Using Nitrogen Purge Gas for US EPA Drinking Water Methods

Application Note

Abstract

The USEPA developed Method 524.4, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (Using Nitrogen Purge Gas)", for identifying and measuring purgeable volatile organic compounds in surface water, groundwater, and drinking water. Due to the economic concerns associated with the cost of helium, this method allows for the utilization of nitrogen as a purge gas. The use of purge and trap gas chromatography is vital to this method because of the required sensitivity. This study will utilize a Purge and Trap concentrator and autosampler in conjunction with a GC/MS. A linear calibration and Method Detection Limits (MDLs) will be established for Method 524.4 compounds.

Background

The United States Environmental Protection Agency (USEPA) has developed methods for the analysis of drinking water, such as the 524 series, to ensure public health and safety. Proposed USEPA Method 524.4 allows for the determination of 76 Volatile Organic Compounds (VOCs) in drinking water using nitrogen (N_2) as the purge gas. VOCs are known contaminants in drinking water with potentially harmful health effects. The methods developed by the USEPA have strict guidelines for drinking water quality and analysis. The use of purge and trap technology allows for the determination of low-level VOCs with a great deal of precision and accuracy.

USEPA Method 524.4 is similar to USEPA Method 524.3 in many regards, but does have several key differences. The most notable change is the purge gas used in the purge and trap concentrator (PTC). The previous USEPA 524 methods call for helium purge gas, while USEPA Method 524.4 calls for nitrogen. With the increasing costs of supplying helium, switching to a nitrogen purge gas allows the same purge efficiency at a lower cost to labs. Another key change is the recommendation of trap to use in the purge and trap concentrator. USEPA Method 524.4 utilizes Supelco K-Trap (Vocarb® 3000) as the analytical trap. The recommended and allowable ranges for the purge and trap variables, which can be found in **Table 1**, have also undergone some changes.

Parameters	Recommended		Allowable	
	Minimum	Maximum	Minimum	Maximum
Sample Temperature	Ambient	40 °C	Ambient	60 °C
Purge Flow Rate	40mL/min	55mL/min	20mL/min	80mL/min
Purge Volume	360mL	520mL	320mL	520mL
Desorb Time	1min	2min	0.5min	2min
Purge Volume + Dry Purge Volume	360mL	820mL	320mL	820mL

Table 1: Recommended and Allowable Ranges for Purge and Trap Variables for proposed USEPA Method 524.4

For this study, a Stratum Purge and Trap Concentrator (PTC) was used in conjunction with an AQUATek 100 Autosampler. This set-up allows for complete automation of the analysis of liquid samples for Purge and Trap. Through the features the AQUATek 100 provides, such as the 100-position sample tray and 2 standard addition vessels, efficiency and throughput can be greatly increased, leading to cost and time savings. A recirculating chiller bath was also employed to hold vials below 10 °C, per method 524.4 requirements.[1]

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Using Nitrogen Purge Gas for US EPA Drinking Water Methods

Application Note

Utilizing an Agilent 7890A GC System/5975 inert XL MSD with Triple Axis Detector, calibrations and Minimum Reporting Levels (MRLs) were determined for the full list of compounds. A 5mL purge volume was used and requirements of the Initial Demonstration of Capability (IDC) for USEPA Method 524.4[1] were met.

Methodology/Procedure

The Stratum PTC and AQUATek 100 Autosampler equipped with chiller were coupled to an Agilent 7890A GC System/5975C with Triple Axis Detector for analysis. Supelco's Vocarb® 3000 (K-Trap) trap was used as the analytical trap. The GC was configured with a J&W DB-624 20m x 0.18mm x 1.0µm column. **Tables 2 and 3** outline the GC/MS conditions. **Table 4** outlines the Purge and Trap parameters.

