A Comparative Study of TOC and THM Analysis of Municipal Drinking Water Using Heated Sodium Persulfate Oxidation and a Novel Approach to EPA Method 524.4

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Introduction

Total organic carbon is an important indicator of water quality throughout the water treatment process. Raw source water is progressively treated to remove particulate matter and natural organic matter (NOM). Humic acid and fulvic acids contained in the residual NOM of water undergoing disinfection by chlorination react with chlorine to form by-product compounds, such as trihalomethanes (THMs) and haloacetic acids (HAAs), which have been linked to cancer. THMs continue to form during drinking water distribution due to excess chlorine levels required to maintain microbial disinfection.

TOC analysis is a quick and effective indicator of NOM and THM levels in source water and finished water. However, TOC analysis cannot be substituted for THM analysis, which requires significantly more time. The relationship between TOC from natural organic matter (NOM) in raw water, TOC levels reduced during treatment, TOC and THMs in finished drinking water, and TOC and THMs from points in the distribution system must be established in a timely manner for effective operation of the water treatment process.

Most United States Environmental Protection Agency (USEPA) methods for analysis of volatile organic compounds (VOC's) call for extraction of the analytes by purging with helium for 11 minutes at 40 mL/minute, making purge-and-trap (P&T) one of the largest consumers of helium in the laboratory. Many labs are seeking less expensive alternatives to the gas and have turned to nitrogen as a viable option. Compared to helium, nitrogen is abundantly available, inert, safe to use, and currently a third of the price of helium, resulting in significant cost savings.

This whitepaper will present comparative data from TOC analysis employing the heated sodium persulfate oxidation technique in USEPA-approved Standard Method 5310C, and an improved approach to THM analysis using USEPA Method 524.4. Any relationship between TOC and THM concentration will be demonstrated and an understanding of the influence of chlorine dosing, time and other factors on each measurement parameter investigated.

Experimental

Heated Persulfate Oxidation

Virtually all organic compound dissolved in water can be oxidized by heated sodium persulfate ($Na_2S_2O_8$) oxidation. Concentrated solutions (1 or 1.5 M) can effectively oxidize organic matter in the form of colloids, macromolecules, and suspended solids.

Sodium persulfate is highly soluble in water:

$$Na_2S_2O_8 + H_2O \longrightarrow Na^+ + S_2O_8^{(-2)}$$

When heat is applied sulfate and hydroxyl radicals are formed by the following reactions:

$$S_2O_8^{(-2)} + 2H_2O \longrightarrow 2SO_4^{(-2)} + 2H^+ + 2OH$$

$$S_2O8^{(-2)} + 2H_2O \longrightarrow 2SO_4^{(-2)} + 2H^+ + H_2O_2$$

$$2H_2O_2 \longrightarrow 2OH^- + O_2$$

The oxidation of organic molecules requires 2.5 – 3 sulfate or hydroxyl radicals per carbon atom.

Instrumentation used in this study included an OI Analytical Aurora 1030W laboratory TOC analyzer equipped with a model 1088 rotary autosampler. Instrument settings for this study are summarized in Table 1.

Table 1. OI Analytical Aurora 1030W Instrument Settings

Parameter	**Aurora 1030W**
Analysis Mode	NPOC
Sample Volume	5.0 mL
Phosphoric Acid Volume	0.5 mL
Persulfate Volume	2.0 mL
TIC Reaction Time	1.5 min
TOC Reaction Time	3.0 min
TOC Detection Time	3.0 min
Calibration Standard	KHP – C9H8O4K
Calibration Points	0, 1.0, 5.0, 10, 25 ppmC

The Aurora 1030W and 9210p TOC analyzers both remove inorganic carbon internally by acidification followed by purging with nitrogen (1030W) or air (9210p). Once inorganic carbon is removed, the persulfate reagent is added and the sample is quantified by a non-dispersive infrared detector (NDIR) and the result reported as TOC content in both mass and concentration.

Calibration

The same analyst using the same source of neat material prepared reagents for each analyzer. Low TOC laboratory reagent water was used to prepare rinse water and reagents. Certified calibration standards were obtained from ULTRA Scientific and are available from OI Analytical. Both instruments were calibrated using potassium hydrogen phthalate (KHP) as a carbon standard. Carbon-free water was used as a zero standard and for the preparation of reagents.

