

Free and total chlorine analyzer verification

DOC316.53.01302

Method

0.05 to 4.00 mg/L as Cl₂

Scope and application: Drinking water.



Test preparation

Introduction

Use the test procedures that follow with the USEPA Method 334.0, *Determination of Residual Chlorine in Drinking Water using an On-line Chlorine Analyzer*. The test procedures in this document are for use by drinking water facilities for compliance with daily monitoring requirements. The applicable section of the USEPA method is referred to in each test procedure.

USEPA Method 334.0 summary:

An online chlorine analyzer is used to continuously monitor the chlorine concentration at a sample point of drinking water. The instrument is calibrated with aqueous standards or the results from two grab samples collected at the same sample point and time. The grab samples are analyzed for chlorine (free or total) with a method that is approved for compliance monitoring of drinking water. The online analyzer accuracy is verified and/or adjusted at regular intervals with the results from grab sample analyses.

Before starting

Fully read the procedures. Identify the reagents and reagent quantities necessary for the procedures. Identify the correct cleaning procedures for labware.

Read the instructions and precautions in the procedures to get the precision and accuracy requirements of Method 334.0.

Identify if free chlorine or total chlorine will be measured.

Read the instrument-specific procedures for chlorine determination (Method 10245, DPD Free Chlorine, or Method 10250, DPD Total Chlorine) for more test instructions.

Use dedicated labware and reagents to decrease preparation and analysis time and to prevent analysis errors.

Identify if there are more test requirements added by the primacy agency.

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Startup procedures

Verification of the chlorine calibration for grab samples

EPA Method 334.0 reference: Start-up procedures section—Grab sample method, paragraph 10.1.1

Scope and application

A requirement of USEPA Method 334.0, Section 10.1.1, is to verify the internal, factory-set calibration curve for grab-sample instruments used to measure the chlorine concentration of water samples.

Three chlorine standard solutions that are approximately the expected high, mid-range and low concentrations and one method blank are used. The lowest concentration standard must be 0.2 mg/L or less, or the minimum chlorine residual requirement set by the primacy agency or less.



For Hach DPD Methods 10245 and 10250 for free or total chlorine, 0–4 mg/L Cl₂, use internal factory-set calibration curves. Use the procedures that follow to verify the factory-set calibration curves.

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	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900 DR300	The fill line is to the right.	2427606 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Analyze the chlorine standard solutions immediately.

Use only glassware that has no chlorine demand.

Use only water that has no organic material or water that has no chlorine demand water (e.g., Hach organic-free water). To prepare water with no chlorine demand, refer to ASTM-D 1253-06 and Standard Method 4500-Cl C.

Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach added to 1 liter of deionized water) for a minimum of 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.

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
Chlorine Standard Solution Ampule, 50–75 mg/L	varies
Water with no organic content	varies
DPD Free Chlorine Reagent Powder Pillow, 25 mL	4
Or	
DPD Total Chlorine Reagent Powder Pillow, 25 mL	4

Refer to [Consumables and replacement items](#) on page 14 for order information.

Prepare the standard solutions

Prepare three chlorine standard solutions that are approximately the expected high, mid-range and low sample concentrations.

Note: *The lowest concentration standard must be 0.2 mg/L or less, or the minimum chlorine residual requirement set by the primacy agency or less.*

Items to collect:

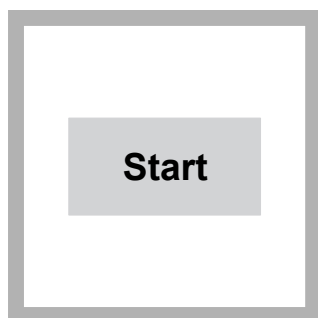
- Chlorine standard solution ampule, 50–75 mg/L Cl₂
- Volumetric flask (50-mL or 100-mL)
- Pipet (0.2–1.0 mL or 1.0–5.0 mL) and pipet tips
- Water that has no organic material

Refer to [Consumables and replacement items](#) on page 17 for order information.

Do the steps that follow to prepare each standard solution.

