APPLICATION NOTE: AN2301
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

US EPA Method 524.4 with the Tekmar Atomx XYZ and the Thermo Scientific™ TRACE™ 1610 GC and ISQ™ 7610 MS System with an HeSaver-H_2Safer™ SSL Injector and an ExtractaBrite Source

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Abstract

As helium supplies become scarcer and more expensive, customers have been seeking alternative carrier gases or ways conserve helium without sacrificing system performance. This application note will evaluate the Teledyne Tekmar Atomx XYZ Purge and Trap (P&T) system in conjunction with a Thermo Scientific TRACE 1610 Gas Chromatograph (GC) equipped with the HeSaver-H_2Safer™ SSL injector and the ISQ 7610 Mass Spectrometer (MS) with an ExtractaBrite source performing US EPA Method 524.4 to determine the concentration of Volatile Organic Compounds (VOCs) in drinking water matrices. Using nitrogen as the purge gas, along with the HeSaver-H_2Safer™ SSL injector, significantly reduces helium gas consumption during analysis. The method was validated by a working linear (r^2) calibration curve, method detection limits (MDL), a mid-point calibration check with accuracy and precision, and Minimum Reporting Level (MRL) confirmation 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 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: 524.3 VOA Mega Mix and 524.3 Gas Calibration Mix. In total, the standard contained 75 compounds.

A nine-point linear (r^2) calibration curve was prepared from 0.2 ppb to 50 parts per billion (ppb) for all compounds with regression value $r^2 \geq 0.995$. The Relative Response Factor (RRF) 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 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 seven 1 ppb standards were prepared to calculate MRL confirmation. Also, ten 10 ppb standards were prepared for the accuracy and precision calculations of the mid-point calibration check. All calibration, MDL, MRL, 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	140ºC	Methanol Needle Rinse	Off
Transfer Line Temp	140ºC	Water Needle Rinse Volume	7.00 mL
Sample Mount Temp	90ºC	Sweep Needle Time	0.25 min
Water Heater Temp	90ºC	Desorb Preheat Temp	245ºC
Sample Vial Temp	20ºC	GC Start Signal	Begin Desorb
Soil Valve Temp	50ºC	Desorb Time	1.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40ºC	Desorb Temp	250ºC
Purge	**Variable**	**Bake**	**Variable**
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Water Bake Rinses	1
Prime Sample Fill Volume	3.00 mL	Water Bake Rinse Volume	7.00 mL
Sample Volume	5.00 mL	Bake Rinse Sweep Time	0.25 min
Sweep Sample Time	0.25 min	Bake Rinse Sweep Flow	100 mL/min
Sweep Sample Flow	100 mL/min	Bake Rinse Drain Time	0.40 min
Sparge Vessel Heater	Off	Bake Time	2.00 min
Purge Time	8.00 min	Bake Flow	200 mL/min
Purge Flow	55 mL/min	Bake Temp	270ºC
Purge Temp	20ºC	MCS Bake Temp	200ºC
MCS Purge Temp	20ºC		
Dry Purge Time	0.5 min	**Trap**	9
Dry Purge Flow	100 mL/min	**Chiller Tray**	On
Dry Purge Temp	20ºC	**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	
Column	TG VMS, 20m x 0.18 mm, 1µm Film
Oven Profile	35 ºC, 4 min, 12ºC/min to 85 ºC, 25ºC/min to 225 ºC, 2 min Hold, Run Time 15.767 min
Inlet	200 ºC, 50:1 Split, purge flow 5.0 mL/min, 0.4 min Helium Delay
Pressurizing Gas	Nitrogen
Carrier Gas	Helium – 0.3 mL/min
ISQ 7610 MS System Conditions	
Temp	Transfer Line 230ºC; Ion Source 280ºC
Scan	Range 35 amu to 260 amu, Solvent Delay 1.55 min, Dwell/Scan Time 0.10 sec.
Current	Emission Current 25 µA, Gain 3.00E+005

Results

The linear correlation coefficient of the calibration curve (r^2), MDL, mid-point calibration check, and MRL confirmation data are shown in Table III. Figure 1 displays a 10 ppb standard, indicating excellent peak resolution with minimal water interference for all VOCs.

