Application Note

Environmental

Agilent

Trusted Answers

US EPA Method 524.2 - Atomx XYZ and Agilent 7890B GC/5977A MS

Author

Amy Nutter
Applications Chemist,
Teledyne Tekmar

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) system along with an Agilent 7890B GC/5977A MS was used to create two working linear calibration curves and method detection limits (MDLs) for target compounds. One working linear calibration curve used the method recommended four-minute desorb time, while the other used a two-minute desorb time. This study will display the ability of the Atomx XYZ's moisture control system 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. An innovative moisture control system improves water vapor removal by as much as 60%, thereby reducing peak interference and increasing GC column life span. 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

Calibration working standards in concentrations of 10, 25, 50, and 100 ppm were prepared in methanol from the following Restek® standards: Drinking Water VOA MegaMix™, Ketone Mix, and 502.2 Calibration Mix. In total, the standards contained 83 compounds.

The calibration curves were prepared from 0.2 ppb to 50 ppb for all compounds. The 10 ppm calibration working standard was diluted to create 0.2 and 0.5 ppb concentrations. The 25 ppm calibration working standard was diluted to create 1 and 2 ppb concentrations. The 50 ppm calibration working standard was diluted to create 5, 10, and 20 ppb concentrations. The 100 ppm calibration working standard was diluted to create 30 and 50 ppb concentrations. The relative response factor (RF) was calculated for each compound using a Fluorobenzene internal standard. Surrogate standards consisted of: 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, accuracy, and precision calculations. All calibration and MDL standards were analyzed with the Atomx XYZ conditions in Table 1. GC-MS conditions are shown in Table 2.

Experimental Instrument Conditions

Table 1. 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	4.00 min/2.00 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	260 °C
Purge Flow	40 mL/min	Condensate Bake Temp	200 °C
Purge Temp	20 °C		
Condensate Purge Temp	20 °C		
Dry Purge Time	0.00 min	**Trap**	9
Dry Purge Flow	0 mL/min	**Chiller Tray**	On
Dry Purge Temp	20 °C	**Purge Gas**	Helium

Table 2. Agilent 7890B GC and 5977A MSD System Conditions.

Agilent 7890B GC Conditions	
Column	Rtx®-VMS, 20m x 0.18 mm, 1µm Film, Helium – 1 mL/min
Oven Profile	35 °C, 4 min, 15 °C/min to 85 °C, 30°C/min to 225 °C, 2 min hold, Run Time 14.00 min
Inlet	180 °C, 120:1 Split, 19.752 psi
Agilent 5977A MSD Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 m/z to 260 m/z, Solvent Delay 0.50 min, Normal Scanning
Gain	Gain Factor 10.00, Autotune

Results

The relative standard deviation (%RSD) of the response factors (RF) for the calibration curves, MDL, accuracy, and precision data are shown in Table 3 (4-minute desorb) and Table 4 (2-minute desorb).

Figure 1 (4-minute desorb) and Figure 2 (2-minute desorb) display a 30 ppb standard, indicating excellent peak resolution with minimal water interference of all VOCs, including the first six gases.

Table 3. US EPA Method 524.2 Calibration, Accuracy, and Precision Data (4-Minute Desorb).

