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THE DETERMINATION OF THE MAXIMUM TOTAL TRIHALOMETHANE POTENTIAL
METHOD 510.1

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METHOD FOR THE DETERMINATION OF THE MAXIMUM TOTAL TRIHALOMETHANE POTENTIAL

METHOD 510.1

1. Scope and Application

1.1 This method is to be used for regulatory purposes only pursuant to section 141.30 of the trihalomethane (THM) regulation Reference 1. It should not be used to estimate THM concentrations for any other purpose in conjunction with the regulation.

1.2 This method is applicable to the determination of the maximum total trihalomethane potential (MTP) of finished drinking water for those groundwater supplies that have failed the MTP test due to the absence of excess disinfectant after seven days of storage as described in Reference 1.

1.3 The method is designed to yield THM concentrations higher than those normally found in a distribution system. It is neither a predictor of distribution system THM concentrations nor a measure of total precursor and should not be used for these purposes. Precursor tests are more appropriately conducted under sample storage conditions that simulate conditions found at specific locations. Reference 2.

1.4 Other than sample collection, the entire procedure must be performed by a laboratory certified for the analysis of total trihalomethanes (TTHM).

1.5 The method as described is capable of monitoring MTP values between 5 and 200 µg/L for water supplies with a seven day chlorine demand of less than 5 ppm using a sample storage temperature of 25°C (or higher) and a buffered pH range of 9.0 to 9.5.

2. Summary

2.1 Duplicate field samples are collected and transported to the testing laboratory. At the testing laboratory, the pH of the sample is adjusted to 9.2 and the free chlorine residual is increased at least 5 mg/L through the addition of a solution containing a boric acid buffer and hypochlorite. The resulting mixture is hermetically sealed and stored at 25°C or above for seven days. After seven days, the presence of free chlorine residual of at least 0.2 mg/L is verified and then is chemically reduced with a dechlorinating agent. The samples are then analyzed for their TTHM content according to Reference 3 or 4. It is recommended that the TTHM analysis be completed within 14 days following incubation.

3. Interferences

3.1 TTHM precursors, bromine, bromide ion, and to a lesser extent iodine and iodide ion contained in the reagents can add to the MTP value. For this reason, a laboratory reagent blank (LRB) (Section 8) must be routinely monitored. If the LRB appears to add significantly to the MTP value, the source of interferant must be located and eliminated. For field samples, the alternative LRB Procedure (Section 8.3) may be used. LRB values cannot be subtracted except as noted in Section 9.3. Blank water and the combined buffer/hypochlorite reagent are specifically treated by exhaustive chlorination at elevated temperatures to eliminate interferences from TTHM precursors. However, upon storage the combined buffer/hypochlorite reagent and blank water may become contaminated with THM. Indirect tests for halide ion interference can be accomplished by an added precursor test (Section 9) or can be performed by routinely analyzing an EMSL-Cincinnati MTP sample. Excessive bromide ion interference is indicated by these tests when the summation of the brominated trihalomethanes exceed 10 % of the TTHM value.

3.2 Other sources of interferences are discussed in the appropriate sections of the required analytical methods. [3,4]

4. Apparatus

4.1 Constant temperature storage container -- water bath or incubator, 25°C and or above.

4.2 Reagent water system -- Carbon filtered distilled water or carbon filtered deionized water.

4.3 Free available chlorine test equipment -- as required by the choice of method (See Sections 7.7 and 7.7.1).

4.4 Reflux apparatus -- 1 to 3 L boiling flask, Reflux condenser and heater.

4.5 Sample Bottles and Seals

4.5.1 240 mL amber reagent bottles with open top screw caps and Teflon faced silicone septum liners.

4.5.2 25 mL vials with open top screw caps and Teflon faced silicone septum liners.