Table III Method 524.4 Calibration, Method Detection Limit, Mid-Point Check, and Minimum Reporting Level Data

Compound	Calibration (0.2-50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=10, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
Dichlorodifluoromethane	1.77	85	0.998	0.600	0.13	8.05	8.52	97	66	123
Chlorodifluoromethane	1.80	51	0.997	1.45	0.09	5.17	9.25	113	96	128
Chloromethane	1.97	50	0.997	1.37	0.07	3.83	9.01	111	88	129
Vinyl Chloride	2.05	62	0.999	0.777	0.05	2.83	9.31	112	82	133
1,3-Butadiene	2.07	39	0.998	1.04	0.16	9.27	9.62	111	78	142
Bromomethane	2.40	94	0.996	0.557	0.09	5.97	7.41	107	77	127
Trichlorofluoromethane	2.73	101	0.999	0.750	0.11	7.01	8.75	106	85	122
Diethyl Ether	3.14	59	1.000	0.326	0.12	8.20	3.14	104	76	122
1,1-Dichloroethene	3.37	96	0.999	0.186	0.15	9.84	8.70	107	81	133
Carbon Disulfide	3.39	76	0.998	0.172	0.14	9.92	9.16	101	91	102
Iodomethane[1]	3.55	142	0.995	0.244	0.07	3.28	6.96	81	82	116
Allyl Chloride	4.06	76	0.999	0.183	0.16	10.3	7.24	103	92	123

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Table III Method 524.4 Calibration, Method Detection Limit, Mid-Point Check, and Minimum Reporting Level Data

Compound	Calibration (0.2-50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=10, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
Methylene Chloride	4.23	49	0.997	0.952	0.12	8.35	5.71	110	87	114
trans-1,2-Dichloroethene	4.47	61	0.999	0.408	0.12	7.58	7.21	108	78	128
Methyl Acetate	4.55	43	0.998	0.582	0.16	9.38	3.97	105	78	136
Methyl-tert-Butyl Ether-d3 (SURR)	4.64	76	2.11	1.20		4.33	2.15	100	97	105
Methyl-tert-Butyl Ether	4.67	73	1.000	1.32	0.09	5.75	4.02	99	88	117
tert-Butyl Alcohol	5.24	59	1.000	0.158	0.12	8.13	4.10	103	88	127
Diisopropyl Ether	5.25	45	1.000	1.98	0.09	5.98	4.98	99	88	117
1,1-Dichloroethane	5.33	63	0.999	0.871	0.11	6.68	6.75	111	92	124
tert-Butyl Ethyl Ether	5.72	59	1.000	1.32	0.06	3.86	4.72	96	86	111
cis-1,2-Dichloroethene	6.03	96	1.000	0.432	0.09	5.54	6.11	105	87	120
Bromochloromethane	6.25	128	0.999	0.207	0.12	7.60	5.38	108	82	119
Chloroform	6.38	83	0.999	0.905	0.10	6.46	5.54	110	91	121
Carbon Tetrachloride	6.53	117	0.999	0.404	0.08	5.79	7.22	107	73	119
1,1,1-Trichloroehane	6.60	97	0.999	0.546	0.27	17.6	8.18	107	95	112
Tetrahydrofuran	6.61	72	0.998	0.072	0.09	5.52	4.98	105	66	147
1,1-Dichloropropene	6.76	75	1.000	0.388	0.09	6.00	7.66	96	79	107
1-Chlorobutane	6.82	56	1.000	0.648	0.06	4.25	7.91	99	90	102
Benzene	7.04	78	1.000	1.41	0.06	3.91	5.99	99	85	113
tert-Amyl Methyl Ether	7.23	73	1.000	1.15	0.04	2.68	5.11	96	87	112
1,2-Dichloroethane	7.27	62	0.999	0.725	0.07	4.52	3.88	109	88	123
Trichloroethylene	7.73	95	0.997	0.429	0.22	14.0	6.00	116	71	147
1,4-Difluorobenzene (IS)	7.77	114								
tert-Amyl Ethyl Ether	8.05	59	1.000	1.07	0.06	4.14	4.98	101	92	112
Dibromomethane	8.18	93	0.999	0.317	0.11	7.39	4.61	107	82	121
1,2-Dichloropropane	8.29	63	1.000	0.552	0.08	5.45	5.13	102	83	116
Bromodichloromethane	8.38	83	0.999	0.722	0.05	3.00	4.92	107	79	121
cis-1,3-Dichloropropene	9.00	75	1.000	0.754	0.07	5.25	4.79	94	83	98

