Trihalomethanes

DOC316.53.01143

THM Plus™ Method

Method 10132

10 to 600 ppb as Chloroform

Water Bath Method

Scope and application: For screening THMs in drinking water samples and Formation Potential tests.

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Measurement cell orientation	Mixing cell	Measurement cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2427606 	2495402 
DR 5000 DR 3900	The fill line is toward the user.		

Before starting

Analyze the samples immediately after collection or refrigerate the samples until the analysis is complete.
If the samples are refrigerated before analysis, keep the samples cool to minimize volatilization of the disinfection by-products (DBPs). During the procedure, keep these samples in the hot water bath for 2 additional minutes (7 minutes total).
If analyzing more than four samples, use 450 mL of water in the water bath.
It is **necessary** that the THM Plus Reagent 2 is at room temperature before use.
A bottle-top dispenser can be used instead of the TenSette Pipet.
Trihalomethane compounds are extremely volatile. Immediately put the cap on the sample cell after it is filled with a sample.
A reagent blank is stable for 1 to 2 hours. It is not necessary to prepare the reagent blank for each sample.
Do not mark the cell below the 10-mL fill line.
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
THM Plus reagent set	varies
Beaker, 600-mL	1

Items to collect (continued)

Description	Quantity
Cell holder assembly, TTHM	1
Evaporating dish, 125 mm x 65 mm	2
Hot plate, 7 x 7 in.	1
Pipet, TenSette®, 0.1—1.0 mL with pipet tips	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Ice[1]	varies
Wipers, disposable	varies

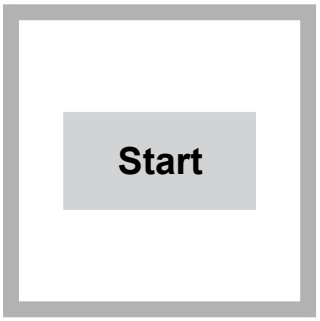
Refer to Consumables and replacement items on page 7 for order information.

Sample collection

- Collect samples in 40-mL glass bottles with Teflon®-lined septa caps.
- Slowly fill the bottles to overflowing so that no air is included with the sample.
- Put the caps on the bottles tightly. Invert the bottles to make sure that no air is in the bottle.
- Because trihalomethane compounds (THMs) are extremely volatile, immediate analysis gives the best accuracy.
- If immediate analysis is not possible, keep the samples at 6 °C (43 °F) in air with no organic vapors. The cool temperature slows the formation of additional THM compounds in chlorinated samples.
- Refrigerated samples can be kept for a maximum of 14 days. For longer periods, add 1 drop of 0.1 N Sodium Thiosulfate per 125-mL bottle of sample to dechlorinate a finished or a distribution system sample.

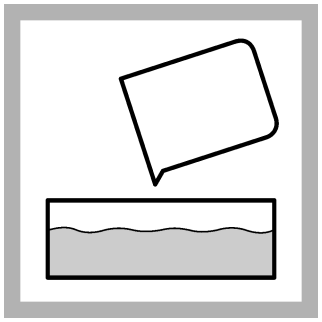
Trihalomethanes Plus Method

Do steps 4 to 9 quickly to prevent loss of THMs from the sample. To analyze more than one sample, complete steps 4 to 9 for one sample before another test starts. If a pipet is used to dispense a sample, make sure that the pipet can quickly release the sample without causing aeration or back pressure.

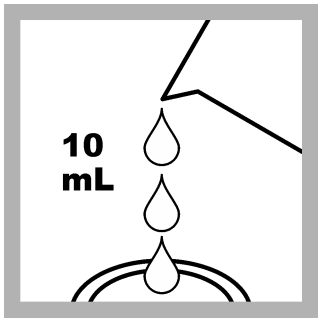


1. Start program **725 THM Plus**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

2. Add 500 mL of water to an evaporating dish to prepare a hot water bath. Put the dish on a hot plate and set the heater to high.

