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

## Application Note

## 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 524.2[1]. 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 to 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.

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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 524.2[1] 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<br>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<br>35-260 4.0 min to 21.0 min |

*Tables 1 & 2: GC and MSD Parameters*



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| 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)*



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## Data Results

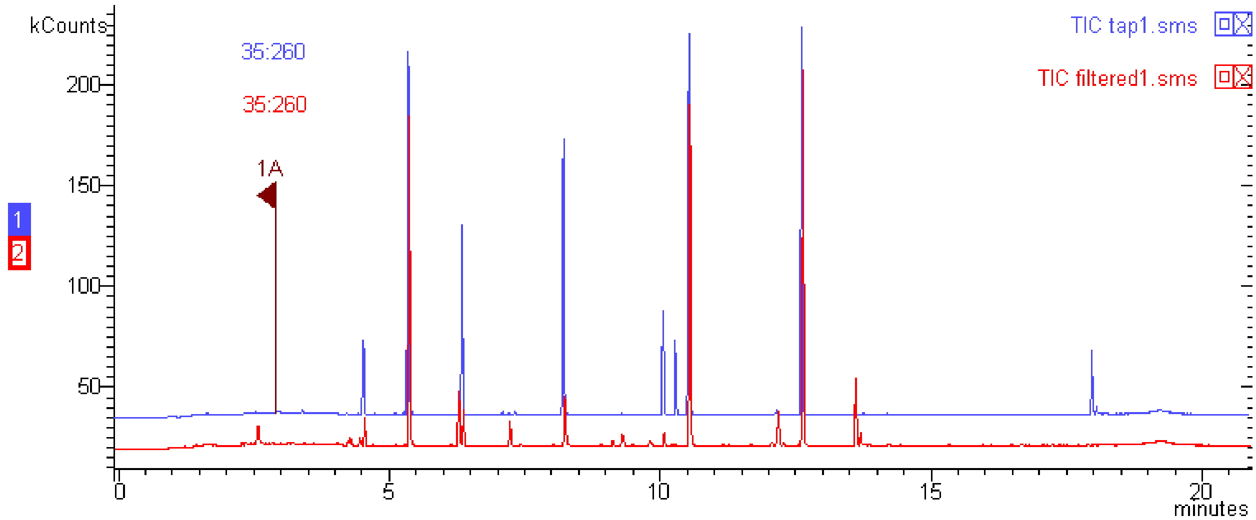


*Figure 1: Comparison of Tap Water and Filtered Water*

| 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)*




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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.