Compound	Calibration			Accuracy and Precision (n = 7, 0.5 ppb)[1]		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Conc. (ppb)	Accuracy (±20 %)	Precision (≤20 %)
Fluorobenzene (IS)						
Dichlorodifluoromethane	13.7	0.17	0.257	0.47	93	11.6
Chloromethane	4.18	0.16	0.230	0.54	108	9.6
Vinyl chloride	10.5	0.15	0.300	0.50	101	9.5
Bromomethane	8.83	0.06	0.311	0.55	109	3.3
Chloroethane	8.05	0.10	0.192	0.52	105	6.3
Trichlorofluoromethane	15.0	0.24	0.516	0.52	105	14.5
Diethyl ether	10.3	0.07	0.202	0.53	105	3.9
1,1-Dichloroethene	2.14	0.19	0.328	0.51	102	11.9
Acetone[2]	0.997	0.19	0.136	0.49	97	12.6
Carbon Disulfide	8.86	0.14	0.877	0.43	85	10.4
Iodomethane[2]	0.998	0.20	0.536	0.42	84	15.5
Allyl chloride	10.8	0.14	0.869	0.43	85	10.6
Methylene chloride	6.92	0.30	0.364	0.53	107	17.7
Acrylonitrile	8.29	0.16	0.086	0.56	111	9.2
trans-1,2-Dichloroethene	8.59	0.15	0.404	0.49	98	9.9
Methyl-*tert*-butyl ether (MTBE)	8.79	0.20	0.824	0.42	85	15.1
1,1-Dichloroethane	7.21	0.11	0.479	0.45	89	8.1
Methyl methacrylate	5.11	0.10	0.168	0.51	102	5.9
2,2-Dichloropropane	7.71	0.25	0.458	0.53	105	15.1
Propionitrile	5.60	0.18	0.034	0.56	111	10.3
cis-1,2-Dichloroethene	3.92	0.13	0.361	0.45	90	9.3
2-Butanone (MEK)	7.28	0.19	0.090	0.59	118	10.4
Methyl acrylate	9.31	0.21	0.236	0.53	107	12.4
Methacrylonitrile	7.49	0.13	0.124	0.57	114	7.2
Bromochloromethane	5.86	0.08	0.238	0.50	100	5.1
Chloroform	8.72	0.15	0.626	0.45	90	10.5
Carbon tetrachloride	6.98	0.10	0.402	0.40	81	8.2
Tetrahydrofuran	0.999	0.09	0.047	0.51	102	5.7
1,1,1-Trichloroethane	8.28	0.10	0.411	0.48	96	6.9
1,1-Dichloropropene	6.77	0.21	0.315	0.42	84	15.9
1-Chlorobutane	4.16	0.27	0.385	0.52	103	16.9
Benzene	5.10	0.11	0.949	0.48	95	7.4
1,2-Dichloroethane	8.86	0.11	0.275	0.46	93	7.3
Trichloroethylene	5.65	0.16	0.281	0.49	97	10.6
Dibromomethane	8.91	0.17	0.183	0.45	89	12.4
1,2-Dichloropropane	7.05	0.15	0.227	0.51	101	9.7
2-Nitropropane[2]	0.995	0.11	0.006	0.52	103	6.7