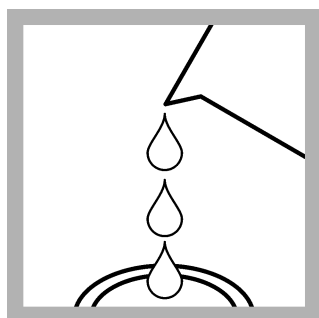
1. Calculate the volume of standard solution and the volumetric flask volume (50 mL or 100 mL) to use to prepare each the standard solution. Refer to [Calculate the concentration of the prepared standard solutions](#) on page 5.
2. Add approximately 25 mL of water that has no organic material to a clean 50-mL or 100-mL volumetric flask.
3. Open the standard solution ampule.
4. Use a pipet to add the calculated volume of standard solution to the volumetric flask.
5. Fill the volumetric flask to the mark with water that has no organic material.
6. Put a stopper in the volumetric flask. Invert to mix.

Verification procedure

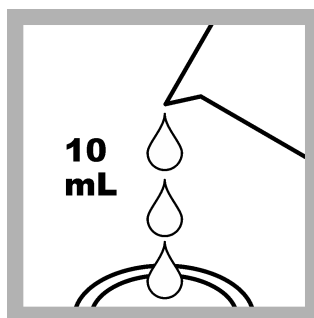


1. Start the program number for Method 10245 (free chlorine) or Method 10250 (total chlorine). For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 2.

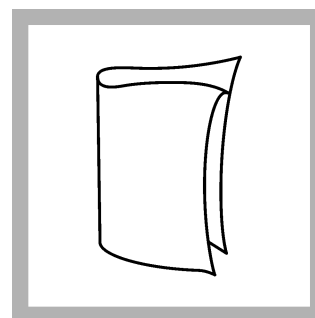
Note: Although the program name can be different between instruments, the program number does not change.



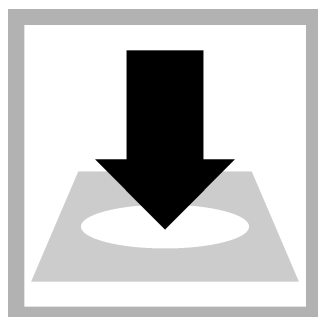
2. Fill the sample cell two times with water that has no organic material. Discard the water.



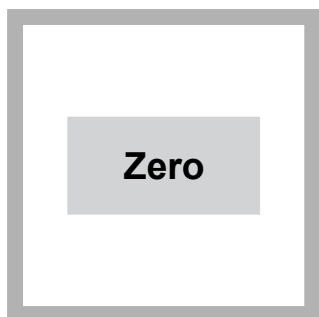
3. Fill the sample cell with 10 mL of water that has no organic material.



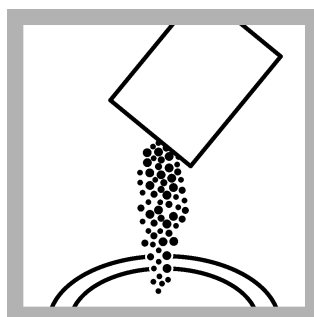
4. Clean the sample cell.



5. Insert the sample cell into the cell holder.

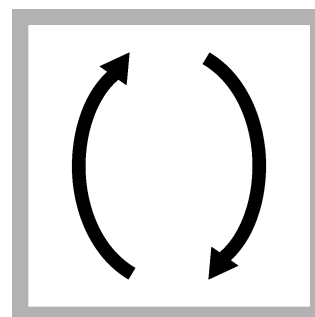


6. Push **ZERO**. The display shows 0.00 mg/L Cl₂.

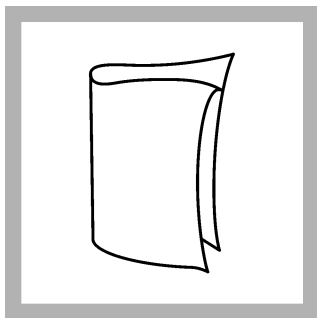


7. **Prepare the method blank:** Add the contents of one DPD Free Chlorine or one DPD Total Chlorine Powder Pillow for 25-mL sample to the sample cell.

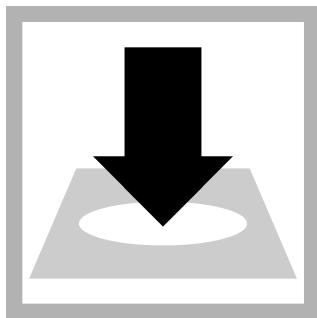
Note: DPD Total Chlorine Reagent can be used for verification of the calibration curve for both free and total chlorine determinations.