4.6 Narrow range pH paper -- pH range approximately 8 to 10.

4.7 TTHM analytical equipment -- See Apparatus in Reference 3 or 4 Section 4.

4.8 Convection Oven - (Optional) Vented, operating temperature near 100°C.

5. Reagents

5.1 Chlorine Solution -- approximately 2000 mg/L.

5.1.1 An aqueous solution of chlorine (hypochlorite) is prepared by either of the following two methods: (1) dilute 40 mL of commercial solution of 5.25 percent sodium hypochlorite (laundry bleach) to 1000 mL with reagent water, or (2) bubble chlorine gas into reagent water until the solution turns dark yellow, then adjust the pH to 9.2 or higher with sodium hydroxide solution.

5.1.2 Reflux the hypochlorite solution for six hours, then remove the condenser and boil for at least 30 minutes longer to remove THM's that may have been produced. Cool and store in an amber glass bottle with a Teflon lined screw cap.

5.1.3 Prior to use, analyze the refluxed chlorine solution to determine the concentration of free chlorine. Use the Iodometric Method 409A for chlorine as described in Standard Methods Reference 5.

NOTE: For this test, dilute the chlorine solution such that 10 to 30 mL of titrant is used.

5.2 Blank Water

5.2.1 Treat the reagent water (4.2) as follows: To each liter of reagent water, add 1.0 mL of 1.0 N sodium hydroxide solution and 5 mg/L of free chlorine (5.1.3). Reflux the mixture for 16 hours. Cool to 90°C then bubble a contaminant free gas such as He or N_2 through the solution at 50 mL/minute for at least one hour. Allow the solution to cool to room temperature, then neutralize with 1.0 mL of 1.0 N sulfuric acid. Check to make certain that a free chlorine residual in excess of 0.2 mg/L remains. If not, repeat the entire procedure using a higher concentration of free chlorine. After this treatment, the water should be free of THM's and THM precursors. Store blank water in a screw cap septum-sealed bottle in an area known to be free of THMs, but be certain to check for THM contamination before using. Blank water is used for the added precursor test (Section 9) and laboratory reagent blank tests (Section 8).

NOTE: As an alternative to refluxing and gas purging, place the mixture in a narrow mouth flask and heat in a convection oven overnight at the boiling point of water. The temperature of the oven must be adjusted so that the mixture does not boil.

5.3 Combined Buffer/Hypochlorite Reagent

5.3.1 Boric acid -- anhydrous, ACS reagent

5.3.2 Sodium hydroxide -- ACS reagent (store in a desiccator).

5.3.3 Dissolve 3.5g of dry sodium hydroxide in 400 mL of reagent water. Add 10.0 g of boric acid. Stir until completely dissolved. Calculate the volume of chlorine solution (5.1.3) that contains 60 mg of free chlorine. Add this volume to the boric acid buffer solution. Reflux the resulting solution using a magnetic stirrer/hot plate for 16 hours. Remove the reflux condensor and gently boil until the volume is reduced to about 250 mL. Cool. Take a small sample and determine the free chlorine residual using one of the methods referenced in Section 7.7.1, and read the special note. The free chlorine concentration of this reagent must be at least 125 mg/L Cl when finally diluted to 300 mL. If sufficient chlorine is not present, then determine the amount of refluxed hypochlorite solution (5.1.3) required to produce this final concentration. Add this amount, then dilute to 300 mL with blank water (Section 5.2). Store this solution in an amber glass bottle with a Teflon lined screw cap. If the free chlorine residual drops below 125 mg/L, then additional refluxed hypochlorite solution may be added. Ten mL of the buffer/hypochlorite solution added to 250 mL of sample should provide a buffered pH of 9.2 (acceptable range 9.0 to 9.5) and a free residual chlorine value of 5 or more mg/L.

NOTE: As an alternative to refluxing and boiling down to 250 mL, place the solution in a narrow mouth flask and heat in a convection oven overnight at the boiling point of water. The temperature of the oven must be adjusted so that the solution does not boil.

5.4 Dechlorinating agent -- sodium sulfite, A.C.S.

5.4.1 Dissolve 2.0 g sodium sulfite in 100 mL of blank water. Discard after one week.

5.5 3,5-dihydroxybenzoic acid (DHBA) - 97% pure.

