US EPA Method 524.2 Using the Teledyne Tekmar Atomx XYZ with Thermo Scientific™ TRACE™ 1610 Gas Chromatograph (GC) and Thermo Scientific™ ISQ™ 7610 MS Mass Spectrometry (MS) System with ExtractaBrite™ Source

APPLICATION NOTE:	AN2205
TECHNOLOGY:	P+T VOC
INDUSTRY:	ENV

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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 TRACE 1610 Gas Chromatograph (GC) and ISQ 7610 Mass Spectrometry (MS) system with an ExtractaBrite Source 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 81 compounds.

The calibration curves were prepared from 0.2 parts per billion (ppb) to 50 ppb for all 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 0.2 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 °C	Methanol Needle Rinse	Off
Transfer Line Temp	140 °C	Water Needle Rinse Volume	7.00 mL
Sample Mount Temp	90 °C	Sweep Needle Time	0.25 min
Water Heater Temp	90 °C	Desorb Preheat Temp	245 °C
Sample Vial Temp	20 °C	GC Start Signal	Begin Desorb
Soil Valve Temp	50 °C	Desorb Time	4.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40 °C	Desorb Temp	250 °C
Purge	Variable	Bake	Off
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	1
Pre-sweep Time	0.25 min	Water Bake Rinses	7.00 mL
Prime Sample Fill Volume	3.00 mL	Water Bake Rinse Volume	0.25 min
Sample Volume	5.00 mL	Bake Rinse Sweep Time	100 mL/min
Sweep Sample Time	0.25 min	Bake Rinse Sweep Flow	0.40 min
Sweep Sample Flow	100 mL/min	Bake Rinse Drain Time	2.00 min
Sparge Vessel Heater	Off	Bake Time	200 mL/min
Purge Time	11.00 min	Bake Flow	260 °C
Purge Flow	40 mL/min	Trap Bake Temp	200 °C
Purge Temp	20 °C	MCS Bake Temp	
Condensate Purge Temp	20 °C		
Dry Purge Time	1.00 min		
Dry Purge Flow	100 mL/min	Trap	9
Dry Purge Temp	20 °C	Chiller Tray	Off
		Purge Gas	Nitrogen

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Table II Thermo Scientific TRACE 1610 GC and ISQ 7610 MS System Conditions	
Thermo Scientific TRACE 1610 GC Conditions	
Column	TG-VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 0.8 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, Purge Flow 0.5 mL/min
Thermo Scientific ISQ 7610 MS Conditions	
Temp	Transfer Line 230 °C; Ion Source 280 °C
Scan	Range 35 *amu* to 260 *amu*, Solvent Delay 0.50 min, Dwell/Scan Time 0.15 sec.
Current	Emission Current 25 µA, Gain 3.00E+005

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 RF (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Dichlorodifluoromethane	1.17	85	8.6	0.335	0.06	8.7	6.2	109
Chloromethane	1.33	50	6.5	0.634	0.04	7.1	5.1	114
Vinyl Chloride	1.41	62	8.0	0.330	0.06	8.2	5.9	115
Bromomethane	1.64	94	11.9	0.279	0.04	5.0	7.9	119
Chloroethane	1.77	64	18.8	0.229	0.04	5.7	4.9	115
Trichlorofluoromethane	1.85	101	7.9	0.443	0.05	7.6	5.5	114
Diethyl Ether	2.17	59	4.5	0.217	0.09	14.4	3.2	119
Carbon Disulfide	2.32	76	11.3	0.369	0.05	6.5	5.3	107
1,1-Dichloroethene	2.34	96	10.1	0.234	0.04	5.9	5.2	105
Iodomethane	2.44	142	9.5	0.386	0.03	8.4	7.3	90
Allyl Chloride	2.79	76	7.0	0.142	0.05	8.4	5.2	109
Methylene Chloride	2.91	84	16.5	0.325	0.05	5.0	4.1	102
Acetone1,2,5	2.99	43	0.998	0.114	0.86	12.5	3.0	130
trans-1,2-Dichloroethene	3.10	96	11.9	0.253	0.05	7.4	5.3	107
Methyl-t-Butyl Ether	3.28	73	5.5	0.678	0.03	4.2	2.6	119
1,1-Dichloroethane	3.79	63	5.9	0.454	0.04	6.2	4.2	115
Acrylonitrile	3.85	52	8.4	0.100	0.05	6.5	3.6	113
cis-1,2-Dichloroethene	4.36	96	7.1	0.299	0.01	2.0	3.9	109
2,2-Dichloropropane	4.46	77	8.3	0.317	0.07	11.1	7.5	82
Bromochloromethane	4.57	128	7.3	0.142	0.02	3.1	3.8	107
Chloroform	4.66	83	8.5	0.470	0.04	5.2	4.2	114
Carbon Tetrachloride	4.74	117	6.4	0.306	0.09	11.6	5.0	116

