

Determination of Volatile Organic Compounds (VOCs) in Various Drinking Water Sources by GC/MS

Application Note

By: *Nathan Valentine*

Abstract

Consumers have become increasingly concerned with the quality of their drinking water. So much so, that bottled water is a multi-billion dollar industry. But are such concerns over water quality justified? This study will evaluate drinking water sources with concern to volatile organic compounds (VOCs), of regulated sources, such as tap and well water, as well as largely unregulated sources used in bottled water. VOC data will be presented from various drinking water sources using a Teledyne Tekmar Stratum Purge and Trap Concentrator (PTC) and an AQUATek 100 Autosampler in conjunction with a Varian 210-MS Ion Trap GC/MS. Differences in VOC content of the samples will be discussed.



Introduction

With Americans becoming increasingly health conscious and concerned with potential exposure to chemicals, businesses have made movements to create more products that are safer for the consumer and the environment. Bottled water has also greatly benefitted from these health concerns and is seen as a safer, cleaner alternative to tap water.

Unlike tap water, which has USEPA mandated testing for contaminants; bottled water is regulated by the FDA as a beverage and with much less stringent demands for testing with regards to frequency and transparency. In this study, the volatile organic compound (VOC) content of different sources of drinking water will be compared using USEPA method 524.2¹. VOCs are known drinking water contaminants with potentially harmful long- and short-term health effects. Comparison of the results of the various water sources will help determine the validity of concerns over tap water safety and if bottled water is worth the cost.

For this study, a Stratum PTC was used in conjunction with an AQUATek 100 Autosampler. This set-up allows for complete automation of sample preparation for the analysis of liquid samples for purge and trap. Through the features the AQUATek 100 provides, such as the 100-position sample tray and standard addition vessels, efficiency and throughput can be greatly increased, leading to cost and time savings.

Utilizing a Varian 210-MS Ion Trap GC/MS, a linear calibration was performed and percent Relative Standard Deviation (%RSD) was evaluated over the entire calibrated range using Relative Response Factors (RRFs). Additionally a Method Detection Limit (MDL) study was performed for the full list of compounds. A 25mL purge volume was used and all performance criteria required by USEPA Method 524.2¹ were met.

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 Autosampler were coupled to a Varian 431-GC and a Varian 210-MS Ion Trap Detector for analysis. Teledyne Tekmar's proprietary #9 trap was the analytical trap used. The GC was configured with a Varian FactorFour VF-624 20m x .15mm x .84µm column. The GC/MS parameters are outlined in Tables 1 and 2. Table 3 outlines the Stratum PTC and AQUATek 100 Autosampler conditions.

GC Parameters	
GC:	Varian 431-GC Gas Chromatograph
Column:	Varian FactorFour VF-624 20m x .15mm x .84µm (P/N CP9100)
Oven Program:	35° C for 2 min, to 200° C at 10° C/min, for 0 min, to 240° C at 50° C/min
Inlet:	220° C
Column Flow:	0.8mL/min
Gas:	Helium
Pressure:	28.7 psi
Injector:	1177 Split/Splitless 1.0mm ID open liner
Split Ratio:	20:1 initial, 100:1 for 5 min, 20:1 after 5 min

MS Parameters	
MSD:	Varian 210-MS Ion Trap Detector
Manifold Temp:	60° C
Transfer Line Temp:	220° C
Ion Trap Temp:	190° C
Solvent Delay:	1.0 min
Target TIC:	12,000
Scans Average:	4µscans
Multiplier Offset:	±100
Max Ionization Time:	25,000
Scan Range:	47-150 1.0 min to 2.40 min 35-260 4.0 min to 21.0 min

Tables 1 & 2: GC and MSD Parameters

Stratum PTC and AQUATek 100 Parameters			
Variable	Value	Variable	Value
Pressurize Time	0.95 min	Purge Time	11.00
Sample Transfer Time	1.25 min	Purge Temp	20° C
Rinse Loop Time	0.85 min	Purge Flow	40mL/min
Sweep Needle Time	0.35 min	Dry Purge Time	0.0 min
Bake Rinse	On	Dry Purge Temp	20° C
Bake Rinse Cycles	1	Dry Purge Flow	100mL/min
Bake Rinse Drain Time	0.60 min	GC Start	Start of Desorb
Presweep Time	0.35 min	Desorb Preheat Temp	245° C
Water Temp	90° C	Desorb Drain	On
Valve Oven Temp	150° C	Desorb Time	2.00 min
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	4.00 min
Condenser Ready Temp	40° C	Bake Temp	280° C
Condenser Purge Temp	20° C	Bake Flow	200mL/min
Standby Flow	5mL/min	Condenser Bake Temp	200° C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0mL/min		
Sample Heater	Off		
Sample Preheat Time	1.00 min		
Sample Temp	40° C		