5.5.1 Stock DHBA solution: dissolve 0.154 g of DHBA in 1000 mL of reagent water (4.2).

6. Sample Collection and Handling

6.1 All samples are collected in duplicate, Field Sample 1 (FS-1) and Field Sample 2 (FS-2), in 240 to 300 mL narrow mouth amber glass bottles with Teflon lined screw caps.

6.2 Samples are collected from a point in the distribution system reflecting the maximum residence time.

6.3 Samples are collected headspace free according to the sampling procedure described in the TTHM analytical method Reference 3 or 4.

6.4 Store all samples at 4°C in the dark in a protected area known to be free from contamination. Process all samples within 14 days of collection.

7. Procedure

7.1 Pour about 20 mL of the FS-1 sample into a clean beaker.

7.2 Add the combined buffer/hypochlorite solution (Section 5.3) to the FS-1 sample contained in the FS-1 sample bottle at the rate of 1.0 mL solution/25 mL sample. Check the pH of the buffered sample with narrow range pH paper to make certain that the pH is within the acceptable range (9.0 to 9.5).

NOTE: Do not dip the pH paper into the sample. Touch the pH paper to a sample wetted stirring rod.

7.3 Fill the FS-1 bottle with the aliquot removed in 7.1.

7.4 Seal the bottle with a Teflon lined septum seal according to the TTHM method used Reference 3 or 4. Shake for one minute.

7.5 Store the modified FS-1 sample in the dark at 25°C or higher for seven days.

7.6 After the storage period, aliquots of the FS-1 sample are transferred (with minimum agitation) into two 25 mL screw cap septum seal vials containing 0.2 mL sodium sulfite solution (Section 5.4). Seal both vials according to the TTHM procedure. Identify these containers as Field Sample 1A (FS-1A) and Field Sample 1B (FS-1B). It is recommended that the FS-1A sample be analyzed for TTHM within 14 days following incubation, provided the test is valid (See Sections 7.7 and 7.8).

7.7 Analyze the remaining FS-1 sample to determine the free chlorine residual content.

7.7.1 Use Standard Methods 409C, 409E, or 409F. [5]

NOTE: The buffer required in the Standard Method (Section 7.7.1) for free chlorine residual may not be strong enough to overcome the boric acid buffer that is already present in the sample, and therefore, the sample pH may need to be adjusted to the required value with 1.0 normal sulfuric acid before proceeding with the free chlorine residual test.

7.8 The free chlorine residual must be at least 0.2 mg/L. If it is not, then the entire test is invalid. If the test is invalid, discard the vials prepared in Section 7.6.

7.8.1 The procedure may be repeated using duplicate or fresh samples for those Water Supplies that have failed 7.8. Additional combined buffer/hypochlorite solution should be added at 7.2 to ensure that the free chlorine residual is in excess of 0.2 mg/L after 7 days of incubation (7.8).

7.9 If the test is valid, then determine the TTHM content of FS-1A, or FS-1B if a duplicate is needed, according to the TTHM methods Reference 3 or 4.

7.10 Use the FS-2 sample as a duplicate for Section 7.8.1, quality control, or in case of shipping or laboratory accidents only if the 14 day holding time has not been exceeded.

8. Procedure for Laboratory Reagent Blank (LRB) Test

8.1 Substitute blank water (Section 5.2) in the sample bottle for the sample and analyze according to Section 7.

8.2 An LRB of less than 5 µg/L TTHM should be obtained, otherwise, abnormally high TTHM values for the field samples will result. If LRB values are in excess of 5 µg/L TTHM then the laboratory should obtain a new source of reagent water and/or reagents. If the contamination source is the reagent water, the alternate procedure for measuring the LRB in <u>field samples only</u> may be used as described in Section 8.3; this is allowed only because reagent water is not added to the field samples.

8.3 Alternate Field Sample Blank.

8.3.1 Purge approximately 100 mL of blank water (Section 5.2) and the combined buffer/hypochlorite reagent (Section 5.3) in separate containers for approximately 30 minutes with nitrogen to remove any THMs.

