Trihalomethane Formation Potential (THMFP)

DOC316.53.01147

THM Plus Method[1] Method 10224

Scope and application: To determine the potential of potable source waters that form trihalomethanes and other disinfection by-products in the influence of direct chlorination. For water treatment processes, water sources or for predicting THM concentrations evaluation in a distribution system. For Simulated Distribution System Trihalomethanes (SDS-THM) studies.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Section 5710.

Test preparation

Before starting

Prepare the sample containers, test bottles and labware before use. Refer to Prepare analysis labware on page 2.
Make a test plan to determine the THMs formation. Refer to Test plan on page 5.
Make sure that the sample temperature agrees with the temperature in the test plan before analysis.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
DPD Free Chlorine reagent, powder pillows, 10-mL or 25-mL	varies
Chlorine Dosing Solution ampules	varies
THM Plus reagent	varies
Sample bottles and caps	6
Bottle labels	6
pH meter	1
Thermometer	1
Pipet, TenSette, 0.1–1.0 mL and tips	1
Stir plate	1
Stir bar magnets	6
Cell holder assembly and evaporating dish (water bath)	1
Spectrophotometer	1

Refer to Consumables and replacement items on page 6 for order information.

Sample collection

- Collect samples in clean glass bottles with TFE-lined screw caps.
- Analyze the samples as soon as possible for best results.
- To preserve samples for later analysis, add 1 drop of thiosulfate solution at each 125-mL sample bottle. If the sample is tested immediately, no acid addition is necessary.
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 24 hours.

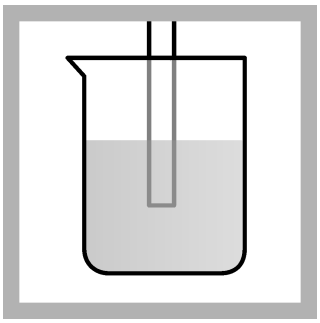
Prepare analysis labware

Pretreat the labware to remove any chlorine demand.

1. Add 1 mL of commercial bleach to 1 liter of water.

   As an alternative, add 2.0 mL of the Chlorine Dosing Solution to each bottle and fill to overflow with deionized water.
2. Soak the labware in this solution for a minimum of 1 hour.
3. Fully rinse the labware with deionized water.

Test procedure

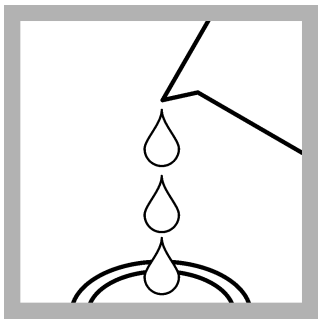


1. Measure and record the temperature and pH of the sample.

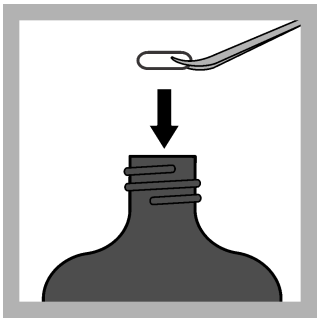
Make sure that the sample temperature agrees with the temperature in the test plan before analysis. If necessary, increase or decrease the temperature of the collected sample.

2. Prepare six chlorine demand-free bottles. Identify and put a label in bottles 1 through 6.

3. Rinse each bottle with sample.

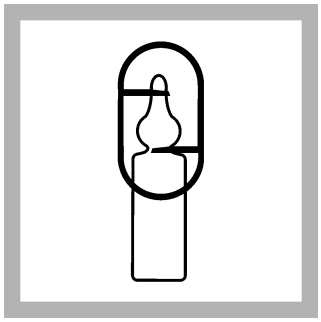


4. Fill each 118-mL bottle with approximately 100 mL of the collected sample. If constant pH is required, add the pH buffer to the sample before the bottles are filled.