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Compound	Calibration (0.2-50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=10, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
Toluene	9.22	91	1.000	1.638	0.24	12.5	5.97	100	104	141
Tetrachloroethylene	9.55	164	0.997	0.613	0.08	4.11	5.80	119	112	143
trans-1,3-Dichloropropene	9.57	75	0.999	0.690	0.10	8.23	4.05	90	69	109
1,1,2-Trichloroethane	9.70	83	1.000	0.388	0.08	5.44	4.20	97	93	116
Ethyl Methacrylate	9.72	69	1.000	0.624	0.12	8.48	4.07	96	85	116
Dibromochloromethane	9.85	129	0.999	0.404	0.06	4.63	4.28	93	66	111
1,3-Dichloropropane	9.92	76	0.999	0.816	0.05	3.87	3.38	96	86	106
1,2-Dibromoethane	10.03	107	1.000	0.400	0.11	7.71	4.69	94	80	104
Chlorobenzene-d5 (IS)	10.43	117								
Chlorobenzene	10.44	112	1.000	1.14	0.07	4.75	5.17	99	84	119
Ethylbenzene	10.47	91	1.000	1.86	0.06	3.78	5.97	95	82	111
1,1,1,2-Tetrachloroethane	10.49	131	0.999	0.361	0.07	5.06	5.08	95	83	101
m,p-Xylene	10.58	91	1.000	1.55	0.13	4.99	5.91	92	74	102
o-Xylene	10.89	91	1.000	1.65	0.06	4.09	5.74	93	74	105
Styrene	10.93	104	0.999	1.17	0.04	3.18	5.73	89	70	96
Bromoform	10.94	173	0.999	0.310	0.05	4.18	5.64	96	81	100
Isopropylbenzene	11.12	105	1.000	1.76	0.04	2.89	7.28	93	74	98
4-Bromofluorobenzene (SURR)	11.31	95	3.57	0.904		2.80	2.08	97	93	108
Bromobenzene	11.39	77	1.000	1.77	0.06	3.59	5.31	104	91	126
n-Propylbenzene	11.41	91	1.000	3.41	0.06	3.88	7.35	97	84	114
1,1,2,2-Tetrachloroethane	11.45	83	0.998	0.716	0.09	6.80	5.16	91	70	107
2-Chlorotoluene	11.52	91	1.000	2.53	0.07	4.65	6.75	99	81	121
1,3,5-Trimethylbenzene	11.54	105	1.000	2.37	0.07	4.78	6.82	92	76	98
1,2,3-Trichloropropane	11.54	75	1.000	0.982	0.10	5.93	5.11	106	99	137
4-Chlorotoluene	11.63	91	1.000	2.39	0.04	2.75	6.80	98	80	113
tert-Butylbenzene	11.76	119	0.999	2.13	0.10	7.13	7.41	91	75	98
Pentachloroethane	11.76	167	1.000	0.294	0.14	8.44	8.09	99	68	131

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Table III Method 524.4 Calibration, Method Detection Limit, Mid-Point Check, and Minimum Reporting Level Data

Compound	Calibration (0.2-50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=10, 10 ppb)		Minimum Reporting Level (n=7, 1 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
1,2,4-Trimethylbenzene	11.81	105	0.999	2.46	0.05	3.62	5.67	92	72	99
sec-Butylbenzene	11.89	105	1.000	2.83	0.06	3.99	7.29	96	68	105
p-Isopropyltoluene	11.98	119	0.999	2.20	0.06	4.39	7.24	91	65	97
1,3-Dichlorobenzene	12.04	146	1.000	1.81	0.08	4.75	5.50	103	86	118
1,4-Dichlorobenzene-d4 (IS)	12.08	152								
1,4-Dichlorobenzene	12.09	146	1.000	1.80	0.10	6.07	5.46	102	82	124
n-Butylbenzene	12.26	91	0.998	2.25	0.08	5.42	7.38	90	69	102
Hexachloroethane	12.37	201	0.999	0.260	0.09	7.80	7.75	98	77	94
1,2-Dichlorobenzene-d4 (SURR)	12.37	152	1.29	0.976		1.77	2.22	100	90	112
1,2-Dichlorobenzene	12.38	146	0.999	1.79	0.04	2.33	5.94	106	80	135
1,2-Dibromo-3-Chloropropane	12.91	75	1.000	0.213	0.12	7.67	6.12	105	65	138
Hexachlorobutadiene	13.34	225	1.000	0.038	0.17	10.1	9.39	109	82	149
1,2,4-Trichlorobenzene	13.37	180	1.000	0.959	0.11	6.25	5.81	104	77	133
Naphthalene	13.59	128	0.999	2.14	0.07	4.52	4.73	94	77	119
1,2,3-Trichlorobenzene	13.71	180	1.000	0.813	0.12	7.54	5.84	104	78	123

