Determination of Trihalomethanes (THMs), Trihaloacetic Acids (THAAs), and Other Disinfection By-Products (DBPs) in Drinking Water

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THM Application Note

Abstract

The determination of Disinfection By-Products (DBPs) has become extremely important to drinking water companies due to the newly imposed regulatory testing requirements by the EPA[1]. The difficulty and expense involved in regulatory testing has necessitated the need for a low cost, simple, quantitative test for DBPs that can be done in real time. The new method, THM Plus[2], allows for the screening of chloroform, also called trichloromethane (TCM), dibromochloromethane (DCBM), bromodichloromethane (BDCM), tribromomethane (TBM), trichloroacetic acid (TCAA), dichlorobromoacetic acid (DBCAA), bromodichloroacetic acid (BDCAA), tribromoacetic acid (TBAA), chloral hydrate (CH), 1,1,1-trichloro-2-propanone (111-TCP) and 1,1,1-trichloroacetonitrile (TCAN). No extraction or concentration steps are required. No hazardous materials are used or generated in the proposed method. The new colorimetric method can be used to quickly adapt to changing influent water characteristics and to establish trending data for the formation of DBPs throughout the distribution system. Multiple samples from across the United States were analyzed in comparison to the three EPA Methods for DBPs to validate the new method.

Introduction

The EPA's new D/DBP Rule for total trihalomethanes (TTHMs) and haloacetic acids (HAAs), in combination with the complexities and cost of approved testing methods, has created the need for a new simplified method of analysis. In order for a water utility to efficiently manage its disinfection process, real-time data analysis for THMs and THAAs plus other DBPs such as CH, 111-TCP, and TCAN is critical. Most small utilities do not have the equipment or budget to perform the three methods that are required to test for the major DBPs. In addition, the turn-around time for these tests can be anywhere from one to three weeks. A complete DBP screening encompasses three separate EPA methods, as outlined in **Table 1**, in contrast to the proposed method described in **Table 2** that screens for multiple DBPs.

Table 1: Description of EPA DBP Methods

EPA#	Extraction/concentration	Methylation	Separation	Detection	Speciation
524.2	Purge and Trap	None	GC*	MS**	Yes
551.1	Liquid Extraction	Acidic	GC*	ECD***	Yes
552.2	Liquid Extraction	None	GC*	ECD***	Yes

*Gas Chromatograph

**Mass Spectrometry

***Electron Capture Detection

Table 2: Description of Proposed Method

	Extraction/ concentration	Derivatization	Separation	Detection	Speciations
Proposed	None	None	None	Spectrophotometer	No

Utilizing all three EPA Methods to determine an accurate representation of the DPBs in drinking water is necessary due to the multiple classes of DBPs potentially formed. The types of halogenated by-products are formed according

to the organic precursors present, in addition to kinetic factors such as contact time, pH, bromide, chlorine concentration, and temperature. They can be classed in order of abundance in tap water. The first class is the major halogenated by-products THMs and HAAs. Haloacetaldehydes, haloacetones, and haloacetonitriles would be the second class of medium DBPs found in tap water. Halopropionic acids and halonitromethanes are the third and minor class of DBPs[3].

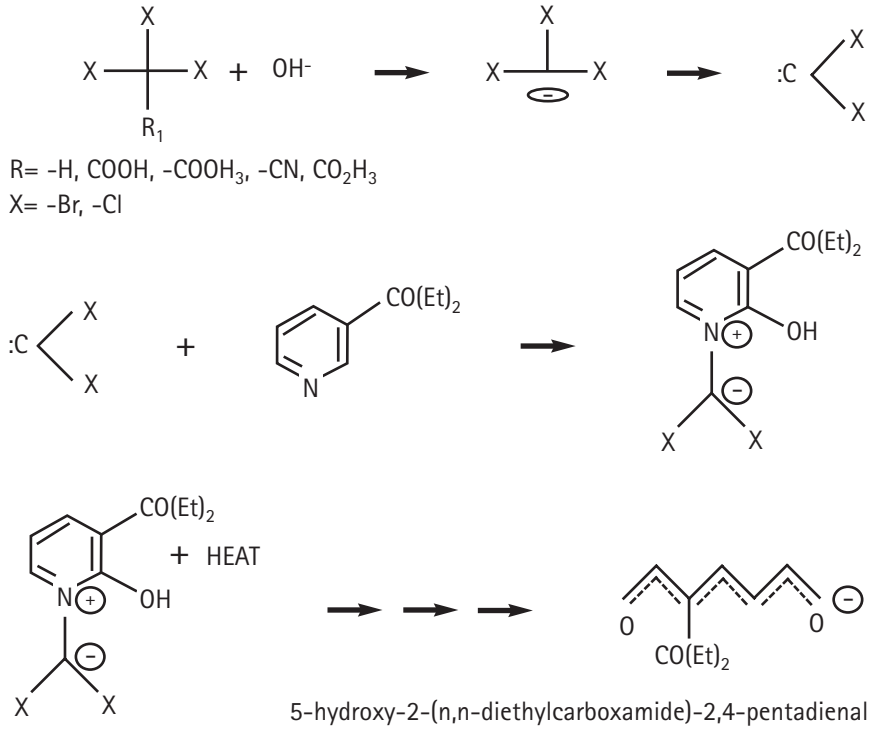
The accuracy, precision, and equivalency of the new method were determined by comparing the new method results to the three EPA-approved methods. Different drinking water samples were analyzed by the new method and by all three EPA methods (524.2, 551.1 and 552.2 expanded to include the mixed halogenated acetic acids). The drinking water samples were spiked with the most abundant DBPs to determine the spike recovery of all methods.