A calibration curve was evaluated from 0.5ppb to 50ppb and MRLs were determined by running seven replicate samples at 0.5 ppb. All samples analyzed for the curve, blanks, and MRLs, were prepared as required by USEPA Method 524.4 using 5g/L maleic acid and 0.625g/L ascorbic acid as preservatives.

GC Parameters	
GC:	Agilent 7890A
Column:	J&W DB-624 20m x 0.18mm x 1.0µm
Oven Program:	35 °C for 3.00min, to 100 °C at 10 °C/min, for 0min, to 240 °C at 25 °C/min for 1.33min
Inlet:	220 °C
Column Flow:	1.0mL/min
Gas:	Helium
Pressure:	19.752psi
Split Ratio:	50:1

MS Parameters	
MSD:	Agilent 5975C w/TAD
Source:	250 °C
Quad:	200 °C
Solvent Delay:	0.5min
Scan Range:	35-300m/z from 0 to 14.3min
Scans:	5.19 scans/sec from 0 to 14.3min
Threshold:	300
MS Transfer Line Temp:	230 °C

Tables 2 & 3: GC and MSD Parameters

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Application Note

Stratum PTC and AQUATek 100 Parameters			
Variable	**Value**	**Variable**	**Value**
Pressurize Time	0.25min	Purge Time	6.00
Sample Transfer Time	0.50min	Purge Temp	20 °C
Rinse Loop Time	0.50min	Purge Flow	60mL/min
Sweep Needle Time	0.30min	Dry Purge Time	2.00min
Bake Rinse	On	Dry Purge Temp	30 °C
Bake Rinse Cycles	1	Dry Purge Flow	100mL/min
Bake Rinse Drain Time	0.50min	GC Start	Start of Desorb
Presweep Time	0.35min	Desorb Preheat Temp	250 °C
Water Temp	90 °C	Desorb Drain	On
Valve Oven Temp	150 °C	Desorb Time	1.00min
Transfer Line Temp	150 °C	Desorb Temp	250 °C
Sample Mount Temp	90°C	Desorb Flow	300mL/min
Purge ready Temp	35°C	Bake Time	2.00 min
Condenser Ready Temp	40°C	Bake Temp	280°C
Condenser Purge Temp	20°C	Bake Flow	400mL/min
Standby Flow	10mL/min	Condenser Bake Temp	200°C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0mL/min		

Table 4: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue)

Results

The calibration curve was prepared from 7 standards from 0.5 to 50 ppb prepared from a 50ppm stock standard. **Figure 1** shows a TIC of a mid range standard with an insert illustrating extracted ions for the six light gases. Calibration curves were generated for all compounds listed in USEPA Method 524.4 using a quadratic regression with inverse concentration weighting. A passing calibration curve must demonstrate that the lowest standard calculates to ±50% of the true values and all other points must calculate to ±30% of the true value. The quadratic regression values (r^2) are shown in the first column of **Table 5**.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Application Note

