

US EPA Method 524.2 using the Teledyne Tekmar Atomx XYZ and Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) System Coupled with a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC)

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Page | 1

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 four-minute desorb time recommendation. The Teledyne Tekmar Atomx XYZ purge and trap (P&T) VOC sample preparation system combined with a Thermo Scientific ISQ 7000 Mass Spectrometry (MS) system and coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph (GC) 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 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 25 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 80 compounds.

The calibration curves were 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.

Seven 0.5 ppb standards were prepared to calculate the MDL and precision for all compounds. Also, seven 5 ppb standards were prepared to calculate accuracy and precision for all compounds. All calibration, MDL, accuracy and precision 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	4.00 min
Condensate Ready Temp	45 °C	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	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 °C	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	280 °C
Purge Flow	40 mL/min	Condensate Bake Temp	180 °C
Purge Temp	20 °C		
Condensate Purge Temp	20 °C		
Dry Purge Time	1.00 min	Trap	K
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

Table II Thermo Scientific TRACE 1310 GC and ISQ 7000 MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	TG VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 1 mL/min
Oven Profile	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min Hold, Run Time 14.767 min
Inlet	200 °C, 50:1 Split
Thermo Scientific ISQ 7000 MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 280 °C
Scan	Range 35 <i>amu</i> to 260 <i>amu</i> , Solvent Delay 0.50 min, Dwell/Scan Time 0.15 sec.
Current	Emission Current 25 µA, Gain 1.00E+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 shows a 5 ppb standard, indicating excellent peak resolution with no water inference for all VOCs.

Table III US EPA Method 524.2 Calibration, Accuracy and Precision Data								
Compound	Calibration			Method Detection Limit (n=7, 0.5 ppb)			Analyte Recovery (n=7, 5 ppb)	
	Retention Time	Linearity RF (%RSD)	Average RF	MDL (ppb)	Average Concentration (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)
Dichlorodifluoromethane	1.31	10.5	0.480	0.146	0.52	8.86	111	7.55
Chloromethane ²	1.48	19.1	1.28	0.167	0.56	9.54	102	4.16
Vinyl Chloride	1.55	9.00	0.675	0.214	0.52	13.0	109	5.71
Bromomethane	1.83	18.2	0.494	0.207	0.68	9.66	107	9.08
Chloroethane	1.94	10.3	0.560	0.128	0.52	7.80	106	4.54
Trichlorofluoromethane	2.07	8.94	0.611	0.191	0.54	11.2	114	6.39
Diethyl Ether	2.40	6.08	0.570	0.075	0.52	4.64	110	2.57
1,1-Dichloroethene	2.57	8.23	0.462	0.158	0.51	9.87	103	6.76
Carbon Disulfide	2.58	9.67	1.99	0.165	0.56	9.44	104	6.05
Iodomethane ^{1,3}	2.71	0.997	0.378	0.052	0.28	5.91	71	19.7
Allyl Chloride	3.09	8.67	0.338	0.153	0.55	8.80	109	5.62
Methylene Chloride	3.22	12.7	1.44	0.166	0.57	9.25	107	4.70
trans-1,2-Dichloroethene	3.40	9.06	0.938	0.154	0.56	8.72	110	4.04
Methyl-t-Butyl Ether	3.57	11.2	0.951	0.075	0.49	4.88	113	1.63
1,1-Dichloroethane	4.08	10.9	1.31	0.177	0.54	10.3	110	5.10
Acrylonitrile	4.15	14.9	0.331	0.172	0.55	10.0	106	3.58
Propionitrile	4.16	14.9	0.331	0.167	0.57	9.25	107	3.58
cis-1,2-Dichloroethene	4.57	10.4	0.991	0.182	0.57	10.2	114	3.81
2,2-Dichloropropane	4.66	7.32	0.633	0.139	0.51	8.76	98	6.71
Bromochloromethane	4.74	18.5	1.09	0.116	0.58	6.39	108	3.74
Chloroform	4.82	10.8	1.03	0.161	0.57	9.07	111	5.26
Carbon Tetrachloride	4.91	12.4	0.374	0.129	0.49	8.41	116	7.32
Methyl Acrylate	4.97	5.09	0.371	0.142	0.50	9.06	107	3.69