Compound	Calibration			Accuracy and Precision (n = 7, 0.5 ppb)[1]		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Conc. (ppb)	Accuracy (±20 %)	Precision (≤20 %)
Bromodichloromethane	9.26	0.12	0.343	0.40	80	9.4
Chloroacetonitrile[2]	0.997	0.09	0.011	0.52	104	5.7
cis-1,3-Dichloropropene	8.43	0.22	0.373	0.42	83	16.9
1,1-Dichloro-2-propanone	7.63	0.09	0.222	0.54	107	5.6
4-Methyl-2-pentanone (MIBK)	6.91	0.12	0.224	0.53	107	7.3
Toluene	4.39	0.08	0.618	0.48	96	5.0
Tetrachloroethene	6.62	0.18	0.555	0.48	96	12.1
trans-1,3-Dichloropropene	6.32	0.09	0.336	0.43	86	6.9
Ethyl methacrylate	7.16	0.13	0.281	0.45	90	9.0
1,1,2-Trichloroethane	11.2	0.15	0.208	0.45	89	11.0
2-Hexanone	17.5	0.23	0.122	0.43	86	17.1
Dibromochloromethane	8.90	0.07	0.340	0.46	92	5.2
1,3-Dichloropropane	6.14	0.20	0.365	0.47	94	13.5
1,2-Dibromoethane	7.68	0.17	0.274	0.41	82	13.6
Chlorobenzene	3.87	0.11	0.790	0.42	84	8.5
Ethylbenzene	5.09	0.08	1.15	0.44	87	5.6
1,1,1,2-Tetrachloroethane	7.93	0.08	0.303	0.40	80	6.5
m-,*p*-Xylene	5.79	0.21	0.484	0.92	92	7.3
o-Xylene	6.82	0.15	0.470	0.45	91	10.3
Styrene	5.11	0.06	0.793	0.48	96	4.2
Bromoform	6.36	0.11	0.263	0.45	90	7.8
Isopropylbenzene	6.91	0.09	1.18	0.44	88	6.3
Bromofluorobenzene (SURR)	2.56		0.303	24	94	5.8
Bromobenzene	6.77	0.14	0.407	0.46	92	9.6
n-Propylbenzene	5.24	0.04	1.34	0.43	87	2.9
1,1,2,2-Tetrachloroethane	9.76	0.12	0.293	0.46	91	8.1
2-Chlorotoluene	5.89	0.08	0.746	0.47	94	5.7
1,3,5-Trimethylbenzene	4.07	0.09	0.986	0.44	88	6.6
1,2,3-Trichloropropane	5.78	0.11	0.342	0.47	93	7.5
trans-1,4-dichloro-2-butene[2]	0.999	0.14	0.047	0.41	81	11.3
4-Chlorotoluene	5.44	0.10	0.862	0.46	93	6.8
tert-Butylbenzene	5.31	0.13	1.11	0.45	89	9.6
Pentachloroethane	14.8	0.14	0.184	0.51	102	8.5
1,2,4-Trimethylbenzene	3.79	0.14	0.972	0.44	87	10.4
sec-Butylbenzene	4.07	0.09	0.986	0.44	88	6.6
4-Isopropyltoluene	6.43	0.12	1.15	0.41	82	9.3
1,3-Dichlorobenzene	4.96	0.06	0.721	0.44	89	4.7
1,4-Dichlorobenzene	4.70	0.12	0.739	0.52	105	7.6
n-Butylbenzene	4.51	0.15	0.928	0.49	98	9.7
Hexachloroethane	8.23	0.11	0.225	0.49	98	8.9
1,2-Dichlorobenzene-d4 (SURR)	2.10		0.451	26	103	3.7
1,2-Dichlorobenzene	3.28	0.12	0.712	0.50	100	7.5
1,2-Dibromo-3-Chloropropane[2]	0.998	0.09	0.046	0.51	101	7.3
Nitrobenzene[2]	0.998	0.09	0.011	0.50	99	6.0
Hexachlorobutadiene	4.78	0.19	0.300	0.48	97	12.2
1,2,4-Trichlorobenzene	7.08	0.21	0.562	0.55	111	12.1
Naphthalene	5.23	0.29	1.08	0.58	116	15.8
1,2,3-Trichlorobenzene	6.16	0.23	0.552	0.57	115	13.0

[1] Data from seven 0.5 ppb samples.
[2] Compounds were linear regressed.

Table 4. US EPA Method 524.2 Calibration, Accuracy, and Precision Data (2-Minute Desorb).