Table 3: Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in Blue)

Data Results

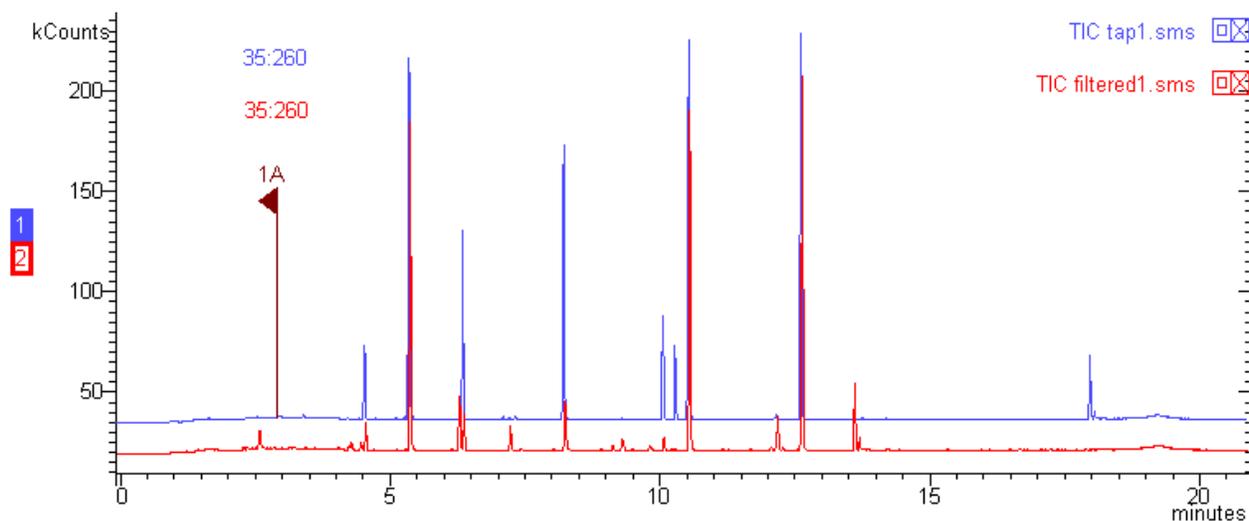


Figure 1: Comparison of Tap Water and Filtered Water

Compound	Tap1	Tap2	Filtered	PurifiedA	PurifiedB	Distilled	SpringA	SpringB	Artesian	Well
Chloromethane	0.261	0	0	0	0	0	0	0	0	0
Acryl Nitrile	0	0	0.792	0	0	0	0	0	0	0
2-Butanone	24.075	0.872	3.039	0	0	0	0.347	0	0	0
Tetrahydrofuran	20.875	0.628	4.049	0	0	0	0	0	0	0
Chloroform	8.413	3.072	1.348	0	0	0	0	0	0	0
1-Chlorobutane	0	0	0	0	0	0	0	0	0.448	0
Bromodichloromethane	15.876	10.341	2.302	0	0	0	0	0	0	0
Toluene	0	0	0.623	0	0	0	0	0	0	0
Dibromochloromethane	28.705	25.306	4.567	0	0	0	0	0	0	0
m,p-Xylene	0	0	0.31	0	0	0	0	0	0	0
o-Xylene	0	0	0.153	0	0	0	0	0	0	0
Bromoform	15.534	18.889	2.614	0	0	0	0	0	0	0
1,2,4-Trimethylbenzene	0	0	0	0	0	0	0	0	0.255	0
1,4-Dichlorobenzene	0	0	1.223	0	0	0	0	0	0	0

Table 1: Results for VOCs in various drinking water sources (ppb)

Even though the FDA does not require the same stringent testing as public water systems, bottled water suppliers obviously do not ignore their water quality in regards to VOCs. Other than tap and filtered water samples, this analysis found little to no contamination. All bottled and well water samples were relatively clear of contamination. On the other hand, tap and filtered water samples contained Trihalomethanes (THMs), which are disinfection by products under normal chlorination practices, Tetrahydrofuran (THF)

and 2-butanone (MEK) which are typical out gassing products associated with plumbing systems.