8.3.2 Add 1.0 mL of the purged buffer/hypochlorite reagent and 0.2 mL of the dechlorinating agent (Section 5.4) to a 25 mL sample bottle. Fill the bottle just to overflowing with the purged blank water and seal. Mix by shaking, then determine the TTHM concentration according to reference 3 or 4 within 14 days. If the solutions were properly purged, the TTHM value will be less than 1 µg/L.

8.3.3 Store an aliquot of the purged buffer/hypochlorite reagent (Sectin 8.3.1) headspace free along with MTP samples at 25°C (or higher) for 7 days.

8.3.4 At the end of 7 days prepare a second LRB according to (8.3.2) using freshly purged blank water, dechlorinating agent and the 7 day old buffer/hypochlorite reagent from (8.3.3); but do not repurge the stored buffer/hypochlorite reagent. The TTHM concentration in this LRB determines the amount of THM produced by the reaction of free chlorine with precursors contained in the buffer/hypochlorite reagent. If the TTHM concentration is less than 5 µg/L, then proceed with the TTHM measurements of field samples using the same batch of buffer/hypochlorite reagent. If TTHM values exceed 5 µg/L, then an alternate source of reagents must be obtained that provide less than 5 µg/L TTHM interference.

9. Procedure for Added Precursor Test

9.1 Fill and seal a tared sample bottle with blank water prepared according to Section 5.2. Reweigh the filled bottle. Determine the volume of water contained in the bottle to the nearest mL assuming that the density of the blank water is 1.0 g/mL.

9.2 Process the blank water according to Section 7 except at Step 7.2 add 10.0 µL of the DHBA solution/25 mL of sample bottle volume (Section 5.5.1) just before the addition of the buffer/hypochlorite solution.

9.3 For 100 % recovery, this test should produce 46 µg/L of TTHM. These data may be corrected for reagent water blanks (Section 8.1 only). See Table 2 for single laboratory test data.

10. Quality Control

10.1 Analyze EMSL-Cincinnati maximum trihalomethane potential quality control samples quarterly.

10.1.1 If the brominated species are abnormally high, check reagents for bromide ion interferences (Section 3.1).

10.1.2 The results must be within 20% of the true value.

10.2 Analyze 10% of all samples in duplicate.

10.2.1 Compare the FS-1A and FS-2A results. The two values must agree within 20 % at concentrations above 50 µg/L TTHM.

10.3 Analyze laboratory reagent blanks according to Section 3.1, and 8.1 only. See Table 1 for single labortory test data.

11. Calculations

11.1 Calculate the concentration of the TTHM by the procedure described in the THM method used, do not subtract LRB concentrations for field samples.

12. Precision and Accuracy

12.1 Single laboratory accuracy and precision data have been collected by the Technical Support Division (TSD), Office of Drinking Water, and the Municipal Environmental Research Laboratory (MERL), Cincinnati, Ohio 45268. These data appear in Tables 1 through 4. At this time no interlaboratory data are available.

References

1. Federal Register, Thursday, Nov. 29, 1979, Volume 44. No. 231 40 CFR 141.30(C)
2. Stevens, A.A., Symons, J.M. Journal American Water Works Association, 69, 546, (1977).
3. Federal Register. Thursday, Nov. 29, 1979, Volume 44. No. 231 40 CFR, Appendix C - Part I
4. Federal Register. Thursday, Nov. 29, 1979, Volume 44. No. 231 40 CFR Appendix C - Part II
5. Standard Methods. 14th Edition. (1975)

TABLE 1

Single Laboratory (MERL) Test Results for Laboratory Reagent Blanks[A]

Sample Number	Concentration µg/l $CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
1	3.0	0.3	< 0.1	< 0.1	3.3
2	1.7	< 0.1	< 0.1	< 0.1	1.7
3	1.3	< 0.1	< 0.1	< 0.1	1.3
4	1.6	< 0.1	< 0.1	< 0.1	1.6
5	2.3	0.2	< 0.1	< 0.1	2.5
6	2.6	0.1	< 0.1	< 0.1	2.7
7	2.5	0.2	< 0.1	< 0.1	2.7
				Average	2.3
				Standard Deviation	0.73
				Relative Standard Deviation	32%