Purge and Trap – GC/MS

This study is based on volatiles analysis by GC/MS; USEPA Method 524.4. Instrumentation for this study included an OI Analytical Eclipse 4660 Purge & Trap Sample Concentrator, an OI Analytical 4100 Sample Processor, and an Agilent 7890A/5975C GC/MS. Because the nitrogen molecule has a higher heat capacity than helium and is able to withdraw more thermal energy from the solution through which it is purged, it is necessary to increase the thermal energy present in the purged volume. For that reason, several changes were made to the standard conditions including slowing purge flow to 35-37 mL/min, increasing purge temperature to 55 °C, and installing a 0.6 mm draw-out plate in the mass spectrometer. Instrument settings for this study are summarized in Table 2.

A ten-point calibration was prepared with concentrations ranging from 0.5 ppb to 40 ppb. Standards were purged for 8 minutes with zero-grade nitrogen. Following purge, the standards were desorbed for 0.5 minutes onto a Restek RTX-VMS 20 meter column. Response factors were calculated using the internal standard approach. Response factors and %RSD for all compounds were checked in accordance with method 524.4.

Table 2. Purge & Trap, 4100 Sample Processor, and Agilent 7890A/5975C GC/MS Instrument Settings

Purge & Trap	**Eclipse 4660 P&T Sample Concentrator**
Trap	#10 trap; Tenax®/Silica gel/CMS
Purge Gas	Zero grade Nitrogen at 45 mL/min
Purge Time	8 min
Sparge Mount Temperature	45 °C
Sample Temperature	45 °C
Desorb Time	0.5 min
Bake Time	4 min
OI #10 Trap Temperature	Ambient during purge 180 °C during desorb pre-heat 190 °C during desorb 210 °C during bake
Water Management	120 °C during purge Ambient during desorb 240 °C during bake
Transfer Line Temperature	150 °C
Six-port Valve Temperature	150 °C
Autosampler	**4100 Water/Soil Sample Processor**
System Gas	Zero grade Nitrogen
Purge Gas	Zero grade Nitrogen
LV20 Pressure	8.0 psi
Gas Chromatograph	**Agilent 7890A**
Column	Restek RTX-VMS 20 meter, 0.18 mm ID, 1 μm film
Carrier Gas	Zero grade helium
Inlet Temperature	250 °C
Inlet Liner	1.5 mm Direct
Column Flow Rate	0.6 mL/min
Split Ratio	40:1
Oven Program	Hold at 40 °C for 1.5 min 16 °C/minute to 180 °C 40 °C/minute to 220 °C Hold at 220 °C for 1.0 min Total GC run is 12.25 min
Mass Spectrometer	**Agilent 5875C**
Mode	Scan 35 – 300 amu
Scans/Second	5.19
Solvent Delay	1.40 minute
Trasfer Line Temperature	250 °C
Source Temperature	300 °C
Quadrupole	200 °C

Results & Discussion

The majority of samples were collected from the greater Bryan-College Station, TX area by the employees of OI Analytical in College Station, TX. In general, most samples were collected in a 45-mile radius of the OI Analytical office. Additional samples were collected from surrounding communities as far away as Houston, TX (90 miles) and Concho County, Texas (approximately 250 miles). Instructions were provided on proper collection techniques. Samples were collected in standard, 40-mL VOA vials. Samples collected for THM analysis were preserved with Ascorbic and Maleic acids according to the method. A summary of the results is shown in Table 3.