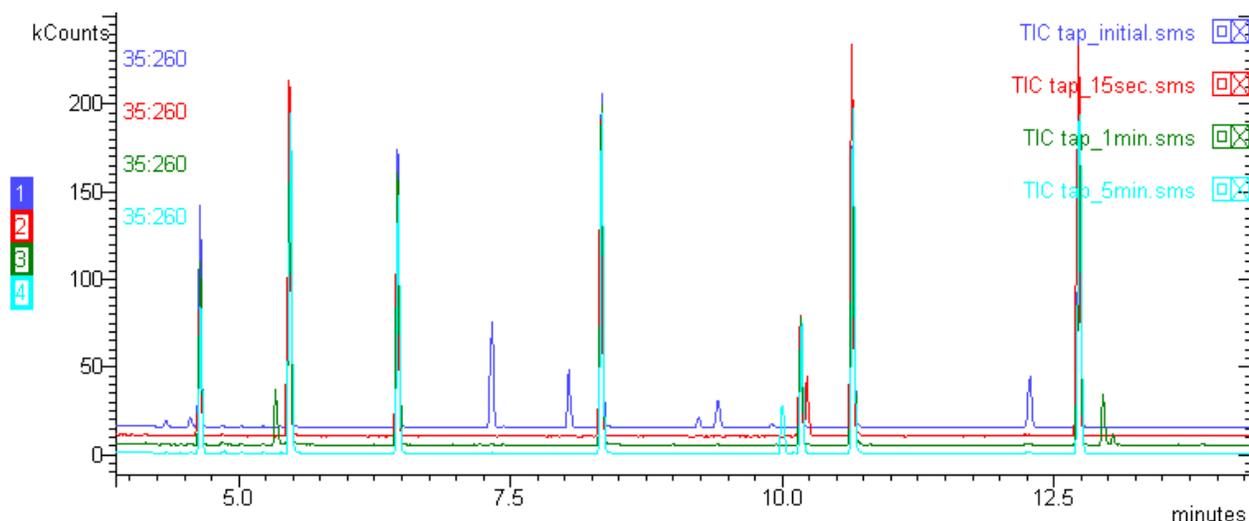


Figure 2: Tap Water VOC Comparison over Time

Compound	Initial	15 sec	30 sec	1 min	2 min	5 min
2-Butanone	4.213	0.458	0.545	0.664	0.599	0.438
Tetrahydrofuran	5.02	0.498	0.683	0.672	0.817	0.366
Chloroform	10.968	6.638	6.357	9.838	7.445	7.044
Bromodichloromethane	19.164	14.061	13.241	20.307	16.125	16.233
Toluene	2.598	0	0	0	0	0
Dibromochloromethane	38.041	30.565	28.351	41.777	35.143	35.028
Ethylbenzene	0.19	0	0	0	0	0
m,p-Xylene	0.72	0	0	0	0	0
o-Xylene	0.103	0	0	0	0	0
Bromoform	25.566	21.268	22.127	30.488	24.575	27.059
1,4-Dichlorobenzene	1.579	0	0	0	0	0

Table 2: Results for VOCs in Tap Water over Time (ppb)