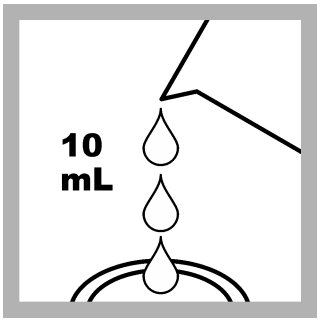


3. Add 500 mL of cold tap water (18 to 25 ºC) to a second evaporating dish. Keep the temperature in this range.

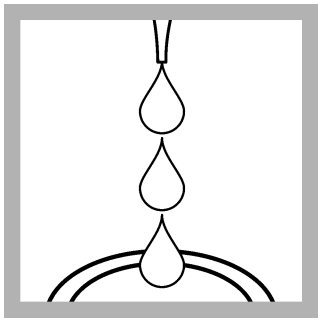


4. Prepare the sample: Put a mark on a round sample cell to identify the cell as the sample. Fill the sample cell with 10 mL of sample.

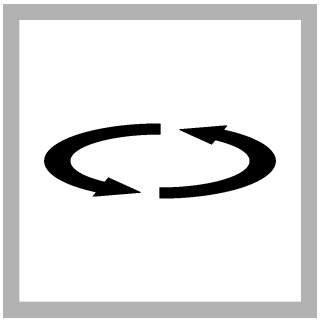
[1] If the tap water is not cool enough for the cooling bath, then use ice.



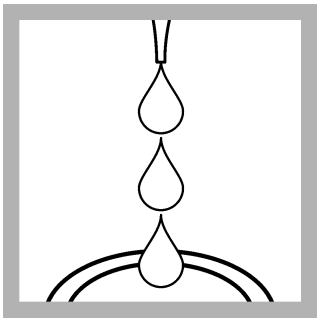
5. Prepare the blank: Put a mark on a second round sample cell to identify the cell as the blank. Fill the sample cell with 10 mL of deionized water.



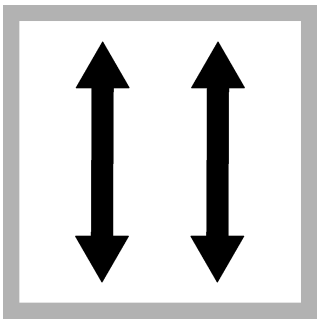
6. Make sure the blank and the sample cells are correctly labeled. Add 3 drops of THM Plus Reagent 1 to each cell.



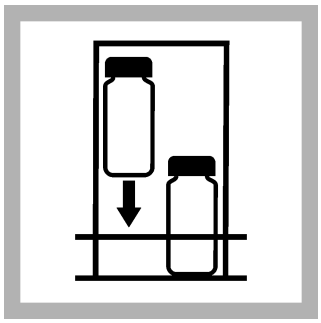
7. Put the caps on both cells. Make sure the caps are fully tightened. Gently swirl each sample cell three times to mix.
Do not vigorously shake the cells because this can cause loss of THMs into the sample cell headspace.



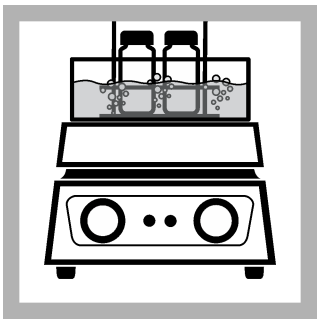
8. With a TenSette® Pipet, add 3 mL of THM Plus Reagent 2 to each sample cell. Prevent agitation of the sample when the reagent is dispensed.
The reagent is viscous and a small amount can remain on the tip after it is dispensed. This does not have an effect on the results.



9. Put the caps on the cells. Make sure the caps are fully tightened.
Fully mix to make sure that all of the THM goes into the liquid and does not accumulate in the air above the sample.

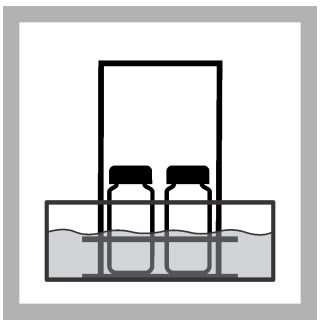


10. Put the cells in the cell holder assembly.



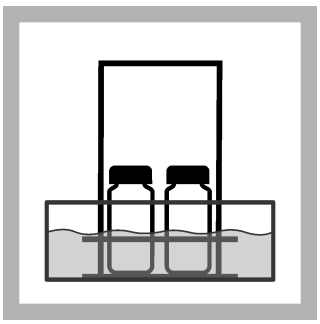
11. When the water boils, put the assembly in the hot water bath.
Do not let the water go above the white "diamond" near the top of the cells.