Theoretical Basis

Prior to development of this new method, most colorimetric testing of THMs has utilized the Fujiwara Reaction[4], using pyridine as a reagent. By contrast, the proposed method does not generate hazardous waste or odor.

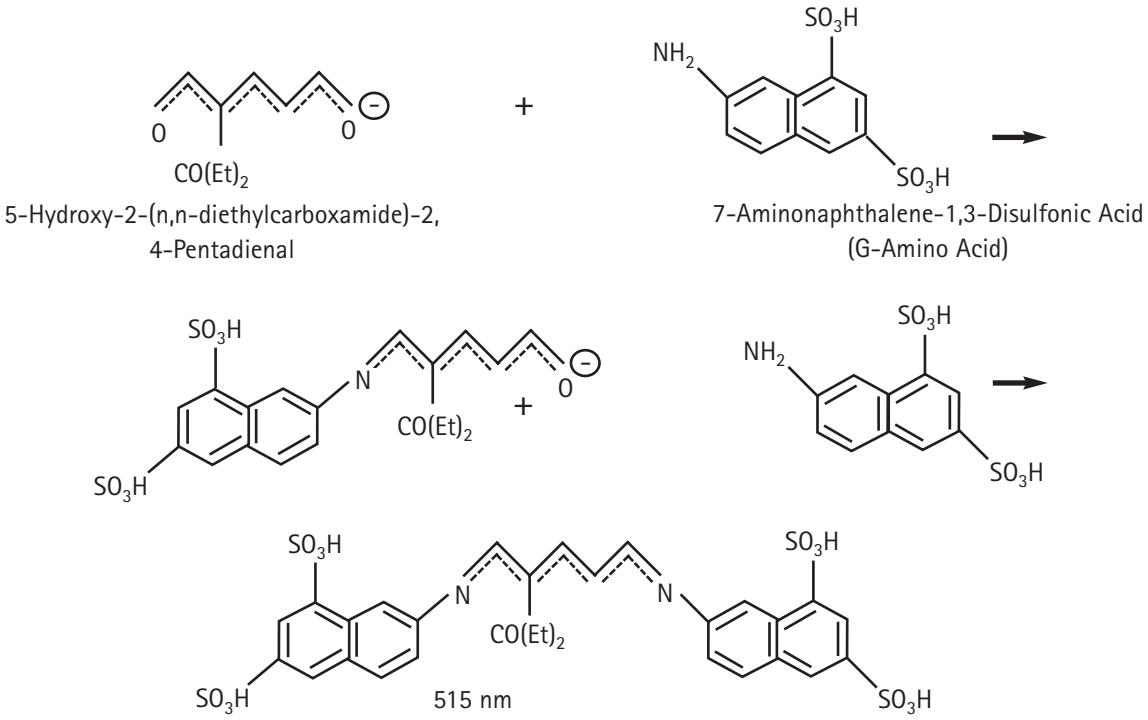
The mechanism of this test is in two stages. In an aqueous sample, trihalogenated species react with n,n-diethylnicotinamide as shown in **Figure 1**. The addition of potassium hydroxide and heat causes the n,n-diethylnicotinamide ring to cleave to form 5-hydroxy-2-(n,n-diethylcarboxyamide)-2,4-pentadienal. This part of the reaction is very analogous to the classical Fujiwara reaction for TCM.

