

Monitoring Trihalomethane Levels¹

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ABSTRACT

Trihalomethanes (THMs) have been found in all chlorinated drinking water. Municipal drinking water is generally the sole source of water used by breweries. The U.S. Environmental Protection Agency liquid/liquid extraction procedure followed by analysis with a gas chromatograph equipped with an electron capture detector was used to determine the levels of THMs in water supplied to 10 Canadian breweries. These levels were all well below maximum acceptable health limits set by governmental regulatory agencies. Brewery in-plant water treatment systems were monitored and found to provide brewing water of better quality with regard to THM content than the municipal water. In a small sampling of market beers, the THM levels detected were lower than those in any of the drinking waters analyzed.

Key words: Chlorination, In-plant water treatment, Liquid/liquid extraction, Trihalomethanes, Water

Trihalomethanes (THMs) are a group of organic compounds, named as derivatives of methane, in which three of the hydrogen atoms of methane are replaced by halogen atoms. Chlorine, bromine, and iodine are the halogen atoms that are important in the formation of THMs in water. Normally only four of the possible 10 THMs that can be formed by these three halogens occur in water in significant concentrations. These are trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform). In the few locations where iodide is naturally present or if iodine is used as a disinfectant, iodine-containing THMs can also be formed.

In 1974, Rook (10), working in Holland and Bellar et al (4) in the United States, reported THMs in chlorinated drinking water. Both researchers suggested that these compounds were formed by the reaction of the chlorine with organics in the raw water supply. They theorized that the chloroform was produced by the haloform reaction of the chlorine, whereas the brominated THMs resulted from the reaction of chlorine with the bromide ion in the raw water. The following year, Bunn et al (5) confirmed this hypothesis by producing in the laboratory all 10 THMs containing chlorine, bromine, and iodine atoms. Rook also demonstrated that, in addition to the classic haloform reaction that occurs with compounds containing the methyl ketone structure ($-\text{CO}\cdot\text{CH}_3$), haloform reaction can occur with compounds containing resorcinol (1,3-dione) structures. These structures, present in water as part of the complex structures of the naturally occurring humic and fulvic acids, were shown to be the main source of THMs in chlorinated drinking water (10).

THM formation is dependent on the chlorine demand and the pH of the raw water (2,9,13). Ground water supplies produce low levels of THMs, whereas surface water, which often contain large amounts of color, turbidity, and organic matter, have higher potential for THM formation (2). Seasonal variations have been reported that correlate with supply water temperatures, such that average THM levels recorded during the summer months were as much as 10 times higher than those found during winter surveys from the same sites (2,13).

Chloroform, the most commonly found THM, has been detected in nearly every drinking water supply that uses chlorine as a disinfectant. Its health effects are better understood than those of the other THMs; however, based on structural similarities, a reasonable assumption is that these compounds have similar toxic effects. The concern for the deleterious health effects of THMs in drinking water is reflected in governmental regulations. Health and Welfare Canada (8) has set the maximum acceptable concentration

(MAC) of total trihalomethanes (TTHMs), that is, the sum of the concentrations of chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3), in drinking water at $350 \mu\text{g/L}$. The objective concentration, the ultimate quality goal for both health and aesthetic purposes, for TTHMs is $0.5 \mu\text{g/L}$ or less. A 1980 U.S. Environmental Protection Agency (USEPA) amendment to the Safe Drinking Water Act provides a maximum contaminant level (MCL) for TTHMs of $100 \mu\text{g/L}$ (12).

Breweries are consumers of large quantities of water. The source of this major brewing raw material is normally municipally supplied drinking water, which in most localities has been disinfected with chlorine and therefore contains at least trace levels of THMs. Government regulations ensure the quality of the water for human consumption; however, this could still leave the water unsuitable for the production of beer. For this reason, many breweries have installed in-plant water treatment facilities that include a chlorination step. With such treatment, another parameter of the water supply, the concentration of the unreacted THM precursors, becomes important.

The maximum total trihalomethane potential (MTP) values are used to determine whether ground water systems require monitoring and to evaluate the precursor reduction in treatment facilities that have prechlorination steps for the removal of organic compounds. Acceptable levels of TTHM potential have not been set because, although water leaving municipal treatment plants contains residual chlorine, residence time in the distribution system is relatively short, and tap water samples normally show only slightly higher THM levels than water sampled at the utility. Where breweries operate in-plant water treatment units, the MTP provides an indication of the THM concentrations that might be produced by the additional chlorination and that in turn should be reduced by subsequent treatment such as activated carbon purification.

