

Occurrence of Volatile Organic Compounds in Tap Water: Demonstration of Performance of a New GCMS and a Novel BFB Tune

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1. Introduction

The United States Environmental Protection Agency (EPA) method 524 was implemented to analyze drinking water with the objective of monitoring Volatile Organic Compounds (VOCs) contaminants. The analytical robustness of this method can depend on the purge and trap GC-MS system, which has been designated by the EPA as the analytical instrument to analyze water samples. Shimadzu manufactured the GCMS-QP2010 SE with the intent to be used with method 524 as well as other EPA methods for volatile organic analysis. This instrument has been successful for these methods. However, recently there was a released of the new GCMS-QP2020 Nexis (NX) instrument that has high capabilities of conquering the challenges of method 524. These challenges consist of method robustness and the ability to pass BFB tuning.

The objective of this study is to challenge the capabilities of the new GCMS-QP2020 NX for the analysis of drinking water samples. For this purpose, the target list of volatile organic contaminants included in EPA 524.2 were analyzed in three hundred and eighty-four drinking water samples.

2. Experimental

In the study, an EST Analytical Econ Evolution purge and trap (P&T) concentrator and Centurion WS autosampler were interfaced to the Shimadzu GCMS-QP2020 NX (Figure 1) A VOCARB 3000 (k) analytical trap was configured with the P&T unit. A narrow bore inlet liner was used to improve peak shape and allow high split injections when transferring sample from the purge and trap concentrator. Data was acquired in full scan mode from m/z 35 to 330. Prior to the performing this study, both the GC-MS and P&T instruments were conditioned. The P&T was conditioned by baking the VOCARB 3000 trap at 260 °C for 8 minutes. The GC-MS column was conditioned by removing the column from the MS, but still being connected to the GC inlet, the GC oven temp was ramped from 35 °C to 280 °C and held for 20 mins before returning to the starting method conditions. The experimental parameters for both GC-MS and purge and trap systems are listed in Table 1.

Table 1. GCMS and P&T operating condition

Gas Chromatography	Nexis GC-2030
Injection port mode	Split mode, 40:1 split ratio
Carrier gas	Helium
Injection port temperature (°C)	200
Column	SH-Rxi-624Sil MS, 30 m x 0.25 mmID x 1.4 µm
Flow control mode	Linear velocity, 32 cm/sec
Oven Temperature	35 °C (4.0 minutes), 14 °C/minutes to 220 °C (7minutes)
Mass Spectrometer	QP2020 NX
Interface Temperature (°C)	180
Ion Source Temperature (°C)	200
Detector Voltage	Relative to Tune -0.2 kV
Threshold	100
Scan Range	m/z 35 to 330
	Event time 0.18 seconds
Purge and Trap Concentrator	EST Econ Evolution and Centurion Autosampler
Trap	VOCARB 3000
Trap Ready Temp (°C)	35
Mort ready Temp (°C)	39
Desorb Preheat Temperature (°C)	245
Desorb Temperature (°C)	250
Trap Bake Temperature (°C)	260
Mort Bake Temperature	210
Purge Flow Rate (ml/min)	Helium, 40
Dry Purge Flow Rate (ml/min)	Helium, 40
Desorb time (min)	1
Bake time (min)	8
Dry purge time (min)	2
Purge and Trap Autosampler	EST Centurion WS
Sample loop size (µl)	5
Sample fill mode	Loop
Internal standard volume (µl)	5
Surrogate standard volume (µl)	5
Analysis Time	
GC Run Time	34 min



Figure 1 Shimadzu GCMS-QP2020 NX

In this study, there were 77 compounds analyzed in 384 samples. All target compounds were purchased from o2si Smart Solutions, while internal and surrogate standards were purchased from Restek Corporation. Individual stock standard solutions of analytes were prepared by dissolving the target compound in methanol, purge and trap grade, at 100 ppm. Internal and surrogate standards for purging were prepared at 50 µg/L.