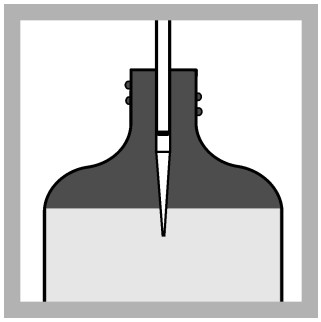


5. Use tweezers or tongs to put a stir bar magnet into each bottle. Do not touch the stir bar.

6. Put Bottle #1 on the stir plate. Set a low stir speed. A small vortex will show on the surface of the liquid.



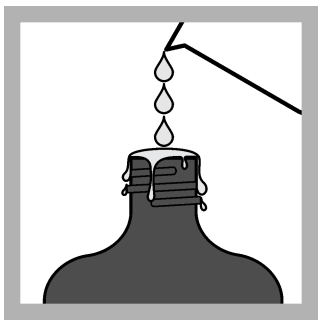
7. Use the ampule breaker to open a Chlorine Dosing Solution Ampule.



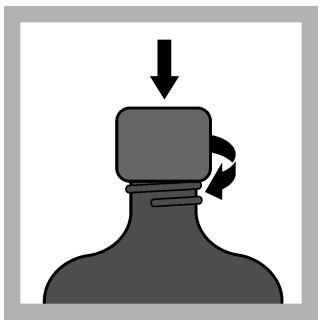
8. Use a TenSette Pipet to add 0.2 mL of the chlorine solution to Bottle #1 while stirring. Put the end of the pipet tip under the water to dispense the chlorine. To prevent highly localized areas of chlorine concentration is mandatory to stir the sample while the chlorine is added.

Each 0.2 mL of Chlorine Dosing Solution will add approximately 2.0 mg/L Cl_2 to the sample.

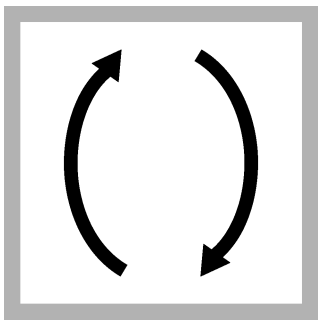
9. Set the stirrer to off.



10. Fill the bottle with sample until it overflows.

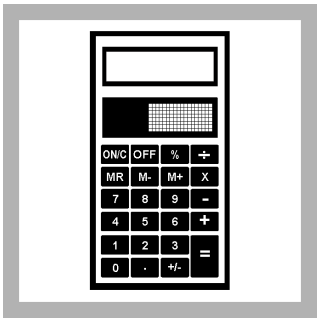


11. Put the cap on the bottle.



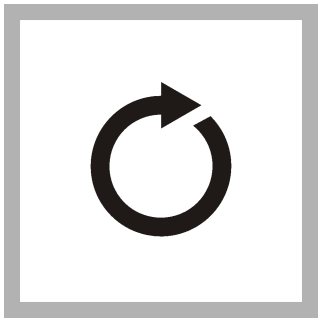
12. Invert to mix.

13. Put the sample bottle in a dark location or wrap with foil.

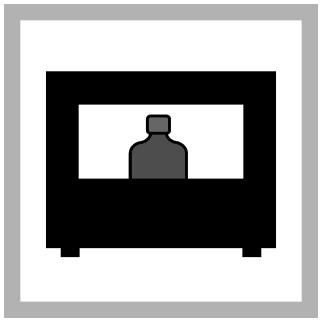


14. Calculate the actual amount of chlorine concentration. Refer to Chlorine addition calculation on page 4.

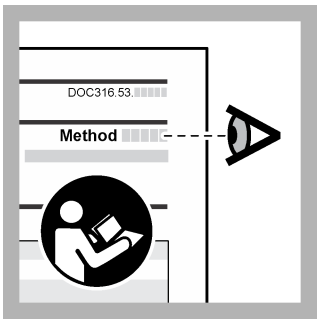
Increase or decrease the quantity of Chlorine Dosing Solution based on the estimate organic level of the sample water and chlorine contact time.



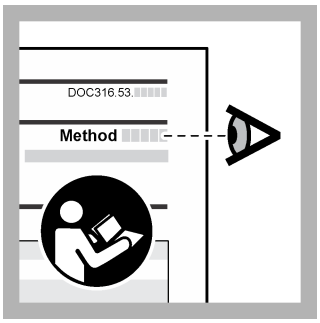
15. Do steps 8–14 again for the remaining bottles. Increase the dose of Chlorine Dosing Solution in increments of 0.2 mL. Refer to Incremental reagent dose on page 5.