12. Start the instrument timer. A 5-minute reaction time starts.
Refrigerated samples: Set the timer for 7 minutes instead of 5 minutes.

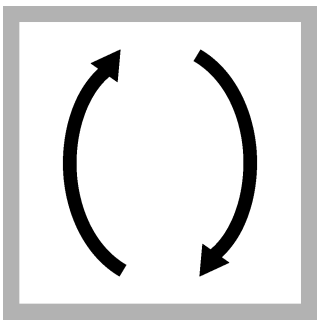


13. When the timer expires, remove the assembly from the hot water bath. Put the assembly in the cooling bath.
If necessary, use ice to cool the tap water.

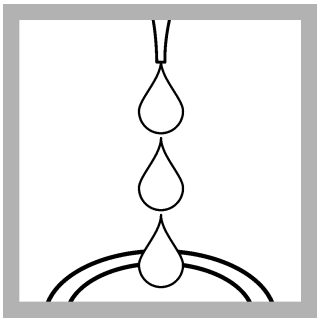
14. Start the instrument timer. The reaction time starts.



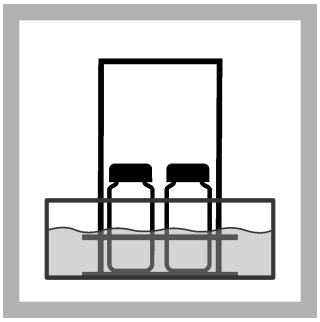
15. When the timer expires, remove the assembly from the cooling bath.



16. Invert each cell at least three times to make sure that a uniform temperature of the sample is maintained.

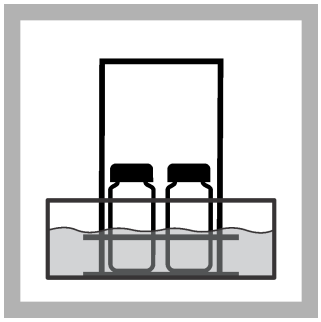


17. Use a TenSette Pipet to add 1 mL of THM Plus Reagent 3 to each sample cell. The sample and the blank will become warm.

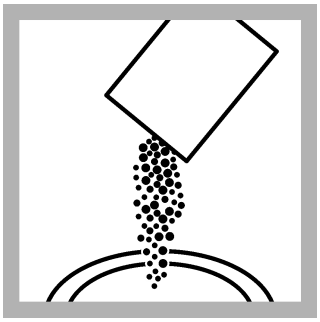


18. Replace the water in the cooling bath with new cold tap water. Put the assembly with the cells into the cooling bath.
If necessary, use ice to decrease the temperature of the tap water.

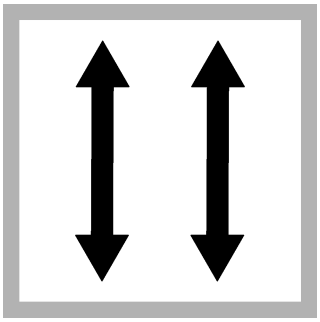
19. Start the instrument timer. The reaction time starts.



20. When the timer expires, remove the assembly from the cooling bath. Remove the sample cells from the assembly rack. Make sure that the temperature of the sample is 15–25 °C.



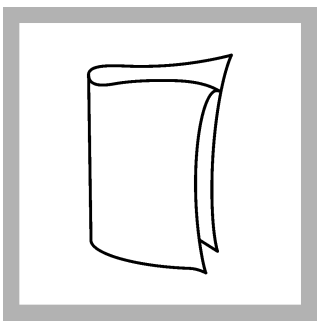
21. Add the contents of one THM Plus Reagent 4 Powder Pillow to each cell.



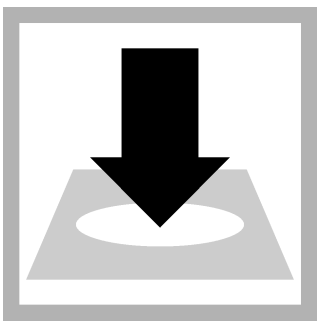
22. Put the caps on the sample cells and fully tighten the caps. Shake the sample cells until all of the powder dissolves.
The powder dissolves slowly. Intermittent shaking during the first 5 minutes of the color development will help dissolve the reagent powder.