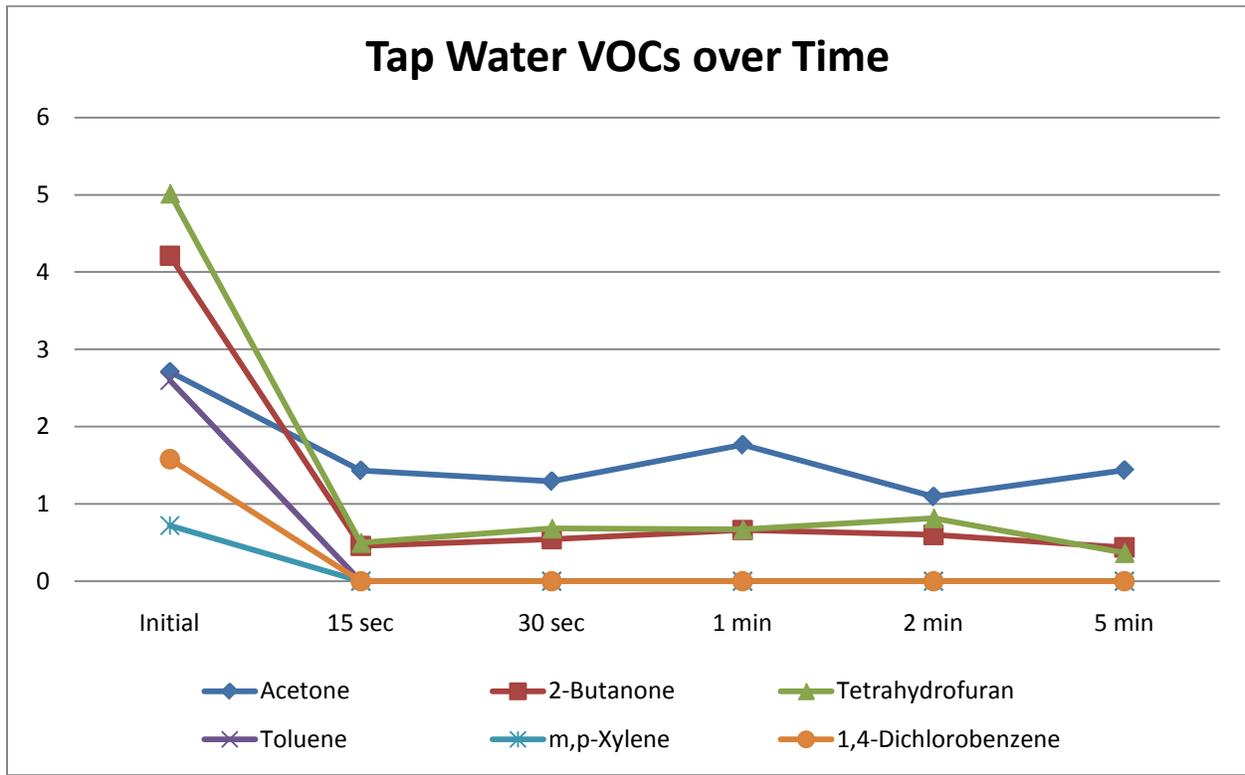


Figure 3: VOCs in Tap Water over Time (ppb)

Inconsistencies in the data led to additional analyses to determine the sources of VOC contamination. The great disparity between the tap water samples could cause issues with reproducibility in this study, requiring further analysis to determine potential causes and replicate the VOC content of tap water over time. Notice that while many of the contaminants diminish over time, the trihalomethanes – chloroform, bromodichloromethane, dibromochloromethane, and bromoform – remain at consistent levels even after five minutes. Trihalomethanes are disinfection byproducts created from the interaction between chlorine and/or bromine and the organic matter in the water being treated. These compounds are inherent to all public drinking water systems which explain their consistency. Since their concentrations decrease over time, the other VOC contaminants are likely extracted at some point between the treatment facility and the tap. The old adage that running the tap for a few minutes to lower the amount of lead in the water also holds true for many of the VOCs. While much of the drinking water lead is associated with older pipes or hot water heaters, these volatile compounds are out gassing compounds that accumulate in the water as it sits in the plumbing lines. Fortunately, simply running the tap for fifteen seconds eliminated or vastly decreased these contaminants.