Standards were prepared in volumetric flasks with syringes of the appropriate volume and immediately transferred into amber 40 mL Teflon lined septa vials and brought to a pH <2 (typically 2 drops of 1:1 HCl).

The samples for the study were collected from multiple undisclosed locations. The source of tap water were a combination of surface and groundwater. Samples were preserved with ascorbic acid to eliminate residual chlorine. These samples were refrigerated at <4 °C and analyzed within 14 days from sampling.

3. Results and Discussion

Quantitation was conducted between the range of 0.25 – 200 µg/L; calibration curves for selected compounds are displayed in Figure 2.

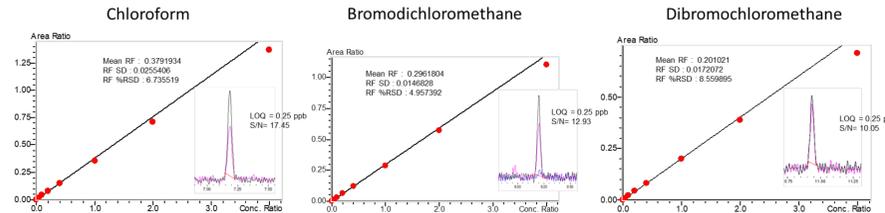


Figure 2. Calibration curves for selected compounds

In addition to monitoring the stability of BFB responses during the BFB daily check, the internal and surrogate standards were analyzed to determine the stability of the overall BFB tune. The number of injections per sequence ranged from 6 to 60. Using %RSD of the analyte peak area as an indication of the stability of the BFB tune, the results indicate that the tune remained stable for at least the length of this study (384 samples, equivalent to approximately 187 hours of operation).

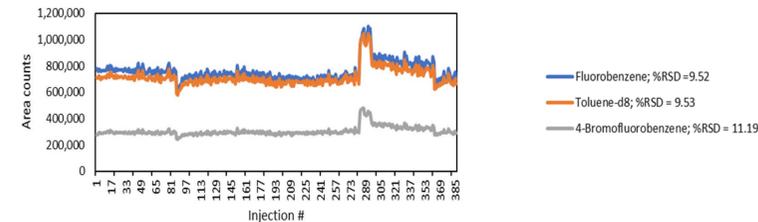


Figure 3. Stability of IS (Fluorobenzene) and SS Peak Area (SS#1:Toluene-d8; SS#2: 4-Bromofluorobenzene) for all injections.

The results indicated that most (96%) target compounds in EPA 524.2 list were non-detected (Figure 4).

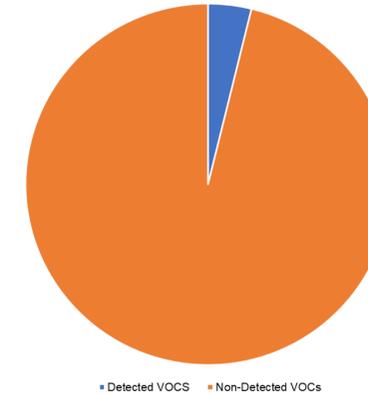


Figure 4. %Occurrence of Volatile Organic Compounds in tap water (n=384)

The compounds detected were chloroform, bromodichloromethane and dibromochloromethane, which are trihalomethanes (THMs) and are bi-products of water disinfection. An average concentration of the detected analytes per sampling location was calculated. Figure 6 displays the average concentration as well as the standard deviation for the detected compounds. As expected, the THMs detected in the samples presented higher concentrations in locations serviced by utilities treating surface water than in those with private wells as the source, since the later are not normally disinfected with chlorine before distribution.

During this study, the impact of filtration on the removal of THMs was also observed. In one sampling location (Sample # 9) both tap water and filtered tap water were collected and analyzed. Figure 5 illustrates the percent removal of THMs by two different water filters.