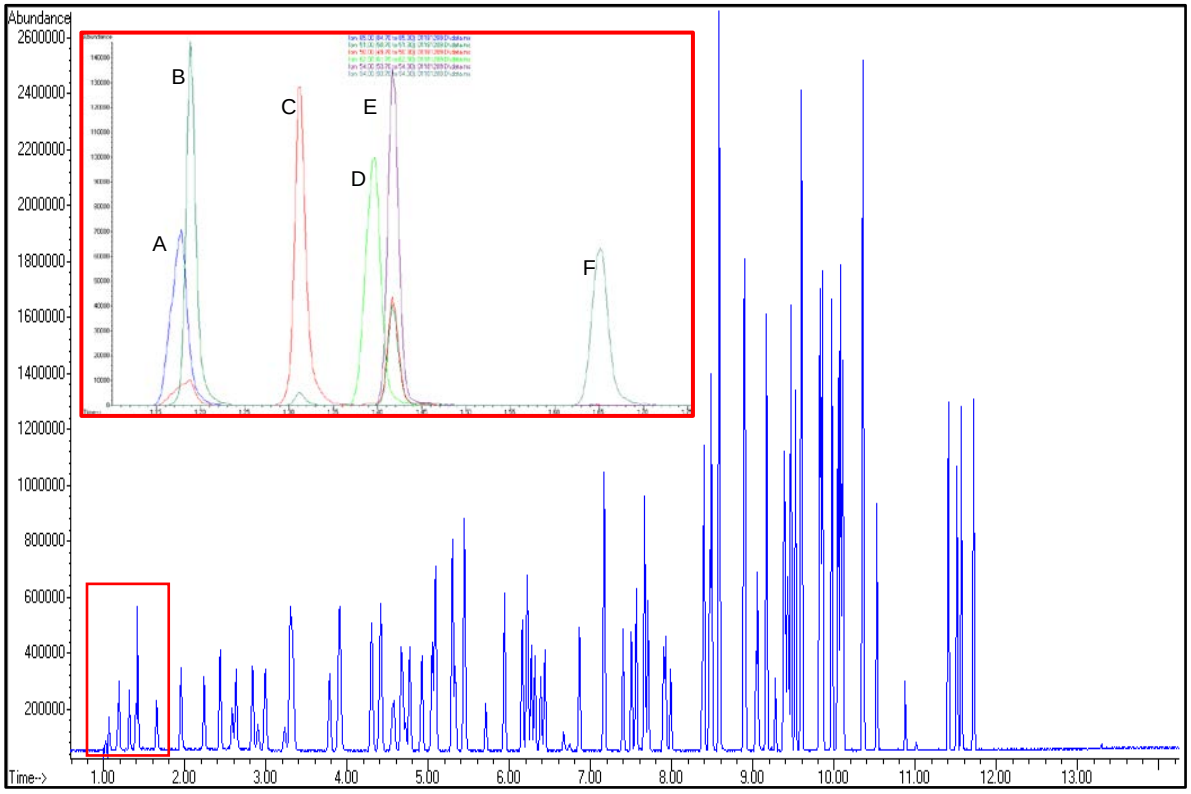

Figure 1: TIC of a 20ppb standard for the proposed USEPA Method 524.4. The insert illustrates the six light gases: Dichlorofluoromethane (A), Chlorodifluoromethane (B), Chloromethane (C), Vinyl Chloride (D), 1,3-Butadiene (E), Bromomethane (F).

The Minimum Reporting Level (MRL) is the minimum concentration that can be reported by a laboratory. This value must be no lower than the lowest calibration standard for each point. The MRLs were established for the USEPA compounds by running seven samples at a concentration 0.5ppb and evaluated as required by the proposed USEPA Method 524.4. A passing MRL has an Upper Prediction Interval of Results (PIR) ≤150% and a Lower PIR ≥50%. The Results of the MRL analysis can be seen in **Table 5**.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Using Nitrogen Purge Gas for US EPA Drinking Water Methods