In the autumn of 1981, we conducted a survey to determine the THM concentrations and the MTP of the waters being supplied to 10 Canadian breweries. Winter samples were taken at each location in January, 1982. In-plant water treatment facilities were monitored for their effects on the THM levels of the water processed, and a small sampling of market beer was analyzed.

EXPERIMENTAL

The USEPA method for the analysis of THMs by liquid/liquid extraction (3) was used.

Gas Chromatographic Instrumentation and Conditions

All THM analyses were done with a Hewlett-Packard 5840 gas chromatograph equipped with a linearized electron capture detector and a $\frac{1}{4}$ -in. o.d. (2 mm i.d.) \times 8-ft glass column packed with 3% SP-1000 on Supelcoport. The inlet and detector temperatures were 200 and 300°C, respectively. The carrier gas was argon-methane (95:5) at a flow rate of 25 ml/min. The column temperature was isothermal at 60°C for 10 min, then increased to 80°C at 20°C/min and held at 80°C for 20 min. A typical chromatogram of a standard 5- μl injection of the pentane phase is shown in Fig. 1.

Sample Collection

All samples were collected in duplicate in 40-ml glass screw-cap septum vials sealed with Teflon® silicone disk cap liners (Pierce #13075 and #12722). The vials were laboratory-washed in detergent, rinsed with tap water followed by distilled water,

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allowed to air dry, placed in a hot-air oven at 105°C for 1 hr, then cooled and stored in an organic-free area. Seals were similarly prepared with hot-air exposure restricted to 15 min. Three drops of a 10% sodium thiosulfate solution was added to the sample vials just before sampling or shipping to arrest the formation of THMs after sample collection. Where the MTP was to be determined, the dechlorinating agent was not added until seven days after the sample was collected.

The water to be sampled was allowed to run at full force for 5 min before sampling, then the flow was reduced to enable the sample to be taken without air passing through or being trapped in the water as the vial filled. The vial was filled just to overflowing and placed on a level surface. The Teflon-lined side of the septum seal was

positioned on the water and the screw-cap tightened. To verify the success of the sampling and seal, the vial was inverted and the cap lightly tapped on a solid surface. If air bubbles were present the bottle was opened, topped-up with a few drops of sample, resealed, and again examined for entrapped air.

Sample blanks were used to monitor any contamination that might have occurred from diffusion of volatile organics through the septum seal during storage and shipment of the vials. These blanks were prepared by filling the vials, each containing three drops of 10% sodium thiosulfate solution, with organic-free water and ensuring an air-free seal. The blanks were shipped to and from the sampling site and stored with the sample vials.

Extraction and Analysis

A 10-ml sample was extracted with one 2-ml portion of pentane. The plunger was removed from a 10-ml syringe equipped with a 22-gauge needle, and the water sample was carefully poured into the syringe barrel until it overflowed. The plunger was replaced, the sample compressed, and any residual air vented while the sample volume was adjusted to 10 ml. This volume was slowly injected into a 15-ml screw-cap centrifuge tube containing 2 ml of pentane and sealed with a Teflon-lined cap. The tube was shaken vigorously for 1 min and allowed to stand until the phases separated. The pentane phase was transferred to a 2-ml crimp-top vial and closed with a one-piece Teflon-lined septum seal. The sample extracts were found to be stable for three weeks at room temperature.

For the determination of TTHM levels, the dechlorinating agent was not added to the vial before sampling. These water samples were allowed to stand in the sealed vials at room temperature for seven days, then three drops of a 10% sodium thiosulfate solution were added, and the water was extracted by the TTHM procedure.

Beer samples were cooled to 0°C. The cold beer was drawn into a 10-ml syringe through the needle, and any gas bubbles that formed were expelled as the sample was adjusted to exactly 10 ml. The beer was carefully injected into a centrifuge tube containing 2 ml of pentane. The tube was capped, vigorously shaken for 1 min, then centrifuged to facilitate the separation of the phases. The extracts were transferred and stored in the same manner as those from water samples.

A 5- μ l volume of each pentane extract was chromatographed using the conditions described.

Calibration

Calibration curves were prepared using reference standards (Aldrich Chemical Co.) of chloroform (99%), bromodichloromethane (97%), dibromochloromethane (GC grade), and bromoform (96%). A standard stock solution containing 5 μ g/ μ l of each THM was prepared by weighing aliquots of each reference standard into methanol. This solution was found to be stable for four weeks when stored in vials sealed with Teflon-lined caps and stored at 0°C. Intermediate standard solutions of 50 ng/ μ l and 5 ng/ μ l were used to prepare the aqueous standards, which were extracted and analyzed using the sample procedure. Figure 2 shows the calibration curves used to calculate the THM levels in water.