Table 3. Summary of Water Sample Results

Location	Source	$CHCl_3$	$BrCl_2CH$	$ClBr_2CH$	$CHBr_3$	Total THM (ppb)	TOC (ppm)
Wellborn	Tap	7.22	4.51	1.66	0.22	13.61	1.987
Bryan	Tap	0.18	0.34	1.00	1.18	2.70	0.480
Wickson	Tap	0.48	0.80	1.37	0.73	3.38	0.415
Somerville	Tap	1.01	0.77	0.75	0.97	3.50	1.124
Wickson	Tap	1.52	1.37	1.54	0.50	4.93	0.685
Wickson	Tap	4.67	9.92	12.77	4.74	32.10	0.655
College Station	Tap	0.64	1.87	5.52	7.29	15.32	0.384
College Station	Tap	0.64	1.60	4.79	6.20	13.23	0.366
Bryan	Tap	1.67	5.55	14.69	18.26	40.17	0.439
Wickson	Tap	3.98	7.89	11.92	4.10	27.89	0.571
College Station	Tap	0.58	1.55	4.58	6.55	13.26	0.378
Kurten	Well	0.00	0.00	0.00	0.00	0.00	0.791
College Station	Tap	1.69	4.20	12.33	16.02	34.24	0.506
Bryan	Tap	1.56	4.06	11.62	14.81	32.05	0.447
Washington County	Tap	1.06	2.18	4.49	4.40	12.13	0.407
Bryan	Tap	1.34	4.15	11.92	15.18	32.59	0.521
Wellborn	Tap	4.80	2.25	0.84	0.00	7.89	1.707
Montgomery County	Well	0.00	0.00	0.00	0.00	0.00	0.248
Calvert	Well	0.00	0.00	0.00	0.00	0.00	0.485
Calvert	Tap	0.66	1.15	3.97	9.53	15.31	0.496
Hearne	Tap	0.31	0.53	2.01	6.24	9.09	0.350
Bryan	Tap	0.93	2.96	8.73	12.08	24.70	0.642
Bryan	Tap	1.66	5.12	13.95	17.44	38.17	0.641
Bryan	Tap	1.60	4.90	14.43	18.33	39.26	0.500
Houston	Tap	12.68	5.22	1.46	0.27	19.63	3.299
Houston (SE)	Tap	13.50	6.34	1.84	0.00	21.68	4.767
Wellborn	Tap	4.10	2.43	1.00	0.27	7.80	3.302
Navasota	Tap	0.33	1.11	3.44	5.99	10.87	0.443
Concho County	Tap	3.54	10.87	22.57	10.26	47.24	1.801
McCullah County	Tap	0.74	1.16	1.06	0.44	3.40	0.295
Williamson County	Tap	9.18	15.49	16.53	5.16	46.36	2.806
Wellborn	Tap	7.50	4.89	1.73	0.14	14.26	3.946

The private well samples had a TOC range of 0.248 to 0.791 ppm. Total THM concentration for these samples was below the detectable limit. The aquifer that supplies water for these wells was not known. Additionally, the water sources for Hearne, Calvert and other areas not listed below is not known at this time. Likewise, the methods to treat that water are not known.

Water for Bryan-College Station is drawn from wells in the Simsboro Sand that is part of the Carrizo-Wilcox aquifer. Water is pumped from a well at approximately 3000-ft, disinfected with chlorine and distributed to the community. This includes Bryan, College Station and Wellborn. The TOC concentration ranged from 0.384 to 1.987 ppm. The highest TOC samples were from the Wellborn community. Total THM concentration ranged from 2.70 to 40.17 ppb for these samples. On average, the Total THM concentration for Bryan was two to three times the concentration of College Station.

Water for Wickson (Northeast of Bryan) is drawn from the Sparta aquifer from wells at approximately 550 - 900-ft. Water is disinfected, with chlorine and distributed to the community.

Somerville is located approximately 35 miles west of Bryan-College Station and is drawn from Lake Somerville. Water is treated in a conventional water treatment plant through the steps of coagulation, flocculation, filtration, and disinfection before distribution. The TOC concentration was 1.12 ppm and Total THM concentration was 3.50 ppm. This was one of the lowest Total THM concentrations for this study.

Houston is located 90 miles south of Bryan-College station. Surface water sources supply the city with water. Water is treated in conventional water treatment plants before distribution. TOC concentration ranged from 3.23 to 4.77 ppm and Total THM ranged from 19.63 to 21.68 ppb. Surprisingly, of all the samples that were taken for this study, the total THM concentration is primarily the result of the brominated compounds: bromodichloromethane, chlorodibromomethane, and bromoform.

Surprisingly, of all the samples that were taken for this study, the total THM concentration is primarily the result of the brominated compounds: bromodichloromethane, chlorodibromomethane, and bromoform. The percentage of brominated compounds in the total THM concentration ranges from 96 to 37 percent. Of the samples taken in the Bryan-College Station area, the Wellborn sample had the lowest brominated compound concentration of approximately 47 percent. The Houston water samples had the lowest brominated compound concentration at 37 percent.

Figure 1 shows the correlation between TOC and total THM. For total THM, no direct correlation is apparent. In a range of TOC concentration between zero (private well samples) and approximately 0.500-ppm, the total THM concentration ranges from 0 to 40 ppb. This appears to be caused, in large part, to the presence of brominated compounds.