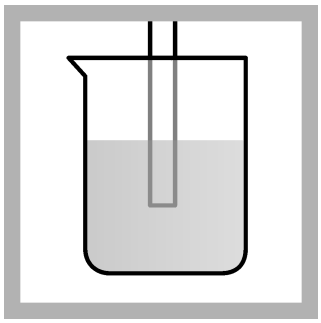
16. Incubate or refrigerate the bottles at the temperature and contact time that is specified in the test plan.



17. After the specified contact time, analyze the samples for residual Free Chlorine. Use the DPD Free Chlorine Reagent procedure (Method 8021 or Method 10069). Follow the chlorine procedure supplied with the spectrophotometer that is used.



18. Select the sample bottle or bottles that have the chlorine residual value from the test plan and analyze for THMs with the THM Plus procedure (Method 10132) . Follow the procedure supplied with the used spectrophotometer. Results are µg/L (ppb) chloroform.



19. Measure the pH of the remaining sample from the analyzed bottle to examine the pH changes that can occur in waters with low alkalinity.

For THMs analysis, immediate analysis is necessary, especially for bottles that had sample removed for chlorine residual analysis. If immediate analysis is not possible, add 1 drop of 0.1 N thiosulfate to each bottle, then keep the samples in storage at 4°C for a maximum of 14 days.

Chlorine addition calculation

Use the following formula to calculate the concentration of the chlorine added to each bottle.

mg/L CL_2 = Volume of standard added × ampule certificate value ÷ 125 mL

Example:

mg/L Cl_2 = 0.2 mL × certificate value of 1250 mg/L Cl_2 ÷ 125 mL = 2.0 mg/L Chlorine

Incremental reagent dose

Table 1 shows the incremental dose of a 1250-mg/L Chlorine Dosing Solution.

Table 1 Incremental dose of Cl_2 Dosing Solution

Bottle #	Cl_2 Dosing Solution (mL)	Cl_2 concentration increment (in mg/L)
1	0.2	2.0
2	0.4	4.0
3	0.6	6.0
4	0.8	8.0
5	1.0	10.0
6	1.2	12.0

Test plan

Tests plans are made to determine the potential of a water to form THMs or other disinfection by-products. This formation occurs under a standard or a user-specified set of reaction conditions. It is necessary to make a good test plan to give the objectives of the study and clearly document the reaction conditions.

Test plans usually have a fixed sample pH, sample temperature, chlorine dose, chlorine contact time and a necessary chlorine residual after the contact time. Test plans with fixed THM formation variables are used to compare different waters. Test plans with fixed variables can also evaluate different source waters and duplicate the results at different utilities or by different analysts with similar reaction conditions.

Some standard or fixed reaction condition plans (also available in the published literature or *Standard Methods for the Examination of Water and Wastewater*) will follow as examples.

- Reaction conditions like the standard 7-day reaction (incubation) period at pH 7.0 ± 0.2 with phosphate buffer at 25 ± 2 °C with a remaining chlorine residual between 3.0 and 5.0 mg/L are not intended to simulate water treatment processes. These conditions are most useful to estimate the concentration of THM precursors in the raw water or to measure the effectiveness of a treatment change under fixed standard conditions.
- A standard method using a 3-day reaction time has also been used. Additionally, a Uniform Formation Conditions (UFC) test is available that uses a contact time of 24 ± 1 hour at 20.0 ± 1.0 °C, a borate buffer at pH 8.0 ± 0.2 with a target-free chlorine residual of 1.0 ± 0.4 mg/L after 24 hours as the sample bottle to be measured for THMs.
- The Formation Potential Plan is also used to make a Simulated Distribution System Trihalomethanes (SDS-THM) study. The objective of this plan is to use the existing treated water pH with variable chlorine doses and contact times that simulate the chlorine levels and water age found in a distribution system. This will estimate the THM formation that occurs in the distribution system.
- Another important use of Formation Potential Test plans is to use a single-water source and vary temperature, pH or chlorine contact times to agree with specific treatment optimization objectives. Again, it is important to document all reaction conditions used in the test plan.

Examples of additional formation potential studies are:

- On settled waters from jar tests to evaluate the effectiveness of coagulant dosage on removing organics responsible for THM formation.
- On chlorine dosage rates and location of chlorine application.
- On the rate of THM formation at variable locations within the treatment stream.
- To correlate THM levels to UV-254, TOC or SUVA values.
- To study the effects of using alternative oxidants.

THMFP procedure modification

If modifications are made, use the guidelines that follow.