Application Note

Compound	Quadratic Regression Factor	Spike Conc. (ppb)	Std. Dev. (ppb)	Mean Compound Response (ppb)	Half Range of Prediction Interval (ppb)	Low PIR (% Recovery) ≥50%	Pass/ Fail	Upper PIR (% Recovery) ≤150%	Pass/ Fail
Dichlorodifluoromethane	0.9996	0.50	0.04	0.49	0.14	70.29	pass	126.28	pass
Chlorodifluoromethane	0.9999	0.50	0.02	0.47	0.06	81.86	pass	107.28	pass
Chloromethane	0.9998	0.50	0.02	0.44	0.07	73.59	pass	103.55	pass
vinyl chloride	0.9998	0.50	0.03	0.52	0.10	83.74	pass	125.40	pass
1,3-Butadiene	0.9996	0.50	0.04	0.50	0.15	70.70	pass	129.30	pass
Bromomethane	0.9996	0.50	0.02	0.41	0.07	66.94	pass	96.49	pass
Trichlorofluoromethane	0.9957	0.50	0.03	0.56	0.13	85.66	pass	137.20	pass
Diethyl Ether	0.9998	0.50	0.02	0.51	0.09	83.29	pass	119.57	pass
1,1-Dichloroethene	0.9998	0.50	0.02	0.47	0.10	73.63	pass	113.22	pass
Carbon Disulfide	0.9999	0.50	0.03	0.51	0.10	81.74	pass	123.40	pass
Methyl Iodide	0.9989	0.50	0.02	0.57	0.07	99.51	pass	129.06	pass
Allyl Chloride	0.9998	0.50	0.03	0.47	0.12	68.89	pass	118.54	pass
Methylene Chloride	0.9995	0.50	0.03	0.46	0.13	64.86	pass	118.00	pass
trans-1,2-Dichloroethene	0.9998	0.50	0.02	0.50	0.09	80.92	pass	117.37	pass
Methyl Acetate	0.9999	0.50	0.02	0.51	0.08	86.82	pass	117.18	pass
MTBE	0.9997	0.50	0.02	0.52	0.06	91.16	pass	115.13	pass
TBA	0.9999	0.50	0.03	0.50	0.11	77.62	pass	121.24	pass
Diisopropylether	0.9994	0.50	0.01	0.55	0.06	99.78	pass	121.93	pass
1,1-Dichloroethane	0.9998	0.50	0.02	0.48	0.08	80.82	pass	111.18	pass
ETBE	0.9996	0.50	0.01	0.53	0.03	98.91	pass	111.38	pass
cis-1,2-Dichloroethene	0.9998	0.50	0.04	0.51	0.18	66.36	pass	136.49	pass
Bromochloromethane	0.9994	0.50	0.02	0.51	0.09	83.70	pass	120.30	pass
Tetrahydrofuran	0.9976	0.50	0.02	0.64	0.09	109.74	pass	145.69	pass
Chloroform	1.0000	0.50	0.01	0.49	0.04	91.12	pass	106.59	pass
1,1,1-Trichloroethane	0.9998	0.50	0.01	0.49	0.06	87.78	pass	109.93	pass
Carbon Tetrachloride	0.9999	0.50	0.02	0.50	0.06	87.24	pass	112.19	pass
1-Chlorobutane	0.9998	0.50	0.03	0.52	0.10	82.24	pass	124.04	pass
1,1-Dichloropropene	0.9998	0.50	0.02	0.52	0.09	87.22	pass	122.50	pass
Benzene	0.9996	0.50	0.02	0.52	0.07	90.23	pass	118.34	pass
TAME	0.9993	0.50	0.01	0.54	0.03	102.24	pass	113.18	pass
1,2-Dichloroethane	0.9998	0.50	0.02	0.50	0.07	84.94	pass	114.49	pass