Compound	Calibration			Accuracy and Precision (n = 7, 0.5 ppb)[1]		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Conc. (ppb)	Accuracy (±20 %)	Precision (≤20 %)
Fluorobenzene (IS)						
Dichlorodifluoromethane	11.5	0.20	0.255	0.41	81	15.4
Chloromethane	10.5	0.13	0.249	0.49	97	8.4
Vinyl chloride	10.8	0.08	0.320	0.43	87	6.2
Bromomethane	13.7	0.20	0.315	0.57	115	11.1
Chloroethane	4.24	0.17	0.197	0.48	95	11.4
Trichlorofluoromethane	6.90	0.11	0.534	0.45	91	7.8
Diethyl ether	10.5	0.16	0.228	0.52	103	9.9
1,1-Dichloroethene	6.25	0.28	0.310	0.54	109	16.1
Acetone[2]	0.995	0.18	0.116	0.49	99	11.8
Carbon Disulfide	9.87	0.07	0.955	0.45	91	5.2
Iodomethane[2]	0.995	0.11	0.461	0.45	91	7.6
Allyl chloride	9.90	0.08	0.955	0.46	91	5.8
Methylene chloride	5.24	0.17	0.342	0.54	108	9.9
Acrylonitrile	4.35	0.10	0.084	0.55	109	6.1
trans-1,2-Dichloroethene	6.80	0.1	0.311	0.50	99	10.0
Methyl-*tert*-butyl ether (MTBE)	10.2	0.13	0.845	0.50	99	8.3
1,1-Dichloroethane	6.61	0.14	0.403	0.46	91	10.0
Methyl methacrylate	10.0	0.17	0.172	0.53	106	10.1
2,2-Dichloropropane	8.67	0.17	0.364	0.45	91	11.6
Propionitrile	16.4	0.15	0.031	0.50	100	9.5
cis-1,2-Dichloroethene	4.23	0.12	0.349	0.53	105	7.2
2-Butanone (MEK)	9.37	0.08	0.075	0.53	107	4.7
Methyl acrylate	2.22	0.30	0.190	0.51	103	18.4
Methacrylonitrile	9.19	0.14	0.106	0.54	109	8.4
Bromochloromethane	9.27	0.26	0.176	0.46	91	18.1
Chloroform	11.5	0.09	0.462	0.45	90	6.5
Carbon tetrachloride	4.91	0.11	0.404	0.44	87	7.9
Tetrahydrofuran	9.62	0.30	0.030	0.48	96	20.0
1,1,1-Trichloroethane	12.1	0.10	0.419	0.44	87	7.2
1,1-Dichloropropene	8.29	0.17	0.316	0.43	86	12.5
1-Chlorobutane	3.65	0.10	0.379	0.51	101	6.1
Benzene	9.85	0.14	0.978	0.47	93	9.4
1,2-Dichloroethane	8.34	0.13	0.281	0.45	89	9.3
Trichloroethylene	4.33	0.20	0.276	0.52	103	12.4
Dibromomethane	13.5	0.13	0.190	0.46	92	8.8
1,2-Dichloropropane	6.71	0.17	0.231	0.47	94	11.8
2-Nitropropane[2]	0.997	0.06	0.005	0.56	112	3.4
Bromodichloromethane	6.71	0.05	0.323	0.49	99	3.1
Chloroacetonitrile[2]	0.995	0.03	0.008	0.53	105	1.9
cis-1,3-Dichloropropene	7.23	0.11	0.394	0.49	99	7.3
1,1-Dichloro-2-propanone	10.9	0.16	0.238	0.51	103	9.9
4-Methyl-2-pentanone (MIBK)	9.99	0.14	0.234	0.52	103	8.7
Toluene	11.2	0.12	0.638	0.44	88	8.8
Tetrachloroethene	11.3	0.13	0.541	0.47	94	9.0
trans-1,3-Dichloropropene	11.8	0.07	0.369	0.42	85	5.4