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

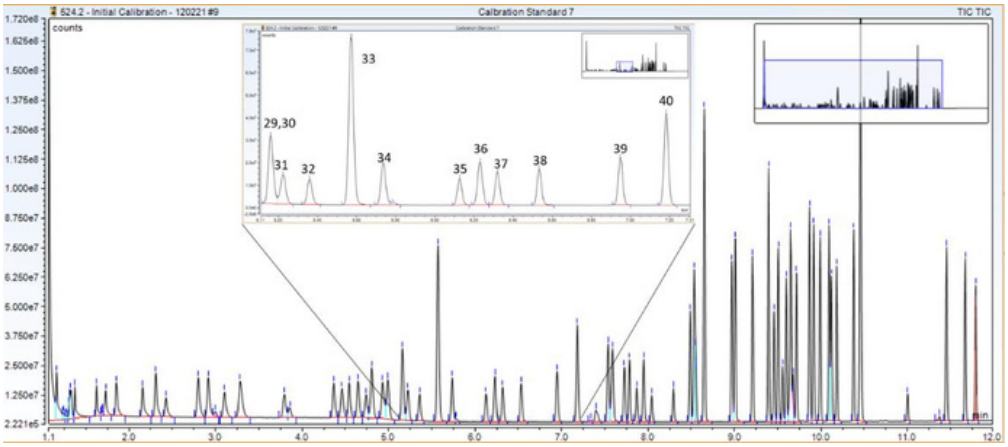
Compound	Calibration				Method Detection Limit (n=7, 0.2 ppb)		Mid-Point Recovery (n=7, 10 ppb)	
	Retention Time	Quant Ion	Linearity RF (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
Tetrahydrofuran[6]	4.79	71	12.9	0.046	0.14	8.5	5.2	112
Methyl Acrylate	4.80	55	5.4	0.204	0.05	7.8	6.8	111
1,1,1-Trichloroethane	4.81	97	7.4	0.350	0.07	10.0	9.2	100
1,1-Dichloropropene	4.95	75	7.3	0.269	0.05	7.5	5.3	111
2-Butanone1,2,5	4.98	43	0.997	0.195	0.57	6.3	6.6	114
1-Chlorobutane	4.99	56	9.0	0.405	0.06	5.2	4.5	113
Benzene	5.15	78	3.1	0.882	0.04	5.9	4.5	104
Propionitrile	5.20	54	7.7	0.045	0.06	7.1	6.3	108
Methacrylonitrile	5.22	67	6.3	0.120	0.02	3.7	3.6	106
1,2-Dichloroethane	5.36	62	4.0	0.288	0.02	3.2	2.9	120
Fluorobenzene (IS)	5.57	96						
Trichloroethylene	5.73	95						
Dibromomethane	6.14	93	5.8	0.247	0.05	6.5	4.8	115
1,2-Dichloropropane	6.25	63	5.1	0.170	0.03	3.9	4.1	106
Bromodichloromethane	6.32	83	3.5	0.255	0.04	6.0	3.5	112
Methyl Methacrylate	6.53	69	3.6	0.330	0.04	6.5	3.2	112
cis-1,3-Dichloropropene	6.95	75	6.9	0.163	0.06	9.6	3.0	108
Toluene	7.19	92	2.7	0.371	0.04	5.9	3.6	106
2-Nitropropane1,7	7.40	46	3.5	0.615	0.03	4.8	4.3	103
1,1-Dichloropropanone[3]	7.41	43	0.997	0.004	0.95	12.7	7.6	103
Tetrachloroethene	7.55	166	11.2	0.090	0.14	8.8	4.8	96
4-Methyl-2-pentanone3	7.58	43	7.2	0.365	0.04	4.8	4.6	130
trans-1,3-Dichloropropene	7.60	75	4.4	0.165	0.12	6.7	3.2	115
1,1,2-Trichloroethane	7.74	83	5.1	0.341	0.04	6.6	2.9	107
Ethyl Methacrylate	7.78	69	3.8	0.212	0.03	5.5	3.3	109
Dibromochloromethane	7.88	129	4.0	0.316	0.02	2.5	2.6	113
1,3-Dichloropropane	7.97	76	6.7	0.217	0.03	5.6	2.7	109
1,2-Dibromoethane	8.05	107	3.5	0.374	0.02	3.5	3.2	112
2-Hexanone3	8.31	43	5.7	0.231	0.04	6.3	3.1	109
Chlorobenzene	8.49	112	10.1	0.133	0.14	8.3	2.7	112
Ethylbenzene	8.54	91	4.1	0.717	0.03	4.9	4.0	102
1,1,1,2-Tetrachloroethane	8.56	131	6.0	1.20	0.03	4.1	4.1	107
m-,p-Xylene	8.66	106	6.7	0.195	0.05	8.4	3.9	110
o-Xylene	8.97	106	5.7	0.511	0.08	6.1	5.4	105
Bromoform	9.01	173	3.9	0.508	0.03	4.4	3.7	102
Styrene	9.02	104	11.8	0.148	0.01	2.5	3.0	116
Isopropylbenzene	9.21	105	6.0	0.870	0.03	4.9	3.9	103
4-Bromofluorobenzene (SURR)	9.40	95	4.1	1.20	0.03	5.2	4.9	105
Bromobenzene	9.46	156	5.4	0.439		3.6	1.1	102
n-Propylbenzene	9.51	91	5.2	0.345		4.6	2.5	105
1,1,2,2-Tetrachloroethane	9.56	83	6.6	1.55	0.03	5.1	4.7	106
2-Chlorotoluene	9.61	91	4.7	0.323	0.03	8.7	4.0	96
1,2,3-Trichloropropane	9.64	75	5.9	0.937	0.05	4.6	4.5	108
			4.9	0.258	0.03	5.0	3.5	112
					0.03			