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Application Note

Trichloroethene	0.9998	0.50	0.03	0.50	0.14	72.84	pass	128.30	pass
t-Amyl Ethyl Ether	0.9991	0.50	0.01	0.54	0.05	97.06	pass	117.23	pass
1,2-Dichloropropane	0.9999	0.50	0.02	0.50	0.08	83.39	pass	114.90	pass
Dibromomethane	0.9994	0.50	0.02	0.64	0.09	111.22	pass	146.50	pass
Bromodichloromethane	0.9998	0.50	0.01	0.53	0.06	94.79	pass	117.21	pass
cis-1,3-Dichloropropene	0.9994	0.50	0.03	0.52	0.13	78.23	pass	131.48	pass
Toluene	0.9995	0.50	0.01	0.54	0.04	98.61	pass	116.25	pass
trans-1,3-Dichloropropene	0.9998	0.50	0.03	0.55	0.10	90.12	pass	130.46	pass
1,1,2-Trichloroethane	0.9999	0.50	0.02	0.51	0.09	83.86	pass	121.28	pass
Ethyl Methacrylate	0.9991	0.50	0.01	0.59	0.03	111.44	pass	123.42	pass
Tetrachloroethene	0.9998	0.50	0.01	0.50	0.05	90.08	pass	109.34	pass
1,3-Dichloropropane	0.9999	0.50	0.02	0.52	0.10	85.31	pass	123.83	pass
Dibromochloromethane	0.9999	0.50	0.02	0.52	0.08	88.24	pass	119.18	pass
1,2-Dibromoethane	0.9998	0.50	0.01	0.55	0.04	101.24	pass	118.19	pass
Chlorobenzene	0.9996	0.50	0.01	0.53	0.06	94.71	pass	118.43	pass
ethylbenzene	0.9992	0.50	0.01	0.55	0.04	101.24	pass	118.19	pass
1,1,1,2-Tetrachloroethane	0.9997	0.50	0.02	0.53	0.08	90.82	pass	121.18	pass
M & P Xylene	0.9989	0.50	0.01	0.58	0.04	109.03	pass	124.11	pass
O Xylene	0.9991	0.50	0.01	0.57	0.03	106.91	pass	119.38	pass
Styrene	0.9986	0.50	0.01	0.60	0.05	110.85	pass	129.15	pass
Bromoform	0.9999	0.50	0.03	0.53	0.13	80.14	pass	130.15	pass
isopropylbenzene	0.9992	0.50	0.01	0.58	0.04	107.87	pass	125.84	pass
Bromobenzene	0.9999	0.50	0.02	0.51	0.06	89.89	pass	114.11	pass
1,1,2,2-Tetrachloroethane	1.0000	0.50	0.02	0.52	0.07	90.27	pass	117.73	pass
n-Propylbenzene	0.9995	0.50	0.01	0.57	0.04	104.16	pass	122.13	pass
1,2,3-Trichloropropane	0.9999	0.50	0.02	0.49	0.09	80.31	pass	116.26	pass
2-Chlorotoluene	0.9998	0.50	0.02	0.54	0.08	92.15	pass	123.85	pass
1,3,5-Trimethylbenzene	0.9991	0.50	0.01	0.58	0.06	104.11	pass	127.32	pass
Pentachloroethane	1.000	0.50	0.04	0.53	0.18	70.85	pass	141.15	pass
4-Chlorotoluene	0.9994	0.50	0.02	0.54	0.07	94.27	pass	121.73	pass
tert Butyl Benzene	0.9981	0.50	0.01	0.50	0.03	94.82	pass	105.76	pass
1,2,4-Trimethylbenzene	0.9992	0.50	0.01	0.58	0.04	106.61	pass	124.25	pass
sec-Butylbenzene	0.9992	0.50	0.01	0.55	0.04	102.07	pass	117.93	pass
4-Isopropyltoluene	0.9989	0.50	0.02	0.60	0.06	107.89	pass	132.11	pass
1,2-Dichlorobenzene	0.9997	0.50	0.02	0.52	0.06	91.24	pass	116.19	pass
1,3-Dichlorobenzene	0.9998	0.50	0.01	0.52	0.04	95.75	pass	113.39	pass

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Application Note

1,4-Dichlorobenzene	0.9997	0.50	0.02	0.50	0.07	86.23	pass	114.34	pass
n-Butylbenzene	0.9991	0.50	0.01	0.57	0.03	107.44	pass	119.42	pass
Hexachloroethane	0.9995	0.50	0.04	0.55	0.16	78.30	pass	141.70	pass
1,2-Dibromo-3-Chloropropane	0.9999	0.50	0.04	0.54	0.15	77.87	pass	136.98	pass
1,2,4-Trichlorobenzene	0.9995	0.50	0.01	0.54	0.04	99.81	pass	116.76	pass
Hexachlorobutadiene	0.9996	0.50	0.02	0.52	0.09	84.72	pass	122.14	pass
Naphthalene	0.9987	0.50	0.01	0.62	0.05	114.85	pass	133.15	pass
1,2,3-Trichlorobenzene	0.9993	0.50	0.01	0.59	0.04	109.87	pass	127.84	pass