Compound	Calibration			Accuracy and Precision (n = 7, 0.5 ppb)[1]		
	Linearity RF (%RSD)	MDL (ppb)	Average RF	Average Conc. (ppb)	Accuracy (±20 %)	Precision (≤20 %)
Ethyl methacrylate	8.57	0.21	0.303	0.49	99	13.8
1,1,2-Trichloroethane	9.04	0.19	0.208	0.53	105	11.4
2-Hexanone	7.09	0.08	0.121	0.56	112	4.7
Dibromochloromethane	12.7	0.12	0.355	0.46	92	8.6
1,3-Dichloropropane	4.10	0.20	0.376	0.47	93	13.8
1,2-Dibromoethane	7.44	0.11	0.270	0.47	94	7.5
Chlorobenzene	9.89	0.07	0.803	0.44	87	5.1
Ethylbenzene	12.3	0.12	1.21	0.44	87	8.5
1,1,1,2-Tetrachloroethane	11.3	0.12	0.315	0.44	88	8.7
m-,*p*-Xylene	10.7	0.25	0.500	0.84	84	9.3
o-Xylene	7.25	0.18	0.474	0.43	87	13.4
Styrene	9.08	0.08	0.819	0.43	86	5.7
Bromoform	9.01	0.10	0.274	0.46	92	6.8
Isopropylbenzene	9.35	0.12	1.23	0.42	84	8.8
Bromofluorobenzene (SURR)	3.31		0.321	24	96	2.9
Bromobenzene	9.22	0.11	0.399	0.45	89	7.8
n-Propylbenzene	5.52	0.11	1.36	0.43	87	8.3
1,1,2,2-Tetrachloroethane	13.7	0.16	0.309	0.49	97	10.6
2-Chlorotoluene	7.19	0.21	0.771	0.47	93	14.6
1,3,5-Trimethylbenzene	8.88	0.11	1.02	0.44	88	7.7
1,2,3-Trichloropropane	11.8	0.18	0.364	0.49	98	11.8
trans-1,4-dichloro-2-butene[2]	0.999	0.22	0.056	0.49	98	14.1
4-Chlorotoluene	5.44	0.15	0.879	0.45	89	10.9
tert-Butylbenzene	4.29	0.08	1.12	0.43	85	6.2
Pentachloroethane	12.4	0.04	0.205	0.41	82	2.9
1,2,4-Trimethylbenzene	4.60	0.13	0.959	0.45	90	9.3
sec-Butylbenzene	8.88	0.11	1.02	0.44	88	7.7
4-Isopropyltoluene	6.80	0.08	1.17	0.42	83	6.5
1,3-Dichlorobenzene	8.03	0.10	0.697	0.46	93	6.8
1,4-Dichlorobenzene	7.04	0.09	0.711	0.48	96	5.8
n-Butylbenzene	12.8	0.08	0.955	0.45	90	5.7
Hexachloroethane	8.24	0.14	0.236	0.43	86	10.4
1,2-Dichlorobenzene-d4 (SURR)	2.94		0.445	25	98	2.2
1,2-Dichlorobenzene	11.2	0.09	0.714	0.47	94	5.8
1,2-Dibromo-3-Chloropropane	9.88	0.31	0.046	0.52	105	18.6
Nitrobenzene[2]	0.996	0.10	0.009	0.54	108	5.6
Hexachlorobutadiene	3.84	0.13	0.289	0.43	85	9.8
1,2,4-Trichlorobenzene	7.83	0.16	0.551	0.45	90	11.5
Naphthalene	7.86	0.10	1.11	0.47	94	6.9
1,2,3-Trichlorobenzene	5.24	0.09	0.522	0.45	91	6.6

[1] Data from seven 0.5 ppb samples.

[2] Compounds were linear regressed.