RESULTS AND DISCUSSION

The USEPA method used in this study is applicable to the analysis of chloroform, bromodichloromethane, dibromochloromethane, and bromoform in raw source water, finished drinking water, and water at any stage of treatment in a range up to 100 μ g/L of each THM. The stated limit of detection for the method is 1 μ g/L for each THM; however, in practice, the detection limits appeared to be close to the 0.03–0.08 μ g/L range reported for a similar British method (7). Relative standard deviations for a solution containing 25 μ g/L of each THM were 6% for CHCl_3 , 6.2% for CHCl_2Br , 8.8% for CHClBr_2 , 6.5% for CHBr_2 , and 4.8% for TTHMs from 10 replicate analyses. The recovery data presented in Table I indicates a tendency toward decreasing

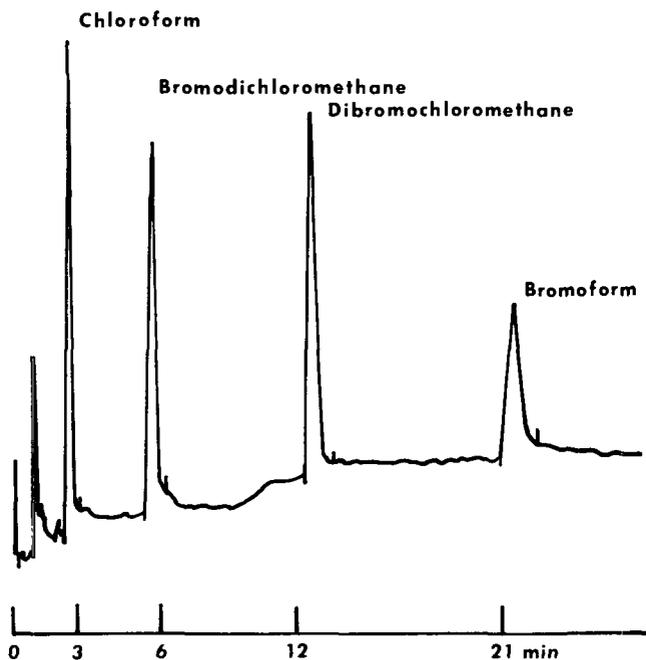


Fig. 1. Typical chromatogram of a standard 5- μ l injection of the pentane phase from the extraction of an aqueous solution containing 5 μ g/L of each trihalomethane.

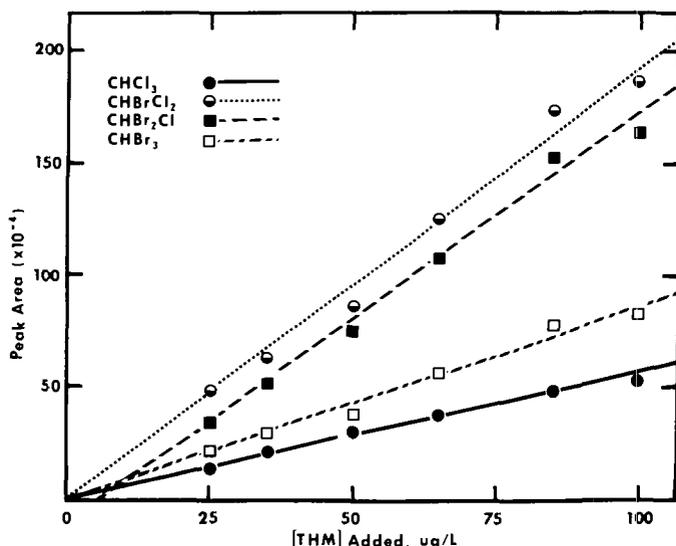


Fig. 2. Calibration curves for the assay of trihalomethanes. The straight lines were fitted by linear regression analysis using peak area as the dependent variable (y) and added trihalomethane concentrations as the independent variable (x).

recovery with decreasing TTHM concentration over the range of the method.