[A] See Section 8

TABLE 2

Single Laboratory (MERL) Accuracy and Precision for Added Precursor Test[A]

Sample Number	Concentration µg/l				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
1	45	3.3	< 0.1	< 0.1	48
2	51	3.9	< 0.1	< 0.1	55
3	39	3.0	< 0.1	< 0.1	42
4	48	3.6	< 0.1	< 0.1	52
5	48	3.7	< 0.1	< 0.1	52
6	43	3.2	0.1	< 0.1	46
7	46	3.6	0.1	< 0.1	50

Average TTHM	49 µg/L
Standard Deviation	4.1
Relative Standard Deviation	8.3%
Average Blank for Test	2 µg/L
Expected test Value	46 µg/L
Total Expected Value	48 µg/l
Recovery	102%

[A] See Section 9

TABLE 3
Single Laboratory (TSD) Accuracy and Precision for Addded Precursor Test[B]

	Concentration µg/l						
Sample	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM	True Value	Percent Error
QC-A	66	0.1	< 0.1	< 0.1	66	78	-15
QC-B	100	1.9	0.1	< 0.1	100	120	-17
QC-B	110	3.3	0.3	< 0.1	110	120	-8

[B] See Section 10.1.

TABLE 4

Single Laboratory (TSD) Maximum Total Trihalomethane Potential For Goundwater

Sample Number	Concentration µg/l				
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	TTHM
1	61	20	8.3	1.5	91
2	67	21	9.8	1.3	99
3	71	22	10	1.4	100
4	63	17	8.1	1.1	89
5	68	22	10	1.4	100
6	64	21	10	1.5	97
7	71	22	10	1.4	104
				Average	98 µg/L
				Standard Deviation	5.3
				Relative Standard Deviation	5%

MAXIMUM TRIHALOMETHANE POTENTIAL (MTP) FOR GROUNDWATERS

#	Sample	Sample Prep.	Free Residual Cl (ng/L)	TOC (ng/L)	THM (µg/L)				TTHM (µg/L)
					$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	
1	Elkhart, Circle R	Inst.	--	2.74	22.0	4.5	1.3	0.1	25.9
	Collected - 5/7/81	MTP-1	NF	3.05	23.7	5.6	1.4	0.2	30.9
	In - 5/12, Out - 5/19	MTP-2	2.0	--	222.1	27.3	4.4	0.3	254.1
2	Oxford, 6557 Todd Rd.	Inst.	< 0.1	1.98	5.6	4.6	3.8	0.4	14.4
	Collected - 5/15	MTP-1	NF	2.88	5.7	4.4	3.0	0.3	13.4
	In - 5/19, Out - 5/26	MTP-2	4.2	--	56.1	17.1	7.9	1.1	82.2
3	Clermont, Gulf, Vera Cruz	Inst.	< 0.1	1.12	4.6	7.5	12.8	2.5	27.4
	Collected - 5/15	MTP-1	NF	1.46	4.5	7.9	12.0	5.1	29.5
	In 5,19, Out 5/26	MTP-2	4.6	--	49.2	18.9	15.3	3.8	87.2
4	Indian Hill, Taft tap	Inst	0.1^+	2.22	5.2	6.1	6.2	0.8	18.3
	Collected - 5/14	MTP-1	NF	2.07	5.3	6.0	6.3	0.9	18.5
	In - 5/19, Out 5/26	MTP-2	3.9	--	66.0	17.7	10.9	1.2	95.8
5	Middletown, 3455 Town Bld.	Inst	< 0.1	1.28	2.9	7.0	12.1	5.5	27.5
	Collected - 5/15	MTP-1	NF	1.18	5.2	8.3	11.5	6.2	31.2
	In - 5/19, Out 5/26	MTP-2	4.8	--	36.6	14.9	13.0	6.9	71.4