23. Start the instrument timer. The reaction time starts.
After the 15-minute development time, the color is stable for at least 30 minutes.

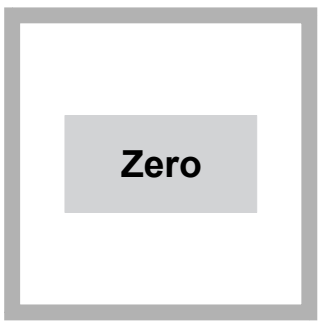
24. When the timer expires, pour the prepared sample and the prepared blank into two square sample cells. Let the sample cells stand undisturbed for 30 seconds to enable any turbidity to settle.



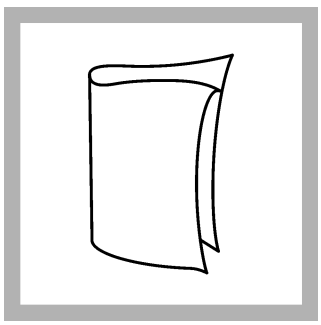
25. Clean the blank sample cell.



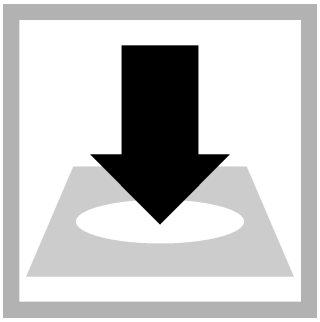
26. Insert the blank into the cell holder.



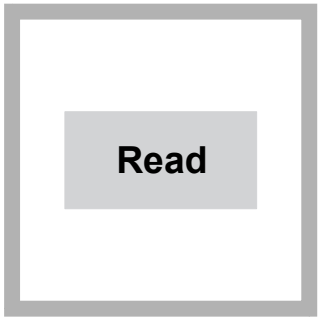
27. Push **ZERO**. The display shows 0 ppb $CHCl_3$.



28. Clean the prepared sample cell.



29. Insert the sample cell into the cell holder.



30. Push **READ**. Results show in ppb $CHCl_3$.

Interferences

Interfering substance	Interference level
Chlorine	10 mg/L
Copper	1000 mg/L
Hardness, Ca	1000 mg/L as $CaCO_3$ May have some turbidity until Reagent 3 is added
Hardness, Mg	4000 mg/L as $CaCO_3$ May have some turbidity until Reagent 3 is added
Iron	10 mg/L
Lead	2 mg/L
Mercury	10 mg/L
Monochloramine	20 mg/L
Nickel	10 mg/L
Sodium Bisulfite	100 mg/L
EDTA	Interferes negatively at all levels

Table 2 Disinfection by-products (DBPs) included in the results

Compound	Effect
1,1,1-trichloro-2-propanone	Interferes positively
1,1,1-tricholoacetonitrile	Interferes positively
Chloral hydrate	Interferes positively
Dibromochloroacetic acid	Interferes positively
Dichlorobromoacetic acid	Interferes positively
Tribromoacetic acid	Interferes positively
Trichloroacetic acid	Interferes positively

Accuracy check

Required for the accuracy check:

- THM Standard Ampule, 10 mg/L as chloroform
- Ampule breaker
- Wiretrol™ Pipet

Note: *When the chloroform is added to the solution, make sure that the chloroform is not lost to volatilization. Keep the chloroform ampule cold in a small ice bath.*

Standard additions method (sample spike)

1. Open a THM Standard Ampule, 10-ppm as chloroform.
2. Use a Wiretrol Pipet to measure 0.100 mL (100 µL) of the chloroform standard into a new 10 mL portion of sample.
3. Put the end of the pipet tip fully under the water, then slowly dispense the chloroform.
4. Immediately put the cap on the sample cell.
5. Swirl the sample cell three times to mix.
   Note: *Careful attention to technique is necessary for the accuracy check methods. It is very easy to lose the chloroform to volatilization when it is added to the solution. Make sure that the chloroform ampule is cold. If necessary, use a small ice bath.*
6. Immediately start step 6 and complete the test procedure to analyze the spiked sample.
7. The value of the spiked sample is expected to increase 100 +/- 20 ppb over the value from the original unspiked sample.
8. Calculate the % Recovery: (A – B) ÷ C × 100 = % Recovery
   A = ppb THMs Spiked Sample
   B = ppb THMs Unspiked Sample
   C = 100 ppb added THM