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 RF (%RSD)	Average RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)
1,3,5-Trimethylbenzene	9.66	105	4.8	1.11	0.03	4.5	5.4	109
trans-1,4-Dichloro-2-butene	9.68	53	3.7	0.113	0.06	8.9	4.1	112
4-Chlorotoluene	9.72	91	7.3	1.01	0.04	5.3	3.8	107
tert-Butylbenzene	9.87	119	4.5	0.990	0.03	5.7	5.2	99
1,2,4-Trimethylbenzene	9.92	105	4.8	1.14	0.03	4.6	4.9	109
sec-Butylbenzene	9.99	105	6.5	1.35	0.04	6.0	5.5	107
p-Isopropyltoluene	10.10	119	5.5	1.11	0.04	7.4	5.6	107
1,3-Dichlorobenzene	10.12	146	7.7	0.701	0.04	6.2	4.5	104
1,4-Dichlorobenzene	10.18	146	10.6	0.725	0.05	7.5	4.9	102
n-Butylbenzene	10.38	91	8.3	1.15	0.05	7.1	6.3	105
Hexachloroethane1,4,7	10.45	117	0.999	2.65	1.06	13.7	7.6	108
1,2-Dichlorobenzene-d4 (SURR)	10.46	152	6.5	0.463		3.8	3.9	104
1,2-Dichlorobenzene	10.47	146	9.2	0.723		3.5	4.2	104
1,2-Dibromo-3-Chloropropane	11.01	75	9.0	0.063	0.02	6.2	4.0	115
Nitrobenzene1,4,8	11.37	51	0.998	0.027	0.04	10.2	3.6	107
Hexachlorobutadiene	11.45	225	7.8	0.113	0.31	6.3	4.4	115
1,2,4-Trichlorobenzene	11.46	180	12.1	0.501	0.04	7.3	5.0	105
Naphthalene	11.67	128	6.5	1.34	0.05	4.6	5.0	104
1,2,3-Trichlorobenzene	11.79	180	7.3	0.494	0.03	6.0	4.9	107
					0.04			

1. Compound used a linear regression calibration
2. Calibration range 2.5-125 ppb Calibration
3. range 0.5-125 ppb Calibration range 0.5-50
4. ppb MDL calculated using n=7, 2.5 ppb
5. MDL calculated using n=7, 0.5 ppb
6. MDL calculated using n=7, 2 ppb
7. MDL calculated using n=7, 1 ppb
8.

Figure 1 Total Ion Chromatogram of a US EPA 524.2 Method 10 ppb VOC Standard with an Inset Indicating Consistent Peak Shapes and Separation for all Compounds with Minimal Water Interference. 29) Benzene, 30) Propionitrile, 31) Methacrylonitrile, 32) 1,2-Dichloroethane, 33) Fluorobenzene (IS), 34) Trichloroethylene, 35) Dibromomethane, 36) 1,2-Dichloropropane, 37) Bromodichloromethane, 38) Methyl Methacrylate, 39) cis-1,3-Dichloropropene and 40) Toluene.



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 1610 Gas Chromatograph (GC) and ISQ 7610 Mass Spectrometry (MS) system. The %RSD of the calibration curve passed all method requirements. Furthermore, the average MDL for all compounds was 0.09 ppb with a 6.5% RSD. Seven 10 ppb mid-point calibration check standards averaged a 109% recovery with a 4.5% 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 12, 2022).

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