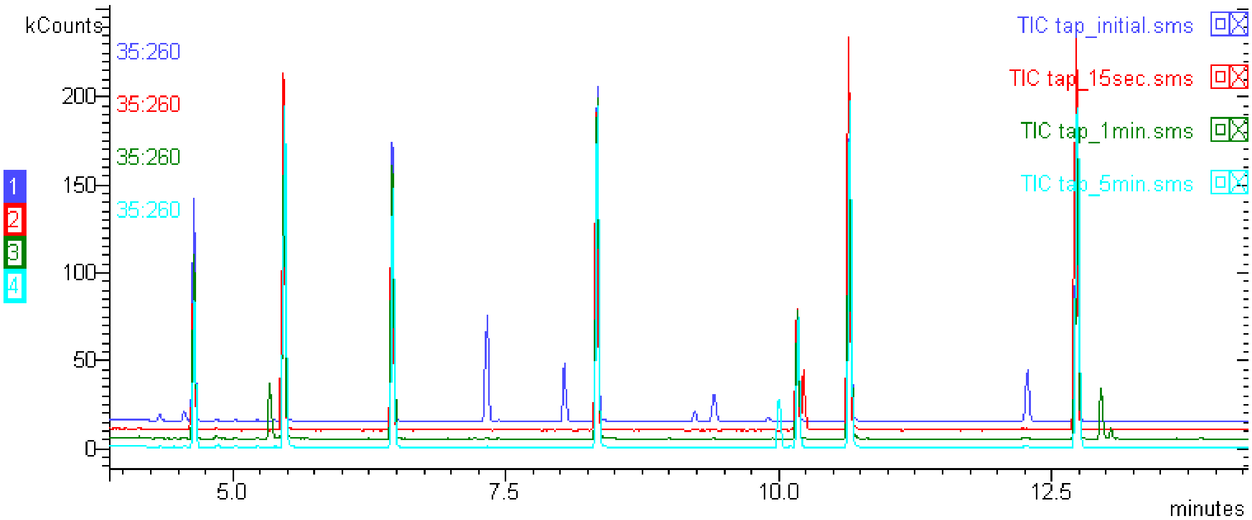


*Figure 2: Tap Water VOC Comparison over Time*

| 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)*



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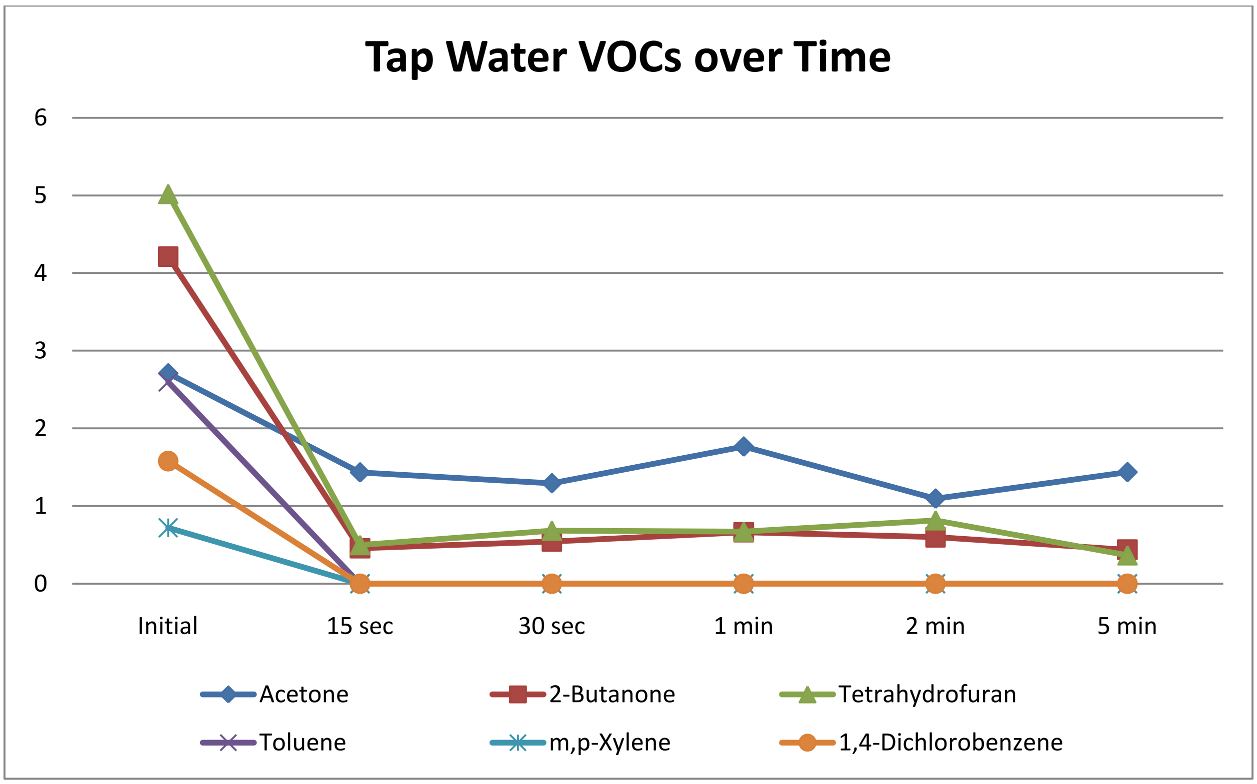


*Figure 3: VOCs in Tap Water over Time (ppb)*

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


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water as it sits in the plumbing lines. Fortunately, simply running the tap for fifteen seconds eliminated or vastly decreased these contaminants.