Standard solution method

Prepare the 99 ppb chloroform standard:

1. Use a pipet to add 10.0 mL of organic-free water into a sample cell.
2. Open a THM Standard Ampule, 10-ppm as chloroform.
3. Use a Wiretrol Pipet to move 0.100 mL (100 µL) of the chloroform standard into the organic-free water.
4. When the standard is added to the sample, slowly release the pipet at or near the bottom of the sample cell with a small swirling movement.
   Note: *When the aliquot of the standard is released too quickly, the solution forms a single bubble that rises to the top of the solution and volitalizes. The aliquot is not absorbed into the solution.*
5. Immediately put the cap on the sample cell.
6. Swirl the sample cell three times to mix.
7. Use test procedure steps 6 to 30 to measure the standard solution. When instructed, prepare the sample and use it immediately.
8. Make slight adjustments to the calibration curve with the reading from the 99 ppb standard solution. Set the standard adjust option with the instrument.
9. Set the standard adjust option with the instrument. Accept the concentration value that shows. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
725	66 ppb $CHCl_3$	53–79 ppb $CHCl_3$	19 ppb $CHCl_3$

Summary of method

The THM Plus method reacts with the trihalogenated disinfection by-products (DBPs) that form as the result of disinfection of drinking water with chlorine when naturally-occurring organic materials are present. DBPs can be produced in the treatment plant or the

distribution system if the water is in contact with free chlorine residual. DBP formation is influenced by: chlorine contact time, chlorine dose and residual, temperature, pH, precursor concentration and bromide concentration.

The predominant DBPs formed by the chlorination of drinking water are trihalomethanes (THMs). The four trihalogenated compounds that form are: chloroform, bromoform, dichlorobromomethane and dibromochloromethane. These four compounds are known as the Total Trihalomethanes (TTHMs) group that is regulated under the Safe Drinking Water Act. The combined concentration of the TTHMs is regulated in drinking water samples. Refer to Interferences on page 5 for other DBPs that can be present and react under the conditions of the THM Plus method.

In the THM Plus method, THM compounds in the sample react with N, N,-diethylnicotinamide under heated alkaline conditions to form a dialdehyde intermediate. The sample is cooled and acidified to pH 2.5. The dialdehyde intermediate reacts with 7-amino-1,3 napthalene disulfonic acid to form a Schiff base. The color that forms is directly proportional to the total amount of THM compounds in the sample. Test results measured at 515 nm and report as ppb chloroform.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Reagent set (50 tests[2]), includes:	—	—	2790800
THM Plus™ Reagent 1	6 drops	30 mL	2753929
THM Plus™ Reagent 2	6 mL	330 mL	2754048
THM Plus™ Reagent 3	2mL	100 mL	2754142
THM Plus™ Reagent 4	2 pillows	100/pkg	2756699

Required apparatus

Description	Quantity/test	Unit	Item no.
Beaker, 600 mL	1	each	50052
Cell holder assembly	1	each	4788000
Evaporating dish, 125 mm x 65 mm	1	each	2764700
Hot plate, 7 x 7 in., 115 VAC, digital	1	each	2881600
Hot plate, stirrer, 220–240 VAC	1	each	2881602
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette® Pipet, 0.1–1.0 mL	2	50/pkg	2185696
Pipet, TenSette®, 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette®, 1-mL to 10-mL	1	50/pkg	2558996
Wipes, disposable	1	280/pkg	2097000

Recommended standards

Description	Unit	Item no.
Chloroform, 10-ppm ampule	7/pkg	2756707

[2] Fifty tests has 25 samples and 25 individual blanks. Multiple samples can be measured with an individual blank.

Optional reagents and apparatus

Description	Unit	Item no.
Pipet filler, safety bulb	each	1465100
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet, Wiretrol™, 50–100 µL	250/pkg	2568905
Vials, glass 40-mL with Septa cap	5/pkg	2794005
Sodium Thiosulfate, 0.1 N	100 mL	32332
Water, organic-free	500 mL	2641549

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