APPLICATION NOTE: AN2209
TECHNOLOGY: P+T VOC
INDUSTRY: ENV

US EPA Method 524.4 Using the Tekmar Atomx XYZ with Thermo Scientific™ TRACE™ 1610 Gas Chromatograph (GC) and ISQ™ 7610 Mass Spectrometry (MS) System with ExtractaBrite™ Source

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Abstract

US EPA Method 524.4 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 1610 Gas Chromatograph (GC)/ISQ 7610 Mass Spectrometer (MS) with an ExtractaBrite source was used to create 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 standards 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) ≥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 20 ppm, after which 5 µL was then mixed with each 5 mL sample for a resulting concentration of 20 ppb.

Seven 0.5 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Also, seven 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	140 ºC	Methanol Needle Rinse	Off
Transfer Line Temp	140 ºC	Water Needle Rinse Volume	7.00 mL
Sample Mount Temp	90 ºC	Sweep Needle Time	0.25 min
Water Heater Temp	90 ºC	Desorb Preheat Temp	245 ºC
Sample Vial Temp	20 ºC	GC Start Signal	Begin Desorb
Soil Valve Temp	50 ºC	Desorb Time	2.00 min
Standby Flow	10 mL/min	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	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	260 ºC
Purge Temp	20 ºC	MCS Bake Temp	200 ºC
MCS Purge Temp	20 ºC		
Dry Purge Time	0.5 min	**Trap**	9
Dry Purge Flow	100 mL/min	**Chiller Tray**	On
Dry Purge Temp	20 ºC	**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, 20m x 0.18 mm, 1µm Film, Helium – 0.8 mL/min
Oven Profile	35 ºC, 3 min, 12ºC/min to 85 ºC, 25 ºC/min to 225 ºC, 2 min Hold, Run Time 14.767 min
Inlet	200 ºC, 50:1 Split, purge flow 0.5 mL/min
ISQ 7610 MS Conditions	
Temp	Transfer Line 230 ºC; Ion Source 280 ºC
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 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 ppb – 50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 0.5 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	1.18	85	1.000	0.468	0.17	11.5	5.6	97	52	139
Chlorodifluoromethane	1.21	51	1.000	1.05	0.13	8.7	4.9	99	62	127
Chloromethane	1.34	50	1.000	0.961	0.15	9.7	3.2	102	63	140
Vinyl Chloride	1.40	62	1.000	0.400	0.14	9.0	4.6	98	61	130
1,3-Butadiene	1.42	39	1.000	0.848	0.10	5.9	8.8	99	83	133
Bromomethane[1]	1.66	94	0.999	0.396	0.17	11.5	3.3	108	51	138
Trichlorofluoromethane	1.89	101	1.000	0.666	0.14	9.9	5.3	95	55	125
Diethyl Ether	2.19	59	1.000	0.383	0.06	3.7	2.3	97	81	109
Carbon Disulfide	2.33	76	1.000	0.951	0.11	6.5	4.7	96	77	132
1,1-Dichloroethene	2.33	96	1.000	0.458	0.13	8.1	4.4	97	67	131
Iodomethane[1]	2.44	142	0.997	0.558	0.07	3.7	2.8	88	99	133
Allyl Chloride	2.76	76	1.000	0.273	0.12	8.3	3.3	97	63	125
Methylene Chloride	2.87	49	1.000	1.32	0.11	6.5	1.5	103	78	133

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Compound	Calibration (0.2 ppb – 50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 0.5 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
trans-1,2-Dichloroethene	3.04	61	1.000	0.593	0.10	6.7	3.2	100	72	124
Methyl Acetate	3.10	43	1.000	0.774	0.10	6.8	2.4	93	71	122
Methyl-tert-Butyl Ether-d3 (SURR)	3.20	76	1.7	1.00		1.7	0.7	99	90	103
Methyl-tert-Butyl Ether	3.21	73	0.999	1.13	0.04	3.0	2.3	94	80	102
tert-Butyl Alcohol	3.39	59	1.000	0.038	0.17	10.0	3.2	90	65	149
Diisopropyl Ether	3.65	45	1.000	2.58	0.04	2.6	2.6	94	77	95
1,1-Dichloroethane	3.67	63	1.000	0.764	0.11	7.3	2.3	99	70	126
tert-Butyl Ethyl Ether	4.04	59	0.999	1.13	0.04	3.4	2.5	91	70	92
cis-1,2-Dichloroethene	4.24	96	1.000	0.499	0.12	7.6	1.6	95	67	125
Bromochloromethane	4.43	128	1.000	0.207	0.12	7.8	1.8	98	69	130
Chloroform	4.53	83	1.000	0.844	0.13	8.4	2.7	99	65	130
Carbon Tetrachloride	4.64	117	0.999	0.435	0.07	5.9	4.0	91	60	96
Tetrahydrofuran	4.70	72	0.999	0.048	0.09	7.2	2.7	87	54	97
1,1,1-Trichloroehane	4.72	97	1.000	0.612	0.08	5.9	4.1	95	67	108
1,1-Dichloropropene	4.85	75	0.998	0.435	0.09	6.9	4.4	89	57	99
1-Chlorobutane	4.91	56	0.998	0.678	0.07	6.1	5.1	91	58	95
Benzene	5.08	78	0.999	1.45	0.06	4.9	3.3	93	66	98
tert-Amyl Methyl Ether	5.28	73	0.999	0.976	0.03	2.7	2.7	92	73	90
1,2-Dichloroethane	5.30	62	1.000	0.532	0.08	5.3	1.3	96	73	111
Trichloroethylene	5.68	95	1.000	0.535	0.09	6.0	5.1	108	76	123
1,4-Difluorobenzene (IS)	5.73	114								
tert-Amyl Ethyl Ether	6.00	59	1.000	0.941	0.06	4.1	2.5	97	75	104
Dibromomethane	6.08	93	1.000	0.299	0.06	4.1	1.5	98	79	109
1,2-Dichloropropane	6.19	63	0.999	0.434	0.03	2.5	2.2	96	78	95
Bromodichloromethane	6.28	83	1.000	0.584	0.07	5.1	2.6	93	67	101
cis-1,3-Dichloropropene	6.93	75	0.998	0.594	0.05	4.5	1.8	89	62	90
Toluene	7.16	91	0.999	1.68	0.05	3.6	4.2	88	70	93