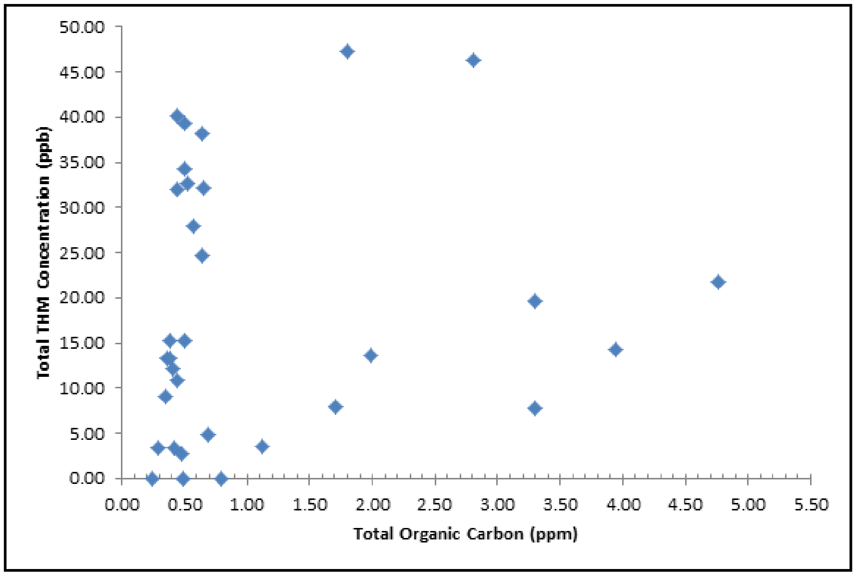

Figure 1. Correlation between TOC and Total THM

Figure 2 shows the correlation between TOC and chloroform. The data shows a direct correlation between TOC concentration and chloroform concentration. However, at approximately equal TOC concentrations some variability in chloroform concentration is found. However, the magnitude of the variability is much less than the brominated compounds.

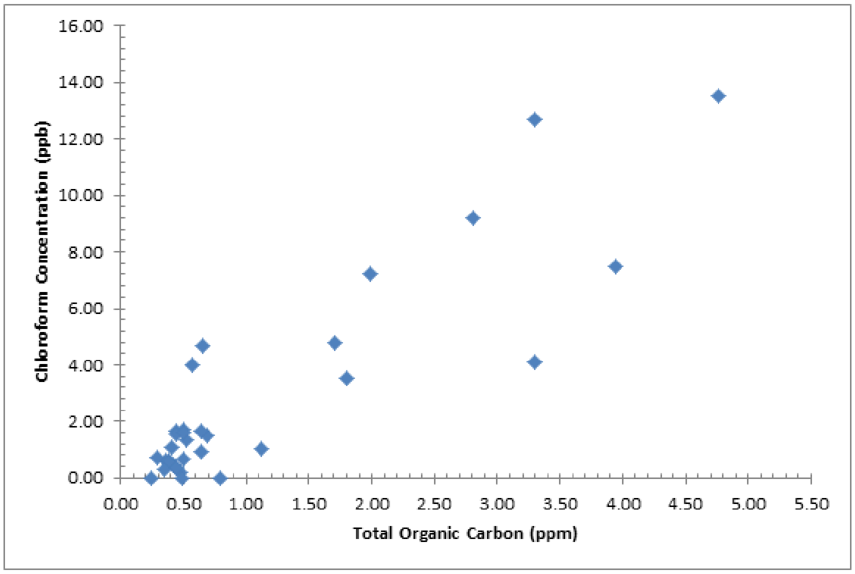

Figure 2. Correlation between TOC and Chloroform

Summary & Conclusions

An approved approach to THM analysis using USEPA Method 524.4 has been demonstrated. This method, coupled with the Model 4100 Sample Processor, should save laboratories both time and money for these analyses.

The total TOC concentration was at an acceptable level for all samples taken for this study. Additionally, the total THM concentration was well below the USEPA requirement of 80-ppb. A direct correlation between chloroform and total TOC was observed for the samples taken for this study. Although no direct correlation between total TOC and total THM was evident, the data shows that the presence of brominated THMs can cause elevated THM concentrations over a very narrow range of TOC concentration.

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Publication 41420416