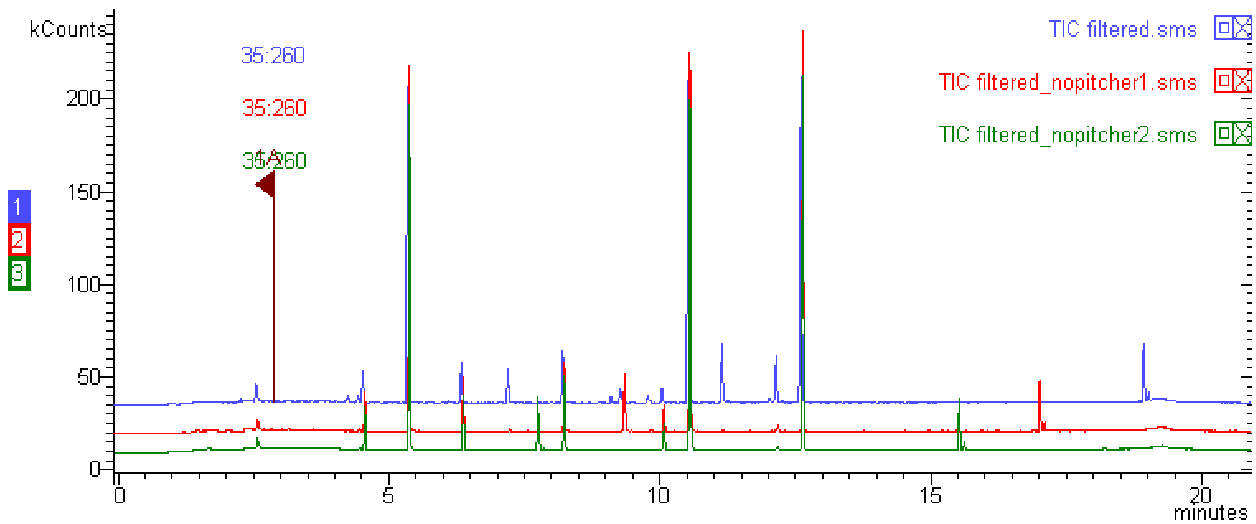


*Figure 4: Filtered Water Comparison Measuring Pitcher Contamination*

| 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 |



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| | | | |
|---|---|---|---|
| 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 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

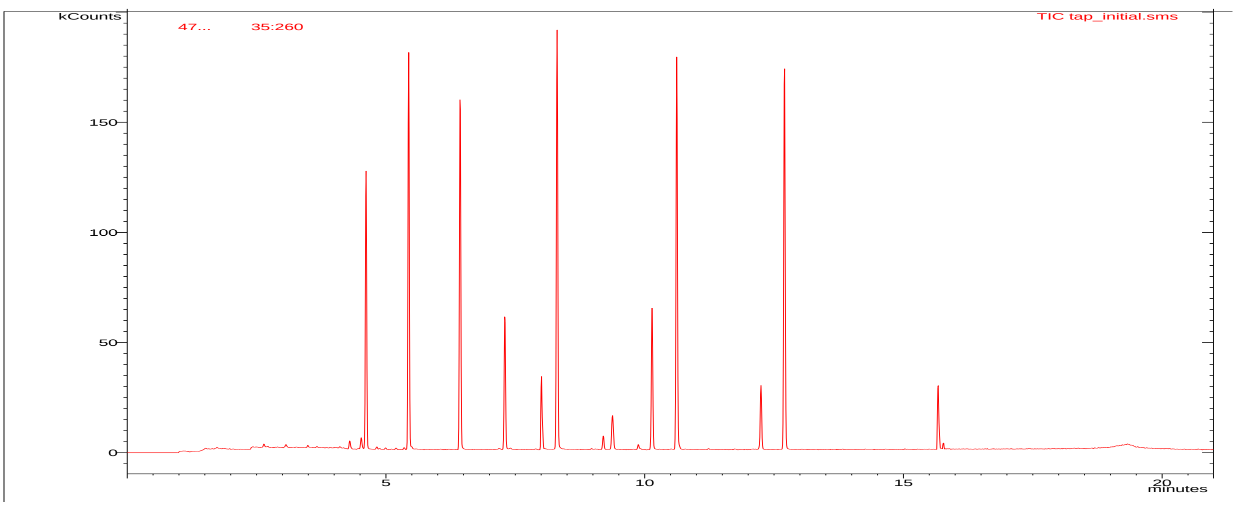


*Figure 5: Total Ion Chromatogram of Tap Water*

Due to the impact on public health and safety, accuracy and precision are critical when dealing with drinking water analyses. EPA Method 524.2[1] 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


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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.




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