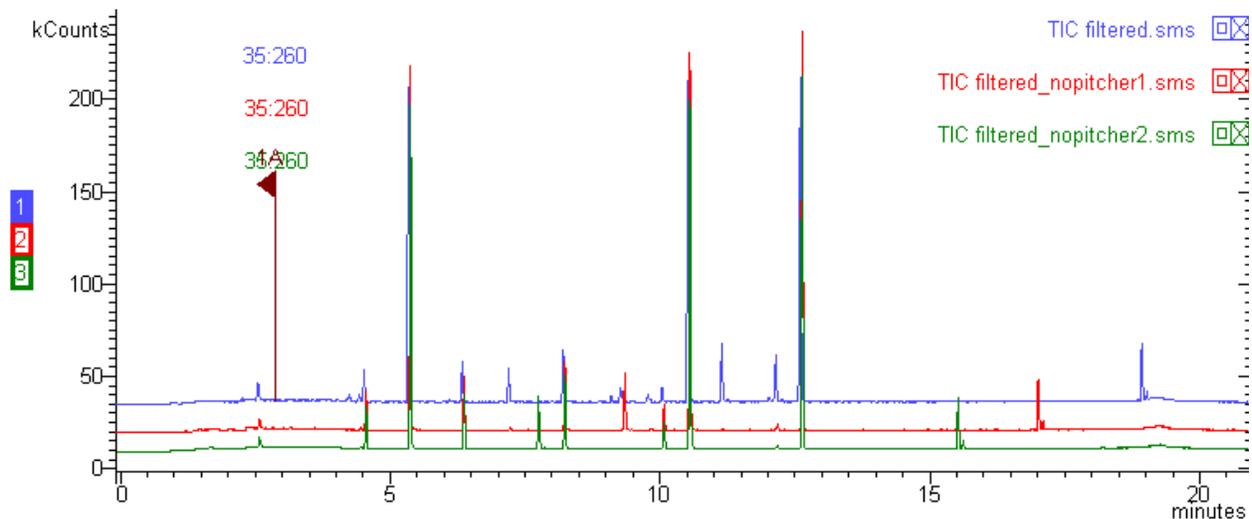


Figure 4: Filtered Water Comparison Measuring Pitcher Contamination

Compound	Filtered from Pitcher	No Pitcher 1st Rinse	No Pitcher 2nd Rinse
Acetone	17.266	7.737	8.736
Acryl Nitrile	0.841	0	0
2-Butanone	2.557	0.429	0.394
Tetrahydrofuran	3.706	1.228	1.048
Chloroform	1.571	1.704	1.945
Bromodichloromethane	2.652	3.092	3.366
Toluene	0.787	0	0
Dibromochloromethane	4.971	6.417	7.159
m,p-Xylene	0.373	0	0
o-Xylene	0.172	0	0
Bromoform	2.998	4.988	5.292
1,4-Dichlorobenzene	1.471	0	0

Table 3: Results for VOCs in Filtered Water (ppb)

Filtered water from a pitcher generated the most VOC contaminants. Determining the source of this contamination required isolating the pitcher and filter. Samples from the pitcher were taken, along with

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samples of water run strictly through the filter into a sample vial. Decreased or lacking concentrations in the filter-only samples showed that these contaminants are likely extracted from the pitcher itself after the water has already been filtered.

Conclusions

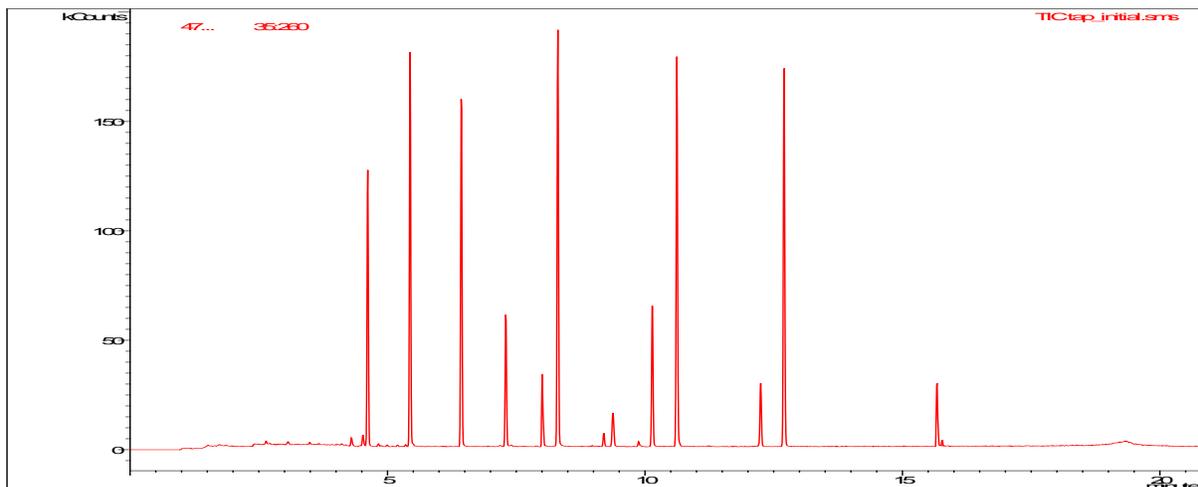


Figure 5: Total Ion Chromatogram of Tap Water

Due to the impact on public health and safety, accuracy and precision are critical when dealing with drinking water analyses. EPA Method 524.2¹ requires strict performance criteria as a result of the development and advancement of Purge and Trap technology. With regards to these stringent requirements, this study demonstrates the capabilities of the Teledyne Tekmar Stratum PTC and AQUATek 100 Autosampler coupled with a Varian 210-MS system. And even though the FDA does not require the same testing protocol as the EPA, analysis of bottled water samples found little to no VOC contaminants. This study found the greatest source of VOC contaminants to be the byproducts (THMs) associated with disinfecting water with chlorine. Due to the nature of public drinking water systems, tap and filtered tap water were the worst culprits, which is why they require the most stringent testing. Since most bottled water is filtered thoroughly and well water is not disinfected, they contain no THMs. They promote cleaner water and, as far as VOC content is concerned, they deliver on that promise. But is the cost - up to 4000+ times more than tap water - worth it?

References

1. USEPA Method 524.2, "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS)," Revision 4.1, 1995.