Figure 1: Mechanism Part 1



The 5-hydroxy-2-(n,n-diethylcarboxyamide)-2,4-pentadienal formed reacts with 7-napthalamine-1,3-disulfonic acid (G-Amido acid) as seen in **Figure 2**. The Schiff Base formed absorbs with a broad peak at 515 nm. This orange species follows Beers Law and directly relates to the quantity of trihalogenated species present.

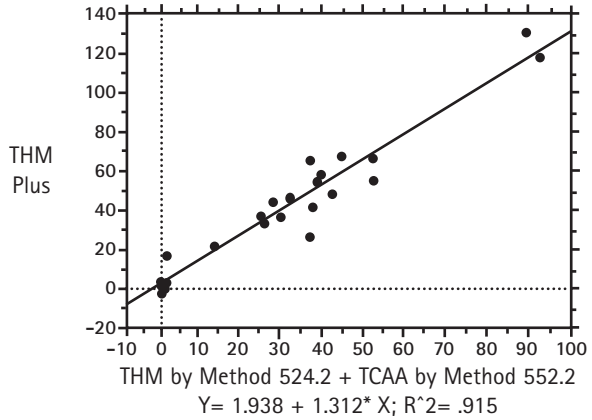
Figure 2: Mechanism Part 2



Preliminary Studies

The first validation study was performed in January 1999. Twenty-seven samples from across the United States were collected and compared to method 524.2, or THMs, and for TCAA from 552.2. Two independent laboratories ran spikes on 13 of the 27 samples for both TCAA and TCM. The proposed method was also spiked to determine recoveries in a wide variety of different water matrices. Samples were collected from sources that were disinfected by chlorination, chloramination, and untreated ground water sources. During the first study, it was observed that the test results were biased high as compared to the reference methods. **Figure 3** represents the first validation study. From this study, the number of DBP methods, which are needed as reference methods, was determined. A correlation was also observed on the ability for the proposed test method test to determine the absence of analytes in samples.

Figure 3: Proposed Method vs. Method 524.2



Spike recovery data is listed in **Table 3**. The excellent recovery of spikes in so many different water sources indicated there was not a matrix effect accounting for the high results. These results suggested using a combination of other methods as the reference values.

Table 3: Spike Recovery Data for 15 Drinking Water Samples from Study 1

	THM Plus 50 ppb as TCM	552.2 TCAA 20 ppb as TCAA	524.2 TCM 20 ppb as TCM
Average	53.8	19.4	21.6
Standard Deviation	3.1	4	2.3
RSD	5.8	20.4	10.7

The second study utilized 13 water samples from the same sources as **study 1**, with the exception that only those water samples containing THM were used. The first study had shown the ability to detect zero when no THM is present. It was here that the independent lab was able to produce peaks on its GC from the 552.2 analysis to show other mixed halogenated acetic acids were present in the water samples. However, this did not account for all of the bias. Further research on the DBPs detected by EPA Method 551.1 were tested for reactivity by the proposed method. It was with this background that the third study, as reported in this paper, was designed and implemented.

Experimental Background

The Hach DR/4000 spectrophotometer was used to read absorbance values. The sodium thiosulfate/potassium hydroxide reagent, n,n-diethylnicotinamide, and G-Amido acid were prepared at Hach Company. Standards were all ordered directly from Chem Services, Inc. from West Chester, Pennsylvania. All standards were diluted using a calibrated positive displacement pipette. The THMs, CH, TCAN and 111-TCP were diluted in isopropyl alcohol and then into water in two to three dilution steps. The THAAs were diluted into organic-free water, also needing one to two additional dilutions. These stock solutions were used as either a spike in samples or in calibrations. All standards were prepared fresh daily.

Experimental Method

For each sample analyzed the following procedure was followed. The reaction and measurements were performed in matched one-inch round glass cells with screw-on Teflon caps. The identical procedure was used for calibration of all eleven analytes. For calibration, organic-free water was used as the blank and digested along with the standards.

1. Five cells were filled with 10 mL of sample. Two were marked "blanks" and three marked "samples."
2. An alkaline solution of sodium thiosulfate was added to dechlorinate the sample and raise the pH.
3. N,N-diethylnicotinamide was added to the samples and the blanks.
4. Three cells marked as samples were placed in boiling water for five minutes.
5. The sample cells were cooled before adding enough acid to lower the pH of the blanks and the samples to 2.5.
6. The samples and blanks were then cooled to room temperature.
7. The G-amino acid was added to all cells.
8. The color was developed for 15 minutes at room temperature.
9. The absorbances of all cells were read at 515 nm on a spectrophotometer using sample water as a blank.
10. The average absorbance of the samples minus the average absorbance of the blanks was used to calculate the amount of trihalogenated DBP present.

