

US EPA Method 524.4 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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Abstract

US EPA Method 524.4 was used to determine the concentration of volatile organic compounds (VOCs) in drinking water. 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 coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph (GC) was used to create a working linear (r^2) calibration curve, method detection limits (MDLs), initial demonstration of capability (IDC) 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 25 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 quadratic (r^2) calibration curve was prepared from 0.2 ppb to 50 ppb for all compounds with regression value (r^2) ≥ 0.995 . The relative response factor (RF) 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 μ L was then mixed with each 5 mL sample for a resulting concentration of 12.5 parts per billion (ppb).

Seven 0.5 ppb standards were prepared to calculate the MDL and MRL confirmation calculations. Also, seven 5 ppb standards were prepared for the IDC, accuracy and precision calculations. All calibration, MDL, MRL and IDC 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			
Purge	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	1.00 min
Purge Ready Temp	40 °C	Drain Flow	300 mL/min
		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	40 °C	Bake Rinse Drain Time	0.40 min
Pre-purge Time	0.00 min	Bake Time	6.00 min
Pre-purge Flow	0 mL/min	Bake Flow	200 mL/min
Purge Time	5.50 min	Bake Temp	280 °C
Purge Flow	80 mL/min	Condensate Bake Temp	180 °C
Purge Temp	20 °C		
Condensate Purge Temp	20 °C		
Dry Purge Time	0.00 min	Trap	K
Dry Purge Flow	0 mL/min	Chiller Tray	On
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

Table II Thermo Scientific TRACE 1310 GC and ISQ LT MS System Conditions	
Thermo Scientific TRACE 1310 GC Conditions	
Column	TG VMS, 20 m x 0.18 mm, 1µm 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, Purge Flow 0.5 mL/min
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 3.00E+005

Results

The linear correlation coefficient of the calibration curve (r^2), MDL, precision and MRL confirmation data are shown in Table III. Due to its limited calibration range, Iodomethane used a higher concentration for its method requirements. Also, Pentachloroethane exhibited poor recovery after breaking down during the IDC. Figure 1 displays a 5 ppb standard, indicating excellent peak resolution with minimal water interference for all VOCs.

Figure 1 Total Ion Chromatogram (TIC) of a Water Method 5 ppb VOC Standard with an Inset Indicating Consistent Peak Shapes and Separation with Minimal Water Interference