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

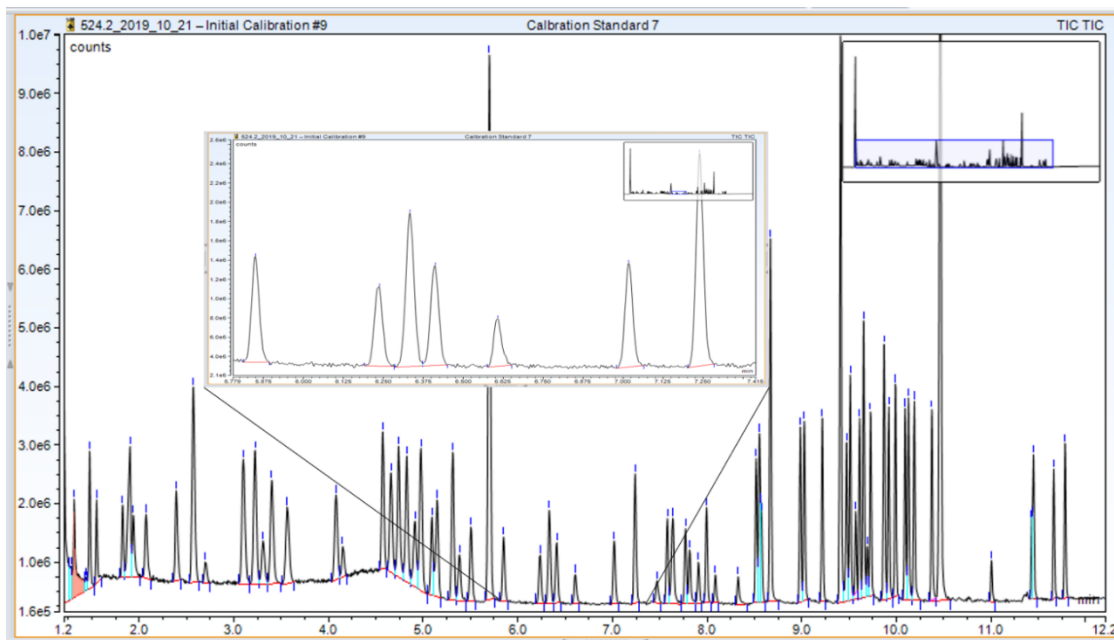
Compound	Calibration			Method Detection Limit (n=7, 0.5 ppb)			Analyte Recovery (n=7, 5 ppb)	
	Retention Time	Linearity RF (%RSD)	Average RF	MDL (ppb)	Average Concentration (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)
1,1,1-Trichloroethane	4.98	7.73	0.569	0.153	0.53	9.14	116	5.69
Tetrahydrofuran ²	4.99	11.3	0.366	0.096	0.62	4.90	111	4.32
1,1-Dichloropropene	5.09	14.1	0.432	0.105	0.44	7.59	98	4.07
2-Butanone	5.12	11.7	0.064	0.263	0.96	8.70	108	5.59
1-Chlorobutane	5.14	13.6	0.691	0.118	0.46	8.24	103	6.14
Benzene	5.31	4.97	1.45	0.092	0.46	6.28	102	4.16
Methacrylonitrile	5.39	10.9	0.160	0.145	0.49	9.52	94	3.47
1,2-Dichloroethane	5.50	7.94	0.643	0.111	0.54	6.57	112	1.50
Fluorobenzene (IS)	5.70							
Trichloroethylene	5.85	6.74	0.288	0.127	0.48	8.37	106	4.92
Dibromomethane	6.23	8.86	0.287	0.091	0.54	5.38	108	3.43
1,2-Dichloropropane	6.33	7.31	0.426	0.056	0.47	3.79	104	1.33
Bromodichloromethane	6.41	6.24	0.483	0.069	0.48	4.59	110	1.63
Methyl Methacrylate	6.62	9.74	0.133	0.153	0.48	10.2	92	2.45
trans-1,3-Dichloropropene	7.01	12.8	0.427	0.043	0.44	3.15	100	1.72
Chloroacetonitrile	7.03	5.98	0.020	0.154	0.48	10.1	103	8.88
Toluene	7.24	8.87	1.11	0.089	0.44	6.40	98	4.65
2-Nitropropane	7.47	7.59	0.307	0.103	0.47	6.96	97	2.76
Tetrachloroethene	7.58	11.9	0.200	0.195	0.52	11.8	111	9.75
4-Methyl-2-pentanone	7.62	7.37	0.394	0.051	0.53	3.09	110	3.69
cis-1,3-Dichloropropene	7.65	14.2	0.365	0.059	0.42	4.47	95	3.71
1,1,2-Trichloroethane	7.78	6.28	0.365	0.083	0.49	5.38	112	2.55
Ethyl Methacrylate	7.82	11.1	0.246	0.041	0.43	3.00	94	3.83
Dibromochloromethane	7.91	6.32	0.274	0.091	0.47	6.19	105	2.45
1,3-Dichloropropane	7.99	6.20	0.210	0.089	0.49	5.78	108	1.70
1,2-Dibromoethane	8.09	9.28	0.493	0.072	0.46	5.02	104	2.78
2-Hexanone	8.32	10.5	0.220	0.124	0.50	7.94	97	3.28
Chlorobenzene	8.52	3.51	0.275	0.113	0.49	7.33	102	2.95
Ethylbenzene	8.55	11.7	0.665	0.059	0.43	4.39	92	4.40
1,1,1,2-Tetrachloroethane	8.57	7.26	1.11	0.122	0.48	8.10	108	2.80
m-,p-Xylene	8.67	16.0	0.164	0.213	0.83	8.16	94	2.92
o-Xylene	8.99	8.21	0.438	0.143	0.44	10.3	92	3.58
Bromoform	9.03	16.5	0.393	0.092	0.43	6.88	99	1.60
Styrene	9.04	10.8	0.673	0.110	0.40	8.73	91	4.40
Isopropylbenzene	9.22	13.6	0.125	0.107	0.41	8.36	95	5.42
4-Bromofluorobenzene (SURRE)	9.41	7.05	0.907		25.0	5.66	97	4.47
Bromobenzene	9.48	6.63	0.412	0.149	0.58	8.21	111	4.07
n-Propylbenzene	9.51	12.0	0.711	0.145	0.46	10.1	102	5.17
1,1,2,2-Tetrachloroethane	9.57	8.42	1.47	0.057	0.48	3.79	102	3.49
2-Chlorotoluene	9.61	5.9	0.447	0.072	0.48	4.85	101	3.35
1,2,3-Trichloropropane	9.65	8.06	0.944	0.082	0.48	5.44	109	4.27
1,2,4-Trimethylbenzene	9.66	19.2	0.369	0.128	0.39	10.5	95	3.40