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Compound	Calibration (0.2 ppb – 50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 0.5 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
Tetrachloroethylene	7.53	164	1.000	0.545	0.09	5.6	3.6	99	80	125
trans-1,3-Dichloropropene	7.58	75	0.995	0.473	0.06	3.8	2.7	87	83	113
1,1,2-Trichloroethane	7.72	83	0.998	0.322	0.07	6.2	2.9	87	58	95
Ethyl Methacrylate	7.78	69	0.999	0.431	0.02	1.9	2.3	88	63	73
Dibromochloromethane	7.86	129	1.000	0.287	0.05	4.5	2.4	94	64	91
1,3-Dichloropropane	7.95	76	0.998	0.557	0.03	2.7	2.5	87	66	81
1,2-Dibromoethane	8.04	107	0.999	0.340	0.06	5.0	2.7	88	60	89
Chlorobenzene-d5 (IS)	8.48	117								
Chlorobenzene	8.49	112	1.000	1.09	0.03	2.4	3.8	92	82	100
Ethylbenzene	8.53	91	0.999	1.92	0.06	4.2	3.4	95	72	101
1,1,1,2-Tetrachloroethane	8.56	131	0.996	0.288	0.05	3.3	3.1	90	84	109
m,p-Xylene	8.66	91	0.999	1.58	0.13	5.1	3.6	97	65	98
o-Xylene	8.98	91	0.999	1.61	0.04	3.0	3.7	91	67	85
Bromoform	9.02	173	1.000	0.187	0.09	7.9	1.7	97	51	97
Styrene	9.02	104	0.999	1.17	0.06	4.6	2.5	92	52	90
Isopropylbenzene	9.22	105	0.999	1.75	0.07	6.4	3.8	92	55	93
4-Bromofluorobenzene (SURR)	9.40	95	1.9	1.08		1.7	1.6	99	94	108
Bromobenzene	9.47	77	1.000	1.29	0.03	2.2	2.2	95	88	105
n-Propylbenzene	9.52	91	1.000	4.01	0.06	4.2	5.1	94	72	100
1,1,2,2-Tetrachloroethane	9.58	83	1.000	0.463	0.10	6.9	4.7	99	64	112
2-Chlorotoluene	9.62	91	1.000	2.42	0.06	4.0	3.4	98	76	105
1,2,3-Trichloropropane	9.66	75	1.000	0.653	0.06	3.7	2.5	100	82	111
1,3,5-Trimethylbenzene	9.66	105	1.000	2.61	0.05	4.2	4.0	96	69	96
4-Chlorotoluene	9.73	91	1.000	2.57	0.07	4.7	4.1	97	73	107
tert-Butylbenzene	9.88	119	0.999	0.027	0.07	5.6	4.4	92	61	95
Pentachloroethane	9.88	167	1.000	2.09	0.14	9.4	13.6	97	59	128
1,2,4-Trimethylbenzene	9.93	105	0.999	2.64	0.07	5.4	3.9	99	64	99