Table 5: Calibration and MRL Data for proposed USEPA Method 524.4

In addition to the calibration curve and the MRLs, samples were collected from local tap water sources to be analyzed. 40mL vials containing the required preservatives (200mg maleic acid and 25mg ascorbic acid) were filled with tap water from Centerville, Deerfield Township, Deer Park, and Mason, OH. These samples were stored in the refrigerator overnight and analyzed using USEPA Method 524.4 to determine the VOCs present in each drinking water source. **Figure 2** illustrates a Total Ion Chromatogram (TIC) of a drinking water sample. Only trihalomethanes (THMs) were observed in these drinking water samples. The USEPA regulations limit the total THM concentrations to below 80ppb because of possible liver, kidney or central nervous system problems and/or increased risk of cancer with long –term exposure. **Chart 1** illustrates the results.

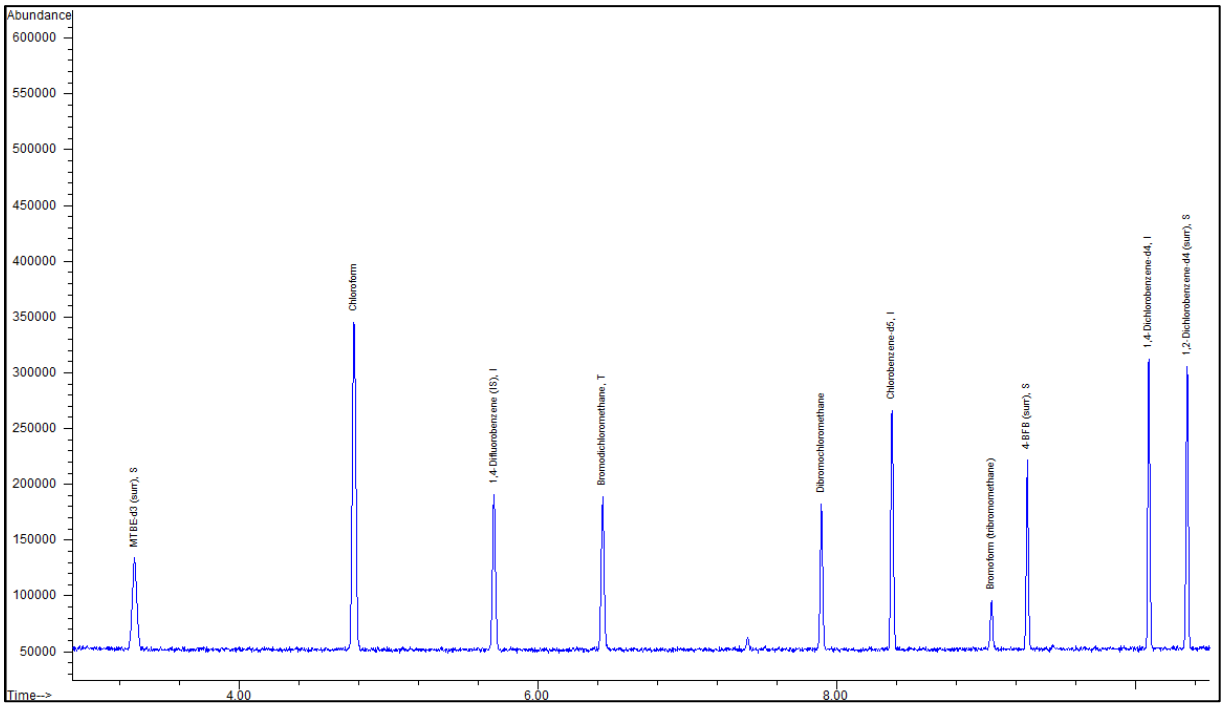

Figure 2: TIC of a Drinking Water Sample from Deerfield Township, Ohio.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Using Nitrogen Purge Gas for US EPA Drinking Water Methods