- Use a larger sample size or smaller chlorine addition to make smaller chlorine concentration additions. A 237-mL bottle (contains 250 mL when filled to overflow) is available for low chlorine demand applications. Each 0.1 mL of Chlorine Dosing Solution dose will increase the chlorine concentration by approximately 0.5 mg/L. For the chlorine addition equation, replace the 250 mL with 125 mL. Refer to Chlorine addition calculation on page 4. A lower concentration Chlorine Standard Solution, 50-75 mg/L as Cl_2 is also available for testing low chlorine demand waters.
- High chlorine demand waters require larger chlorine doses. Add 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL, 2.5 mL and 3.0 mL Chlorine Dosing Solution in the test procedure for high chlorine demand waters.
- Use foil as a light protection for sample bottles made of clear colorless glass. If foil is not used, make sure to keep the sample bottles in a dark location during the contact time.
- Add a fixed amount of a pH buffer solution to each bottle to change the sample pH. Use organic-free water to prepare a reagent blank bottle. Add the same amount of buffer to the blank botlle and complete the test procedure on it. Use the blank bottle to determine the formation potential added by the buffer. Subtract the formation potential of the blank bottle from the sample THM values.

Summary of method

Drinking water source waters contains organic matter that reacts with chlorine to form chlorinated organic species. Some of this chlorinated organic species are trihalomethanes or other regulated disinfection by-products. The potential of various source or treated waters to form disinfection by-products is determined with the addition of chlorine and the control of the dosage rate, pH, temperature and contact time. The THMs formed under these user-defined conditions are determined with the THM Plus method.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Chlorine Dosing Solution ampules, 1190–1310 mg/L as Cl_2, 10-mL ampules	varies	16/pkg	2504810
Chloroform, 10-ppm ampules	varies	7/pkg	2756707
DPD Free Chlorine reagent powder pillows, 25 mL	1 pillow	100/pkg	1407099
THM Plus reagent set	varies	each	2790800
Water, organic-free	varies	500 mL	2641549

Required apparatus

Description	Quantity/test	Unit	Item no.
Bottles, amber glass, 118 mL	6	6/pkg	714424
Cap, with inert Teflon™ liner, for mixing bottle	varies	12/pkg	2401812
Cell holder assembly	1	each	4788000
Evaporating dish, 125 mm x 65 mm	1	each	2764700
Hot plate/stirrer, 7 x 7 inch, 110 V	1	each	2881600
Sample cell, 10-mL round, 25 mm x 60 mm	1	6/pkg	2427606
Stir bar, magnetic	1	each	4531500

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Bottles, amber glass, 237 mL	6/pkg	714441
Bottles, amber glass, 1000 mL	6/pkg	714463
Buffer, pH 6.86	15/pkg	1409895
Buffer, pH 8.0	15/pkg	1407995
Buffer, pH 8.3	25/pkg	89868
Buffer solution, pH 7.0, demand-free	1 L	2155353
Caps, for 237-mL amber glass bottles	6/pkg	2166706
Cap with Teflon™/PE line, for 1000-mL amber glass bottles	6/pkg	2371006
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
DPD Free Chlorine AccuVacs®	25/pkg	2502025
SwifTest™ dispenser for free chlorine[1]	each	2802300
DPD Total Chlorine Reagent Powder Pillows, 25 mL	100/pkg	1406499
DPD Total Chlorine Reagent Powder Pillows, 10 mL	100/pkg	2105669
SwifTest™ dispenser for total chlorine [2]	each	2802400
Graduated cylinder, plastic	100 mL	108142
Incubator, BOD, compact, model 205, 220/240 Vac	each	2616202
Monochlor F Reagent Powder Pillows	100/pkg	2802299
HQ11d portable meter kit with PHC101 pH electrode	each	HQ11D53101000
Sodium Hydroxide Standard Solution, 0.100 N	500 mL	19153
Standard Methods for the Examination of Water and Wastewater (current edition)	each	2270800
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, magnetic	each	2881200
Sulfuric Acid Std. Solution, 0.100 N	500 mL	20253
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Thermometer, enviro-safe, non-mercury, -20 to 110°C (0 to 230 °F)	each	2635702
Tweezers, plastic	each	1428200
Water, organic-free	500 mL	2641549

[1] Includes one vial of 2105560 for 250 tests.
[2] Includes one vial of 2105660 for 250 tests.

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