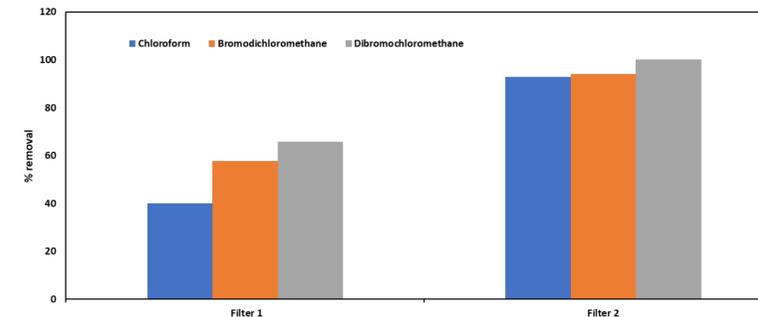


Figure 5. Filtration effect of THM in tap water

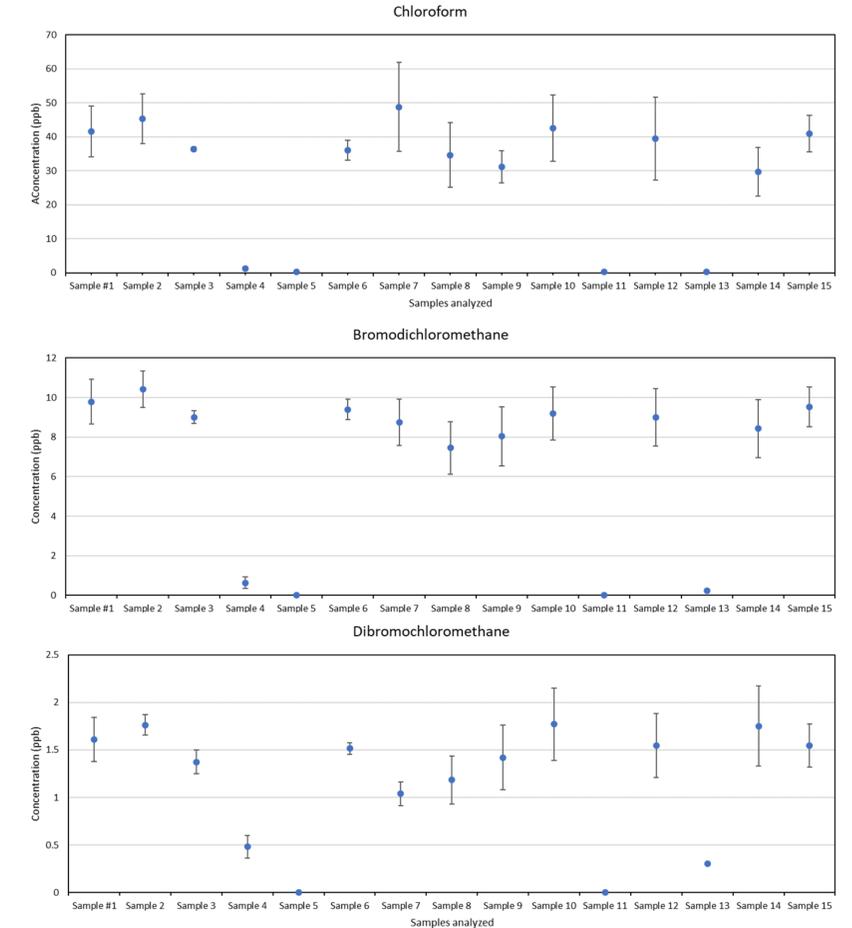


Figure 6 THMs detected in sample analysis

4. Conclusion

The study shows that using the GCMS-QP2020 NX system and the new tuning algorithm, reliable instrument performance and passing BFB criteria evaluations over an extended period can be obtained for the analysis of VOCs. BFB tuning were able to pass the EPA criteria for this method during the analysis of more than 384 samples. As a determination of stability, the precision of internal standards and surrogates was less than 12 %RSD during the study period, thereby indicating that this novel tuning results in a stable instrument and meets the quality assurance criteria included in method 524.2.