THMs in City Waters

The 10 Canadian cities involved in this study are widely scattered throughout the country (Fig. 3) and therefore have vastly different raw water sources. Table II lists the TTHM concentrations and the MTP levels in the city waters sampled during the surveys conducted in October, 1981, and January, 1982. THMs were detected in all waters analyzed, suggesting that the disinfectant used by the municipal water treatment utilities was chlorine. The TTHM concentrations were all below maximum acceptable levels, and precursor levels as shown by the MTPs were in most cases only slightly higher than the TTHM values. This indicates that the source waters were initially of satisfactory quality or that a prechlorination step had been employed that removed most of the organic compounds. The low residue of unreacted material

TABLE I
Recovery of Trihalomethanes (THMs) Added to Water

THM Added ($\mu\text{g/L}$)	Percent Recovered				Total THM
	CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
100	91	93	94	91	92
25	107	88	82	99	94
5	80	84	96	78	85
1	108	80	57	81	81

TABLE II
Trihalomethane Concentration in City Water

Sampling Site	TTHM ^a $\mu\text{g/L}$		MTP ^b $\mu\text{g/L}$	
	October	January	October	January
	1	3.2	3.5	3.4
2	9.9	14.0	12.2	14.1
3	22.5	29.0	32.8	122.3
4	17.5	13.4	22.6	41.0
5	19.7	9.8	24.1	15.7
6	45.7	57.3	46.7	67.1
7	39.0	18.6	42.9	20.9
8	35.7	5.1	41.3	9.1
9	2.0	3.6	4.6	4.5
10	2.8	3.5	4.1	3.7

^aTTHM = total trihalomethanes.

^bMTP = total trihalomethane potential.

suggests that further treatment would not significantly increase the THM content. No correlation existed between the degree of industrialization in the community and the THM concentrations; thus, only the naturally occurring organic compounds appear to be responsible for the THMs in these drinking waters.

Table III presents the concentrations of the individual THMs found in the city waters analyzed during the two surveys. Chloroform was present and in the highest concentration in all samples, whereas bromodichloromethane was found in all but one sample. Dibromochloromethane was present in waters from four cities, and a trace of bromoform was detected in one sample. The potential for the formation of bromoform in significant concentration was found in one sample. The fact that bromoform

TABLE III
Trihalomethanes in City Water

Sampling Site	Sample Date	CHCl_3 $\mu\text{g/L}$	CHCl_2Br $\mu\text{g/L}$	CHClBr_2 $\mu\text{g/L}$	CHBr_3 $\mu\text{g/L}$
1	October	3.2
	January	3.3	0.2	<0.1	...
2	October	9.8	<0.1
	January	14.0	<0.1
3	October	19.8	2.4	0.3	...
	January	27.9	1.1	<0.1	(12.4) ^a
4	October	14.3	2.6	0.6	...
	January	11.4	1.6	0.4	...
5	October	14.1	4.3	1.2	<0.1
	January	7.9	1.3	0.6	...
6	October	41.2	0.8
	January	56.1	1.2
7	October	33.4	5.0	0.6	...
	January	16.8	1.6	0.2	...
8	October	34.2	1.5
	January	5.1	<0.1
9	October	2.0	<0.1
	January	3.6	<0.1
10	October	2.8	<0.1
	January	3.5	(<0.1) ^a

^a Values shown in parenthesis are maximum total trihalomethane potential concentrations.

TABLE IV
Total Trihalomethane Concentrations (TTHM) in Water from Brewery
In-Plant Water Treatment Systems

Sampling Site	TTHM ^a ($\mu\text{g/L}$)									
	City Water		After Treatment						Brewing Water	Dilution Water
	TTHM ^a	MTP ^b	Cl_2	ClO_2	O_3	Sand and Gravel Filter	Carbon Purifier			
1	3.3	5.7	9.6						2.2	4.5
2	14.0	14.1	22.1						18.4	4.5
3	29.0	122.3	34.7					7.0	28.2	
4	13.4	41.0	29.3					5.2	3.6	15.7
5	9.8	15.7	10.4					4.2	3.5	3.7
6	57.3	67.1	59.6				76.0	23.8	27.0	
7	18.6	20.9					19.2	13.5	8.7	
8	5.1	9.1	15.4		17.8			4.8	2.5	
9	3.6	4.5					17.0	3.4	2.5	
10	3.5	3.7			3.6				3.1	

^aTTHM = total trihalomethane.

^bMTP = total trihalomethane potential.



Fig. 3. Map of Canada showing sampling sites.