Application Note

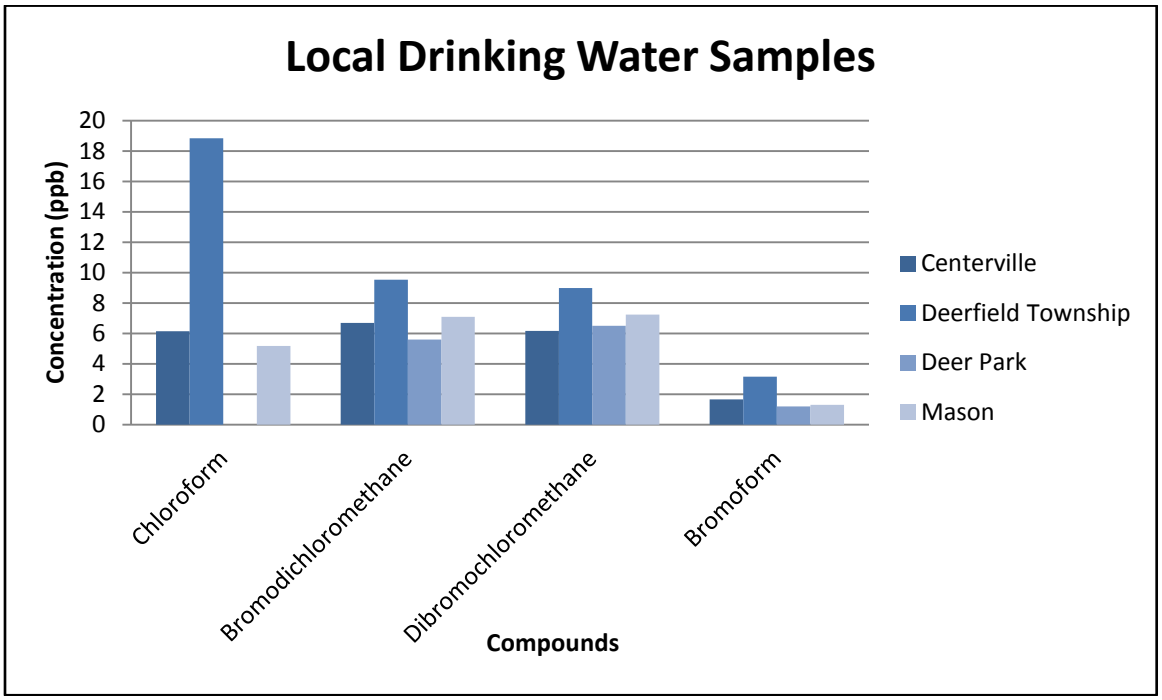

Chart 1: Results for Local Water Samples Analyzed with USEPA Method 524.4

Conclusions

When dealing with drinking water analyses, accuracy and precision are important due to the impact on public health and safety. This study demonstrates the capabilities of the Teledyne Tekmar Stratum PTC and AQUATek 100 Autosampler with a chiller coupled with an Agilent 7890/5975C w/TAD GC/MS. All performance criteria outlined in the proposed USEPA Method 524.4[1] were met. All compounds passed the Minimum Reporting Level (MRL) criteria as outlined in Method 524.4, verifying the suitability of this system for drinking water analysis. The flexibility of the purge and trap parameters allows labs to optimize their methods to increase efficiency and throughput while use of nitrogen as the purge gas allows for labs to reduce costs for analysis.

References

1. USEPA Method 524.4, “Measurement of Purgeable Organic Compounds by Capillary Column Gas Chromatography/Mass Spectroscopy (GC/MS),” Revision 1, 2011.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com