4
1,1,2,2-Tetrachloroethane	8.82	17.5	0.10	0.215	0.42	84	8.32
2-Chlorotoluene	8.87	4.89	0.12	0.944	0.49	98	8.79
1,2,3-Trichloropropane	8.92	3.55	0.08	0.354	0.50	100	5.92

Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data

Compound	Calibration				Accuracy and Precision (n=10, 0.5 ppb)[1]		
	Ret. Time	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Concentration (ppb)	Accuracy (±20%)	Precision (≤20%)
1,3,5-Trimethylbenzene	8.92	7.68	0.10	1.14	0.47	95	7.31
trans-1,4-Dichloro-2-butene	8.96	15.6	0.08	0.074	0.42	83	7.12
4-Chlorotoluene	9.00	5.22	0.12	1.04	0.50	100	8.76
tert-Butylbenzene	9.16	7.33	0.07	0.941	0.44	88	5.87
1,2,4-Trimethylbenzene	9.22	7.99	0.10	1.16	0.46	92	7.87
sec-Butylbenzene	9.30	7.26	0.14	1.39	0.49	97	10.0
p-Isopropyltoluene	9.42	7.59	0.09	1.08	0.46	91	6.78
1,3-Dichlorobenzene	9.46	5.95	0.14	0.782	0.53	107	9.12
1,4-Dichlorobenzene	9.53	8.54	0.08	0.826	0.53	106	5.59
n-Butylbenzene	9.75	7.06	0.12	1.24	0.50	99	8.55
Pentachloroethane	9.84	7.08	0.16	0.004	0.50	101	10.9
Hexachloroethane	9.84	12.3	0.10	0.155	0.44	89	7.76
1,2-Dichlorobenzene-d4 (SURR)	9.85	4.27		0.501	25	100	2.70
1,2-Dichlorobenzene	9.86	5.61	0.11	0.813	0.54	108	7.29
1,2-Dibromo-3-Chloropropane	10.50	7.43	0.13	0.089	0.49	98	9.36
Hexachlorobutadiene	10.90	11.1	0.15	0.000	0.52	105	10.5
Nitrobenzene	10.96	13.7	0.16	0.009	0.50	99	11.5
1,2,4-Trichlorobenzene	11.03	7.46	0.15	0.550	0.56	112	9.21
Naphthalene	11.30	6.35	0.11	1.19	0.51	102	7.50
1,2,3-Trichlorobenzene	11.44	6.47	0.12	0.552	0.56	111	7.83

1. Data from ten 0.5 ppb samples.
2. Compounds were linear regressed.

Figure 1 Total Ion Chromatogram of a Water Method 50 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 water samples following US EPA Method 524.2 with detection by a Thermo Scientific TRACE 1310 GC/ISQ 7000 MS with an AEI source. The %RSD of the calibration curve passed all method requirements. Furthermore, MDL, precision and accuracy for ten 0.5 ppb standards 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. Munch, J.W., US EPA Method 524.2 - Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1, 1995