1. Calibration range from 0.5-50 ppb.

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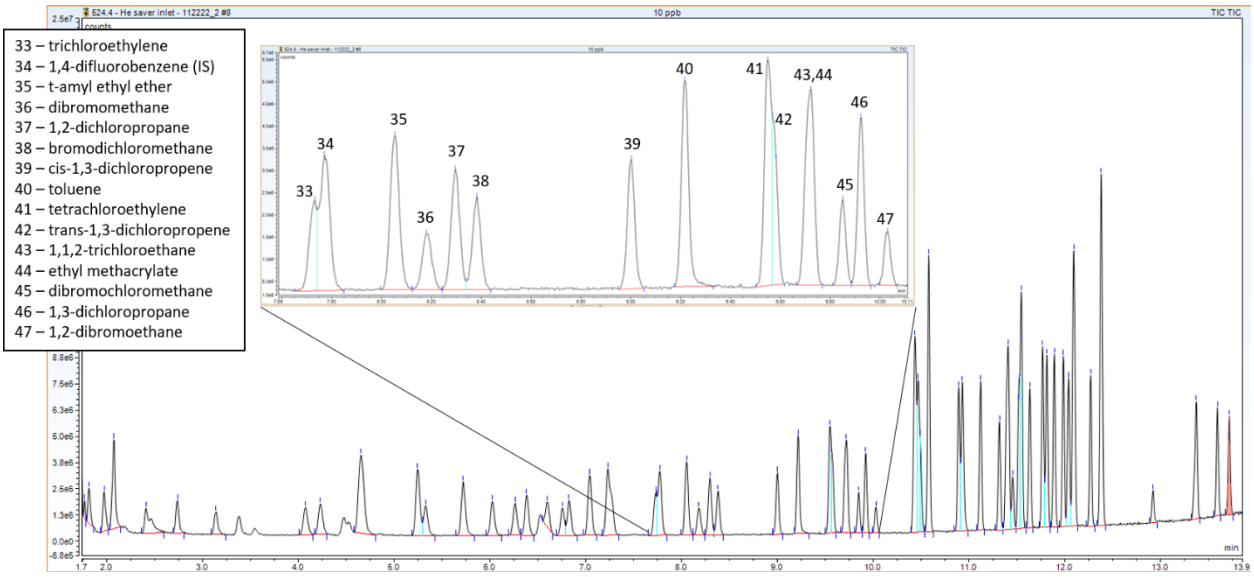

Figure 1 Total ion chromatogram (TIC) of a US EPA 524.4 water method 10 ppb VOC standard with an inset indicating consistent peak shapes and separation with minimal water interference.

Conclusion

This study demonstrates the capability of the Teledyne Tekmar Atomx XYZ P&T system to process VOCs in drinking water samples following the US EPA Method 524.4 with detection by a Thermo Scientific TRACE 1610 GC/ISQ 7610 MS with limited consumption of helium gas while maintaining the performance of the systems. The linearity of the calibration curve from 0.2 ppb to 50 ppb passed all method requirements with no interference from excessive water. Calibration standards met the required ±50% of the true value for first calibration standard and ±30% of the true value for the rest of the calibration standards. The MDL for seven 0.5 ppb standards, MRL confirmation for seven 1 ppb standards, and mid-point calibration checks for ten 10 ppb standards showed no interference from excessive water and displayed very reproducible results. Furthermore, the average MDL for all compounds was 0.09 ppb with a 6.0% RSD. The MRL passed all method requirements of the lower Prediction Interval of Results (PIR) ≥50% and the upper PIR ≤150%. The ten 10 ppb mid-point calibration check standards averaged a 101% recovery with a 6.0% RSD.

Furthermore, the Atomx XYZ and GC-MS conditions displayed in Tables I & 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, D.J..; Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry; US EPA Method 524.3 – Revision 1.0, June 2009.
2. Munch, D.J. and Wendelken, S.C.; Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas; US EPA Method 524.4 – May 2013.

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