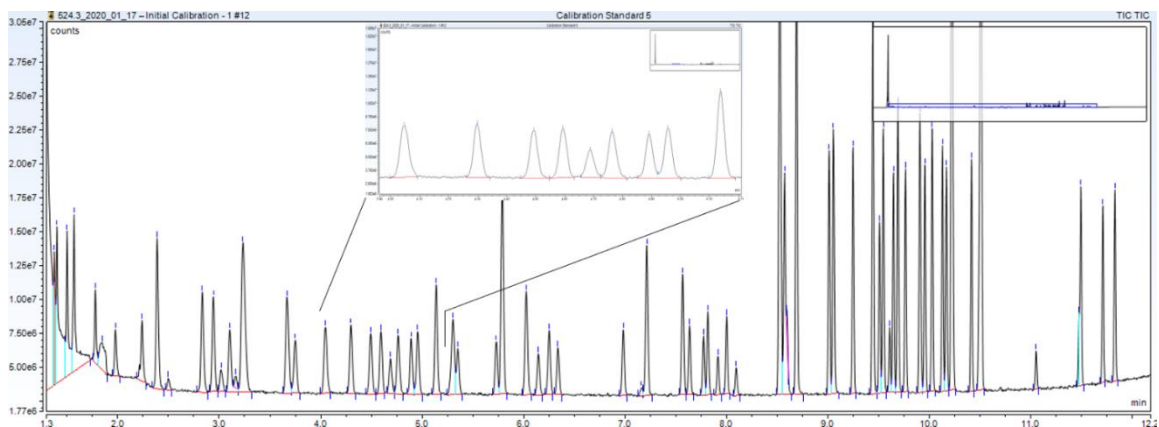


Table III Method 524.4 Calibration, Accuracy and Precision Data

Compound	Calibration			Method Detection Limits (n=7, 0.5 ppb)			Init. Dem. of Capability (n=7, 5 ppb)		Min. Rpt. Lvl. (n=7, 0.5 ppb)	
	Retention Time	Linearity (r ² ≥0.995)	Avg RF	Avg Conc (ppb)	MDL (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Dichlorodifluoromethane ¹	1.38	0.999	0.339	0.49	0.11	7.94	119	5.21	61	117
Chlorodifluoromethane ³	1.41	0.998	0.851	0.60	0.10	5.09	120	4.01	96	144
Chloromethane	1.51	0.999	1.27	0.44	0.14	9.92	119	4.64	53	121
Vinyl Chloride	1.57	0.998	0.470	0.60	0.11	6.00	119	4.76	91	148
1,3-Butadiene	1.58	0.999	0.415	0.58	0.13	7.05	120	7.22	84	149
Bromomethane ¹	1.79	0.997	0.416	0.43	0.13	9.83	117	6.47	52	117
Trichlorofluoromethane	1.99	0.999	0.481	0.58	0.11	6.26	114	5.17	88	146
Diethyl Ether	2.26	0.999	0.337	0.60	0.10	5.12	118	5.87	95	144
1,1-Dichloroethene	2.40	0.999	0.374	0.59	0.11	5.76	116	5.15	90	144
Allyl Chloride	2.41	0.999	1.51	0.60	0.09	4.65	120	5.96	98	142
Iodomethane ^{2,3,5}	2.52	0.999	0.348	5.7	2.7	14.9	113	14.9	46	180
Carbon Disulfide	2.86	0.998	0.284	0.58	0.13	7.19	115	4.24	83	149
Methylene Chloride	2.97	0.997	1.02	0.59	0.10	5.62	120	3.61	91	144
cis-1,2-Dichloroethene	3.13	0.999	0.403	0.57	0.09	5.26	116	4.49	90	138
Methyl Acetate	3.19	1.00	0.445	0.54	0.10	5.81	108	6.89	83	133
Methyl-tert-Butyl Ether-d ₃ (SURR)	3.25	10.7	0.932	12.8		6.43	105	7.86	76	128
Methyl-tert-Butyl Ether	3.27	0.995	0.878	0.54	0.10	5.61	103	7.82	85	133
Diisopropyl Ether	3.68	0.997	1.71	0.57	0.05	2.82	116	3.30	101	127
1,1-Dichloroethane	3.77	0.999	0.891	0.60	0.10	5.52	118	4.17	94	146
tert-Butyl Alcohol	4.07	0.997	1.01	0.56	0.07	3.72	105	4.24	96	129
tert-Butyl Ethyl Ether	4.07	0.997	1.01	0.56	0.07	3.77	111	4.10	96	129
trans-1,2-Dichloroethene	4.32	0.998	0.658	0.58	0.06	3.54	120	3.03	99	132
Bromochloromethane	4.52	0.999	0.201	0.60	0.07	3.74	113	1.58	101	137
Chloroform	4.62	0.999	0.740	0.58	0.07	3.79	118	3.06	98	133
Carbon Tetrachloride	4.71	0.999	0.376	0.52	0.10	5.95	102	6.29	79	128
1,1,1-Trichloroethane	4.79	0.999	0.492	0.55	0.10	5.73	107	5.00	85	135
Tetrahydrofuran	4.79	1.00	0.047	0.56	0.15	8.34	119	8.95	75	149
1,1-Dichloropropene	4.91	0.995	0.432	0.54	0.07	4.07	96	6.52	91	125

Table III Method 524.4 Calibration, Accuracy and Precision Data

Compound	Calibration			Method Detection Limits (n=7, 0.5 ppb)			Init. Dem. of Capability (n=7, 5 ppb)		Min. Rpt. Lvl. (n=7, 0.5 ppb)	
	Retention Time	Linearity (r ² ≥ 0.995)	Avg RF	Avg Conc (ppb)	MDL (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
1-Chlorobutane	4.98	0.996	0.704	0.54	0.06	3.74	102	5.54	92	124
Benzene	5.19	0.996	1.44	0.56	0.06	3.50	105	4.24	97	128
tert-Amyl Methyl Ether	5.33	0.998	0.866	0.57	0.06	3.30	114	3.71	100	130
1,2-Dichloroethane	5.37	0.999	0.518	0.58	0.05	2.80	116	4.05	102	128
Trichloroethylene	5.75	0.996	0.309	0.56	0.11	6.48	100	5.59	84	142
1,4-Difluorobenzene (IS)	5.81									
tert-Amyl Ethyl Ether	6.05	0.998	0.967	0.58	0.07	3.67	114	2.08	99	133
Dibromomethane	6.17	0.999	0.240	0.59	0.05	2.86	115	2.74	105	132
1,2-Dichloropropane	6.27	0.995	0.405	0.55	0.06	3.51	105	4.65	95	126
Bromodichloromethane	6.36	0.997	0.486	0.56	0.09	5.08	107	5.86	89	134
trans-1,3-Dichloropropene	7.00	0.995	0.545	0.52	0.08	5.02	100	5.32	84	125
Toluene	7.23	0.999	1.49	0.54	0.06	3.72	113	4.56	93	125
Tetrachloroethylene ³	7.58	0.998	0.413	0.56	0.08	4.43	116	7.40	93	132
cis-1,3-Dichloropropene	7.65	0.996	0.503	0.55	0.06	3.33	99	3.88	96	126
1,1,2-Trichloroethane	7.79	0.996	0.224	0.57	0.07	3.87	107	6.36	96	131
Ethyl Methacrylate	7.83	0.999	0.463	0.57	0.11	6.24	114	4.66	86	143
Dibromochloromethane	7.93	0.996	0.261	0.53	0.10	6.11	99	5.77	80	132
1,3-Dichloropropane	8.02	0.996	0.503	0.58	0.04	2.23	102	5.21	106	126
1,2-Dibromoethane	8.11	0.997	0.248	0.54	0.08	4.50	107	5.38	89	128
Chlorobenzene-d5 (IS)	8.54									
Chlorobenzene	8.55	0.999	0.920	0.57	0.11	5.92	112	4.19	87	140
Ethylbenzene	8.58	0.998	1.72	0.58	0.09	4.93	109	4.98	93	138
1,1,1,2-Tetrachloroethane	8.61	0.999	0.239	0.55	0.06	3.60	108	5.40	95	127
m,p-Xylene	8.70	0.998	1.50	1.13	0.15	4.32	107	5.03	93	132
o-Xylene	9.02	0.997	1.53	0.56	0.08	4.42	107	3.83	92	131
Styrene	9.06	0.999	1.15	0.55	0.07	4.06	104	4.65	93	128
Bromoform	9.07	0.999	0.211	0.54	0.10	6.15	102	5.17	82	134
Isopropylbenzene	9.26	0.999	1.63	0.54	0.09	5.00	105	5.54	87	130
4-Bromofluorobenzene (SURR)	9.45	4.76	0.863	12.9		3.75	99	1.32	88	119