Calibration on TCM was performed at eight concentrations ranging from 0 to 220 ppb. The slopes from the calibration are reported in **Table 4**. From 159 points, an R Squared of 0.997 was calculated. The P-Value is 0.001, which shows the actual attained significance. The Mean Square of 206382.041 with the F-Value 25223.858 is an indication that the model describes what is happening with the data. The slope was calculated to be 0.473. The 95% confidence intervals for the slope were 0.467 to 0.479. All analytes detected by this proposed method were calibrated by a similar procedure in the 0 to 220 ppbs as TCM range. The calculated slopes for these calibrations are also listed in **Table 4**.

Table 4: Slopes of Each Analyte Proposed Method Detects and Confidence Intervals

Analyte	Slope: mAbs vs. ppb	95% high	95% Low
TCM	0.473	0.479	0.467
DCBM	0.458	0.491	0.425
BDCM	0.421	0.472	0.370
TBM	0.404	0.434	0.375
TCAA	0.315	0.328	0.302
DCBAA	0.475	0.493	0.457
CDBAA	0.541	0.559	0.524
TBAA	0.412	0.425	0.399
CH	0.442	0.454	0.429
111-TCP	0.574	0.587	0.560
TCAN	0.223	0.251	0.195

At concentrations less than 15 ppb as TCM, all analytes give an average response that has a standard deviation of 0.001 absorbance. Precision data on seven replicates of 60 ppb TCM standard shows a standard deviation of 0.001 absorbance or 2 ppb. Therefore, all analytes below 15 ppb give an equivalent response to TCM. THM and TCAA were the only analytes detected in quantities greater than 15 ppb as TCM. It is valid to use the slope for TCM to calculate the concentration of all eleven analytes.

Results

The third study was performed on seven water samples from the Front Range in Colorado to validate the assumption that more DBPs were being detected than were reported by the independent laboratories in the first two studies. Each sample was split prior to analysis by the proposed method, EPA 524.2, EPA 551.1 and EPA 552.2 (expanded to include all mixed HAAs). Samples 1, 3, 5, 7, and 9 are sample waters and samples 2, 4, 6, 8, 10, 12 and 14 are the spiked samples. **Table 5** is a complete list of the analytes detected by the independent lab. All values are reported as TCM.

Table 5: Independent Laboratory Results for All Analytes Reported as ppb TCM

	524.2	524.2	524.2	524.2	551.1	551.1	552.2	552.2	552.2	552.2
#	BDCM	TBM	TCM	DBCM	CH	T-P	TCAA	BDCAA	CDBAA	TBAA
1	2.6	0.0	28.4	0.0	3.3	1.8	7.3	1.0	0.0	1.0
2	2.6	0.0	83.0	0.0	6.5		17.5	1.0	0.6	0.8
3	1.8	0.0	21.4	0.0	1.9	2.1	8.8	1.2	0.0	1.0
4	1.8	0.0	74.7	0.0	4.0	22.9	21.2	1.4	0.0	0.0
5	6.3	0.0	53.1	0.0	3.4	1.8	14.6	1.7	0.0	1.2
6	6.0	0.0	102.0	0.0	5.6	22.2	30.0	2.2	0.9	0.0
7	9.6	0.0	45.8	1.1	2.7	2.3	15.3	2.9	0.9	1.1
8	9.3	0.0	97.2	1.1	4.4	22.9	25.6	3.0	0.7	1.0
9	2.8	0.0	44.4	0.0	3.3	0.0	8.0	1.0	0.0	0.0
10	2.5	0.0	90.9	0.0	4.6	21.4	17.5	1.0	0.0	1.0
11	1.8	0.0	17.5	0.0	1.9	1.8	5.0	1.0	0.0	0.8
12	1.9	0.0	72.9	0.0	3.0	22.9	13.9	1.0	0.0	0.9
13	11.8	0.0	47.9	1.8	6.6	4.4	10.2	2.6	0.9	0.0
14	11.7	0.0	99.4	1.9	6.7	24.4	17.5	2.4	0.8	0.0

The spikes, as TCM, were 50 ppb TCM, 14.4 ppb CH, 13.1 ppb TCAA, and 13.5 ppb 111-TCP. The spike TCM was within acceptable range. The recovery of the CH and TCAA was low as can be seen in **Table 5**. The proposed method was run immediately after splitting, whereas the samples sent to the independent lab were preserved per EPA guidelines.