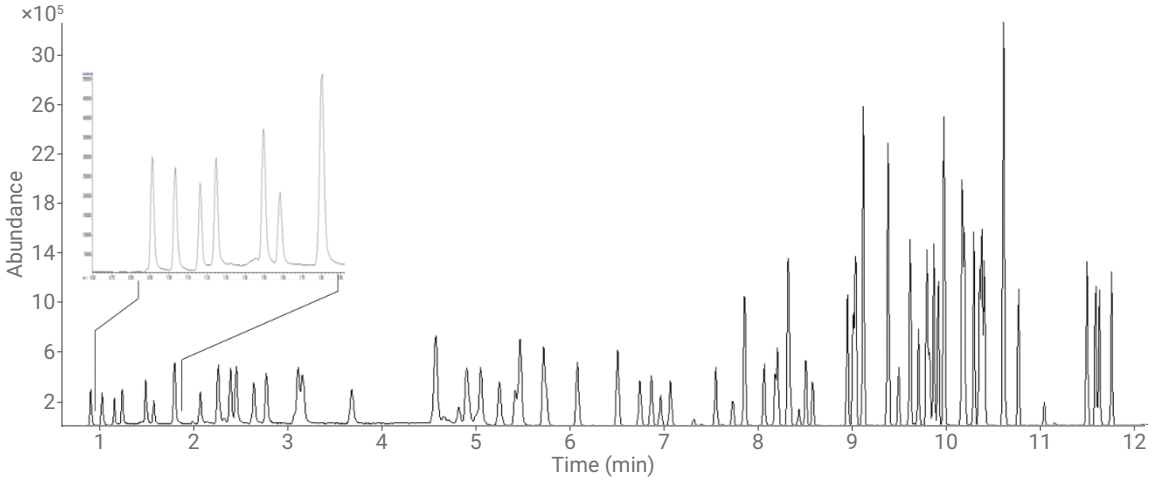

Figure 1. Total Ion Chromatogram of a 30 ppb VOC Standard with an Inset of the Primary Characteristic Ions for the First Six Gases Indicating Consistent Peak Shapes for all Compounds with No Water Interference Using a Four-Minute Desorb.

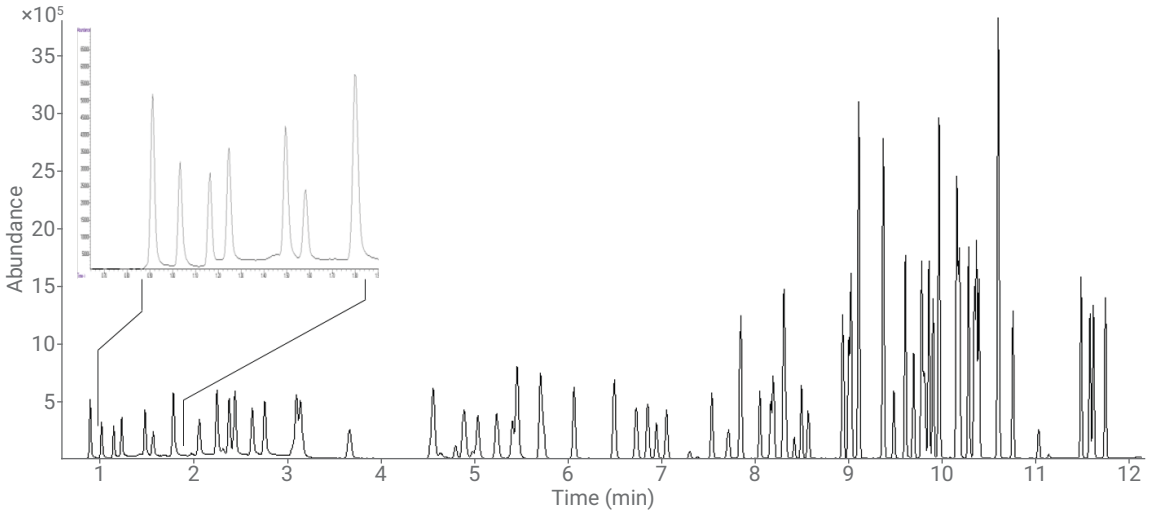

Figure 2. Total Ion Chromatogram of a 30 ppb VOC Standard with an Inset of the Primary Characteristic Ions for the First Six Gases Indicating Consistent Peak Shapes for all Compounds with No Water Interference Using a Two-Minute Desorb.

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 an Agilent 7890B GC/5977A MS. The %RSD of the calibration curve passed all method requirements. Furthermore, MDL and precision and accuracy for seven 0.5 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.

Reference

1. Munch, J. W. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, *US EPA Method 524.2, Revision 4.1*, **1995**.

www.agilent.com/chem

Printed in the USA, April 24, 2018
5991-9260EN

Agilent
Trusted Answers