Table III Method 524.4 Calibration, Accuracy and Precision Data

Compound	Calibration			Method Detection Limits (n=7, 0.5 ppb)			Init. Dem. of Capability (n=7, 5 ppb)		Min. Rpt. Lvl. (n=7, 0.5 ppb)	
	Retention Time	Linearity (r ² ≥0.995)	Avg RF	Avg Conc (ppb)	MDL (ppb)	Precision (≤20%)	Accuracy (±20%)	Precision (≤20%)	LPIR (≥50%)	UPIR (≤150%)
Bromobenzene	9.52	0.998	0.847	0.60	0.06	3.18	112	4.13	104	135
n-Propylbenzene	9.55	1.00	3.02	0.54	0.14	8.09	111	6.22	74	143
1,1,2,2-Tetrachloroethane	9.62	1.00	0.530	0.58	0.10	5.34	116	8.38	92	141
2-Chlorotoluene	9.65	0.999	1.88	0.54	0.12	7.17	111	5.96	78	139
1,3,5-Trimethylbenzene	9.70	0.999	1.93	0.56	0.14	7.76	106	5.81	77	146
1,2,3-Trichloropropane	9.70	0.999	0.498	0.59	0.10	5.51	117	8.20	93	145
4-Chlorotoluene	9.77	0.999	1.96	0.57	0.12	6.70	109	5.79	84	144
p-Isopropyltoluene	9.91	0.999	1.75	0.52	0.14	8.67	101	5.24	68	139
tert-Butylbenzene	9.91	0.999	1.77	0.52	0.15	9.18	101	5.29	66	142
Pentachloroethane ^{3,4}	9.92	0.995	0.153	0.49	0.18	11.9	75	27.7	52	144
1,2,4-Trimethylbenzene	9.96	0.999	1.96	0.56	0.13	7.45	108	5.72	79	145
sec-Butylbenzene	10.03	0.999	2.50	0.53	0.13	7.99	106	6.15	72	139
1,3-Dichlorobenzene	10.18	0.999	1.44	0.59	0.13	6.79	112	5.42	86	149
1,4-Dichlorobenzene-d4 (IS)	10.23									
1,4-Dichlorobenzene	10.24	0.999	1.47	0.57	0.14	7.89	110	6.59	78	150
n-Butylbenzene	10.42	0.999	1.92	0.59	0.13	6.93	107	6.03	85	150
Hexachloroethane	10.50	0.998	0.317	0.60	0.13	7.14	115	6.23	80	143
1,2-Dichlorobenzene-d4 (SURR)	10.51	2.04	0.927	12.7		1.65	102	2.10	95	108
1,2-Dichlorobenzene	10.52	0.999	1.41	0.56	0.14	7.71	110	5.96	77	146
1,2-Dibromo-3-Chloropropane	11.06	0.997	0.137	0.55	0.13	7.75	118	7.50	76	143
Hexachlorobutadiene	11.48	0.999	0.051	0.58	0.12	6.75	112	6.56	84	146
1,2,4-Trichlorobenzene	11.50	0.995	0.922	0.58	0.19	10.2	117	2.36	86	147
Naphthalene	11.72	0.996	1.85	0.58	0.12	6.62	119	6.40	82	143
1,2,3-Trichlorobenzene	11.84	0.995	0.887	0.56	0.15	8.52	120	5.66	74	149

1. Calibration curve 0.5-50 ppb.
2. Calibration curve 1-50 ppb.
3. Calibration curve used a quadratic regression.
4. Analyte is a poor purger and broke down after several injections.
5. 5 ppb MDL.

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 ISQ 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific TRACE 1310 Gas Chromatograph (GC). 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, precision and MRL confirmation for seven 0.5 ppb standards and IDC for seven 5 ppb standards showed no interference from excessive water and displayed very reproducible results.

Furthermore, the Atomx XYZ and GC-MS conditions shown in [Table I](#) and [Table II](#) are capable of analyzing three samples per 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. 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. [Online] <https://nepis.epa.gov/Exe/ZyPDF.cgi/P100J7EE.PDF?Dockey=P100J7EE.PDF> (accessed March 26, 2020).