Table 6: Spike Recovery of Seven Samples by EPA Methods for Study 3

	TCM 524.2	TCAA 552.2	CH 551.1	111-TCP 551.1
Spiked Amount as TCM	50	13.1	14.4	13.5
Average Recovered	51.7	10.6	1.7	20.7
Standard Deviation	3.2	2.6	1.0	0.5
Percent Loss	3.4	-19.1	-88.2	25.5
RSD	6.2	24.5	58.8	2.4

Table 7 shows the result of converting the concentration of the analytes to ppb as TCM. These values are used to compare the results to the proposed method.

Table 7: Concentrations of DBPs by Various Methods

	1	2	3	4
	THMs by Method 524.2	Column 1 plus THAAs by Method 552.2	Column 2 plus other DBPs by Method 552.2	THM Plus
1	31.0	40.3	45.4	53
3	23.2	34.2	38.1	54
5	59.4	76.9	82.1	92
7	56.5	76.7	81.7	99
9	47.2	56.2	59.5	66
11	19.3	26.1	29.9	42
13	61.5	75.3	86.3	106

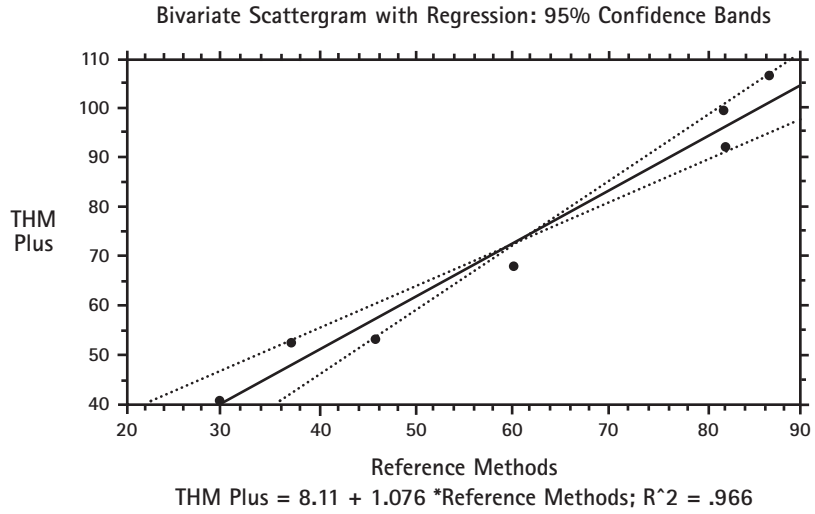
The data generated by comparing method 524.2 versus the proposed method show good correlation but a bias in the results. When the additional DBPs from Method 552.2 and Method 551.1 are incorporated, the proposed method shows a significantly improved statistical correlation. **Table 8** shows improvements in all statistical parameters. The F-Value increasing shows improvement in the model. The decreasing P-Value supports the improvement in the model. R squared values show an improved correlation between the reference methods and the proposed test method.

Table 8: Statistical Analysis of Each Method in Comparison to Proposed Method Results

Method Compared	Slope	95% lower	95% upper	F Value	P Value	R squared
524.2	1.360	1.864	0.856	48.124	.0010	0.906
524.2+552.2	1.133	1.467	0.799	75.933	0.0003	0.938
524.2+552.2+551.1	1.076	1.310	0.843	140.202	<0.0001	0.959

The results from the proposed method versus the sum of the reference methods are shown in **Figure 4**. The 95% confidence error bars were included.

Figure 4 : Plot of Reference Method Concentrations vs. Proposed Method



Discussion/Conclusion

The original scope of this research was to develop a screening method for only THMs. The research shows the test went beyond this scope and developed into a screening test for trihalogenated DBPs. The difficulty in assessing the accuracy and precision of three reference methods, 524.2, 551.1 and 552.2, increased the challenge in determining the accuracy of the THM Plus Method. However, in spite of all these challenges, the data from study 3 clearly shows that the THM Plus Method is fully capable of detecting DBPs and correlates well with instrumental reference methods.

Unlike the reference methods where advanced instrumentation and analytical expertise is required, the THM Plus test allows for quick real-time analysis utilizing equipment readily available in most laboratories. When using the THM Plus method as a screening method for THMs, excellent tracking and process control adjustments can be made immediately and in a cost-effective manner to meet changing influent water conditions. The ability to detect for THAA and other DBPs is also of great value and interest in providing the highest quality drinking water possible.

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References

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