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Compound	Calibration (0.2 ppb – 50 ppb)				Method Detection Limits (n=7, 0.5 ppb)		Mid-Point Check (n=7, 10 ppb)		Minimum Reporting Level (n=7, 0.5 ppb)	
	Ret. Time	Confirm. Ion	Linearity (r^2 ≥0.995)	Avg. RRF	MDL (ppb)	Precision (≤20%)	Precision (≤20%)	Accuracy (±30%)	LPIR (≥50%)	UPIR (≤150%)
sec-Butylbenzene	10.00	105	0.999	3.29	0.07	5.4	4.8	96	63	97
p-Isopropyltoluene	10.10	119	1.000	2.57	0.06	4.7	4.2	93	63	92
1,3-Dichlorobenzene	10.13	146	1.000	1.47	0.05	3.3	2.9	94	78	101
1,4-Dichlorobenzene-d4 (IS)	10.18	152								
1,4-Dichlorobenzene	10.19	146	1.000	1.54	0.08	4.8	2.7	99	82	120
n-Butylbenzene	10.39	91	0.999	2.91	0.07	5.0	4.8	97	68	101
Hexachloroethane	10.46	201	0.996	0.199	0.10	7.2	5.1	100	66	119
1,2-Dichlorobenzene-d4 (SURR)	10.47	152	1.4	0.982		1.5	1.6	100	94	106
1,2-Dichlorobenzene	10.47	146	1.000	1.50	0.04	2.7	1.7	101	89	110
1,2-Dibromo-3-Chloropropane	11.01	75	0.999	0.111	0.06	5.1	2.1	92	63	94
Hexachlorobutadiene	11.46	225	0.996	0.383	0.15	10.0	4.1	98	58	133
1,2,4-Trichlorobenzene	11.46	180	0.999	1.05	0.09	6.1	3.0	91	68	112
Naphthalene	11.68	128	0.999	2.62	0.05	4.3	2.4	87	62	87
1,2,3-Trichlorobenzene	11.80	180	0.998	1.04	0.07	4.7	3.4	91	72	105

1. Calibration range from 0.5 - 50 ppb.

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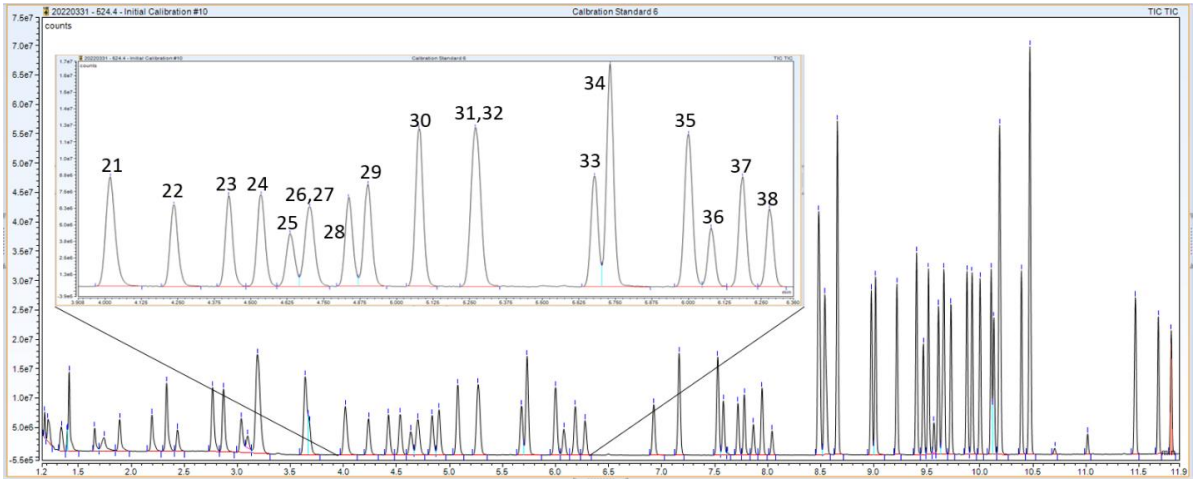
Figure 1 Total Ion Chromatogram (TIC) of a US EPA 524.4 Water Method 10 ppb VOC Standard with an Inset Indicating Consistent Peak Shapes and Separation with Minimal Water Interference.
21) t-butyl ethyl ether, 22) cis-1,2-dichloroethene, 23) Bromochloromethane, 24) Chloroform, 25) Carbon tetrachloride, 26) Tetrahydrofuran, 27) 1,1,1-trichloroethane, 28) 1,1-dichloropropene, 29) 1-chlorobutane, 30) Benzene, 31) t-amyl methyl ether, 32) 1,2-dichlorothane, 33) Trichloroethylene, 34) 1,4-dichluorobenzene (IS), 35) t-amyl ethyl ether, 36) Dibromomethane, 37) 1,2-dichloropropane, 38) Bromodichloromethane.



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. 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 MRL confirmation for seven 0.5 ppb standards and mid-point calibration checks for seven 10 ppb standards showed no interference from excessive water and displayed very reproducible results. The average MDL for all compounds was 0.08 ppb with a 5.5% RSD. The seven 10 ppb mid-point calibration check standards averaged a 95% recovery with a 3.4% RSD.

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. US EPA. 2013. “Method 524.4: “Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas,” Cincinnati, OH. [Online] https://nepis.epa.gov/Exe/ZyPDF.cgi/P100J7EE.PDF?Dockey=P100J7EE.PDF (accessed April 29, 2022).