TABLE V
Total Trihalomethane (TTHM) Reduction by Brewery In-Plant
Water Treatment Carbon Purifiers

Sampling Site	Preceding In-Plant Treatment	Percent TTHM Reduction
3	Chlorine	80
4	Chlorine	82
5	Chlorine	60
6	Chlorine, sand and gravel filter	69
7	Chlorine dioxide, sand and gravel filter	30
8	Chlorine, sand and gravel filter	72
9	Ozone	6

TABLE VI
Trihalomethanes^a Detected^b in Water from Brewery In-Plant Water
Treatment Systems

Sampling Site	City Water		After Treatment						
	TTHM ^c	MTP ^d	Cl ₂	ClO ₂	O ₃	Sand and Gravel Filters	Carbon Purifiers	Brewing Water	Dilution Water
1	1,2	1	1,2					1	1
2	1	1,2	1,2					1	1
3	1,2	1,2,3	1,2,3					1,2	
4	1,2,3	1,2,3	1,2,3					1,2	1,2
5	1,2,3	1,2,3	1,2,3					1	1,2
6	1,2	1,2	1,2				1,2	1,2	
7	1,2,3	1,2,3		1,2,3			1,2,3	1,2	
8	1	1,2	1,2				1,2	1	
9	1	1,2			1		1	1	
10	1	1						1	

^a 1 = chloroform, 2 = bromodichloromethane, 3 = dibromochloromethane, and 4 = bromoform.

^b Detection level was 0.1 µg/L or more.

^c TTHM = total trihalomethane.

^d MTP = total trihalomethane potential.

was not detected in the corresponding city water sample suggests that the residence time in the distribution system was not sufficient for the reaction to occur. Only four city waters show lower chloroform concentrations in the winter samples than in those taken in the autumn; therefore, the majority of the locations do not exhibit the seasonal trend reported in other surveys (2,13).

Brewery In-Plant Water Treatment

In January, 1982, the brewery in-plant water treatment systems and the city waters being supplied to each of our 10 breweries were monitored for THM levels. Table IV presents the TTHM concentrations found in those water samples. Seven of the breweries rechlorinate the city water, one treats with chlorine dioxide (ClO₂), one disinfects with ozone (O₃), and one has no in-plant water treatment facilities.

At all locations where chlorine was used, the TTHM levels rose after in-plant treatment. However, the MTP was reached in only one system. Sand and gravel filtration, which is a phase of three of the systems, increased the TTHM levels to or above the city water potential. In this step, the opportunity for continuing THM formation is provided by the extended chlorine contact time and by the presence of previously trapped organic matter that is available for reaction with excess chlorine. Activated carbon purifiers were quite effective in reducing the THM levels in water.

Table V shows the efficiency of these units in the seven in-plant systems that have carbon purifiers. Where water was passed through activated carbon, as much as 82% of the THM content was removed, and in all cases the THM levels were reduced below those of the original city water supplied to the breweries.

Chlorine dioxide has been found not to produce THMs (1), although it will produce other organic by-products (11). Reactions involving a combination of chlorine and chlorine dioxide have been reported to give products common to both reagents (6), which would include THMs. In our survey, the THM levels in water from the system using chlorine dioxide as a disinfectant appear to be unaffected by either the chlorine dioxide alone or in combination with the municipal treatment. Ozone, as expected, also does not appear to produce THMs, alone or in association with previously chlorinated water. The levels of THM in the brewing and beer dilution waters of the 10 breweries monitored were all well below maximum acceptable standards for drinking water even in those breweries that lack or that have only partial in-plant water treatment facilities.

Table VI shows the individual THMs detected in city water and at various stages during in-plant water treatment. Chloroform was present in all city water supplies and persisted through all types and phases of in-plant treatment. Bromoform was not detected in any of these samples and dibromochloromethane, where present, was completely removed before the waters were used in production. Bromodichloromethane was detected in brewing water from four of the water treatment systems.

Analysis of Beer

Ten Canadian market beers were analyzed. Chloroform and bromodichloromethane were detected in low concentrations, resulting in average TTHM levels of 2.0 µg/L. Dibromochloromethane and bromoform were not present in any of the beer samples analyzed.

SUMMARY

The TTHM concentrations in water supplied to our 10 Canadian breweries were well below maximum acceptable limits. Levels of unreacted precursors indicated that the quality of the source waters was generally satisfactory, resulting in low MTP. Of the four THMs that can occur in significant concentrations in chlorinated water, chloroform was detected most frequently and in the highest concentrations. In-plant water treatment facilities, although initially raising levels during rechlorination, provided brewing water superior in THM content to the original city water supply. The two surveys conducted for this report did not show the reduction in TTHM levels that would be expected with the drop in water temperature from the autumn to the winter sampling dates. TTHM concentrations in beer were on average lower than those of any of the waters analyzed. Thus, the human health hazard posed by the presence of these substances at the concentrations detected appears to be negligible.

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