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	Retention Time	Linearity RF (%RSD)	Average RF	MDL (ppb)	Average Concentration (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)
trans-1,4-Dichloro-2-butene	9.69	8.50	0.921	0.124	0.47	8.44	99	4.94
4-Chlorotoluene	9.73	11.8	0.106	0.105	0.42	7.95	100	3.57
tert-Butylbenzene ²	9.87	10.1	1.01	0.113	0.39	9.15	81	5.13
1,3,5-Trimethylbenzene	9.92	20.0	0.791	0.097	0.37	8.47	95	3.41
sec-Butylbenzene ²	9.99	19.6	0.916	0.095	0.35	8.56	95	5.78
p-Isopropyltoluene	10.09	19.8	1.13	0.106	0.36	9.41	92	4.22
1,3-Dichlorobenzene	10.13	8.00	0.726	0.091	0.47	6.18	111	3.59
1,4-Dichlorobenzene	10.19	8.02	0.629	0.099	0.47	6.70	108	3.49
n-Butylbenzene	10.37	16.6	0.601	0.111	0.43	8.26	97	5.16
Hexachloroethane	10.45	10.8	0.950	0.240	0.50	15.2	104	8.46
1,2-Dichlorobenzene-d4 (SURR)	10.46	6.03	0.371		24.1	5.35	103	3.64
1,2-Dichlorobenzene	10.47	8.38	0.660	0.108	0.49	6.93	106	3.14
1,2-Dibromo-3-Chloropropane	11.01	13.4	0.099	0.146	0.57	8.18	114	5.87
Nitrobenzene ²	11.38	13.7	0.025	0.157	0.45	11.0	110	6.43
Hexachlorobutadiene	11.43	12.4	0.025	0.196	0.62	10.0	120	4.89
1,2,4-Trichlorobenzene	11.45	8.42	0.287	0.167	0.57	9.35	100	2.01
Naphthalene	11.67	5.53	0.797	0.087	0.48	5.76	94	4.30
1,2,3-Trichlorobenzene	11.79	7.52	0.317	0.086	0.48	5.66	93	4.35

1. Compounds were linear regressed.
 2. Calibration curve 0.5 ppb-50 ppb
 3. Compound is a poor purger. Analyte recovery is out of method range.

Figure 1 Total Ion Chromatogram of a Water Method 5 ppb VOC Standard with an Inset Indicating Consistent Peak Shapes and Separation 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 ISQ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph (GC). The %RSD of the calibration curve passed all method requirements. Furthermore, MDL, precision and accuracy for seven 0.5 ppb and 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. 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 March, 26 2020).