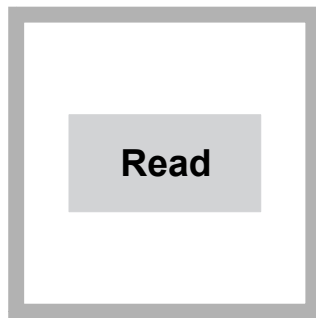
8. Put a cap on the sample cell. Invert the sample cell several times to mix. Go to the next step immediately.



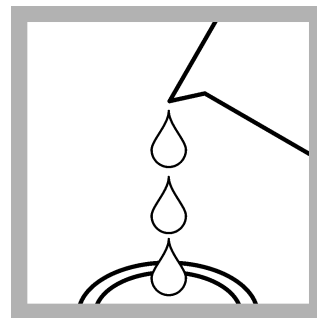
9. Clean the blank sample cell.



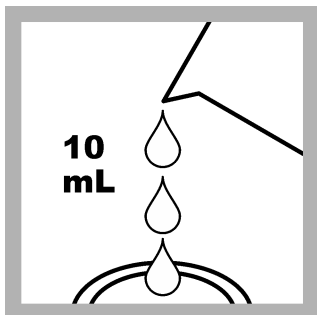
10. Within 1 minute of the reagent addition, insert the sample cell into the cell holder.



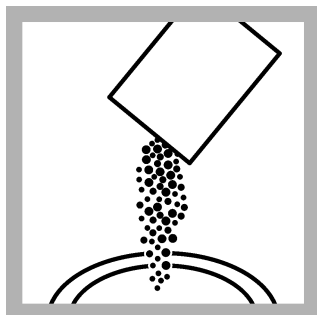
11. Push **READ**. Record the results. Results show in mg/L Cl₂.



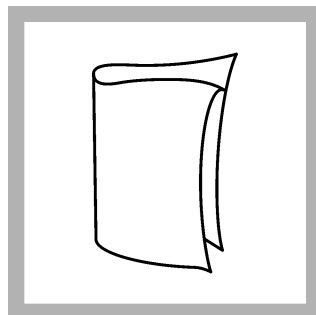
12. Fill the sample cell two times with water that has no organic material. Discard the water.



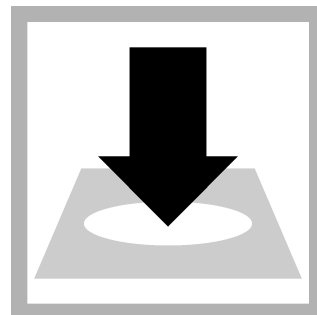
13. Fill the sample cell with 10 mL of the standard solution.



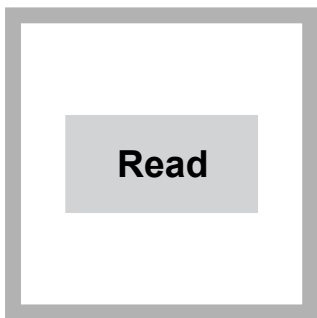
14. **Prepare the standard:** Add the contents of one DPD Free Chlorine or one DPD Total Chlorine Powder Pillow for 25-mL sample to the sample cell.



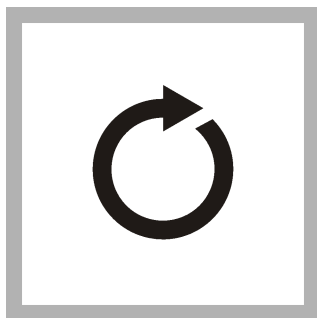
15. Clean the prepared sample cell.



16. Within 1 minute of the reagent addition, insert the sample cell into the cell holder.



17. Push **READ**. Record the results. Results show in mg/L Cl₂.



18. Do steps 12–17 again to measure the remaining two standard solutions.

Calculate the concentration of the prepared standard solutions

Calculate the volume of standard solution and the volumetric flask volume (50 mL or 100 mL) to use to prepare each standard solution.

1. Calculate the standard solution volume to use.
(final chlorine standard concentration × volumetric flask volume) ÷ actual standard ampule concentration = standard solution volume

Note: The actual standard ampule concentration changes for each lot of standard. Refer to the package label for the actual standard ampule concentration.

2. Round the standard solution volume to the nearest 0.05 mL.
3. Calculate the actual concentration of the diluted standard solution.

(actual pipet volume × actual standard ampule concentration) ÷ volumetric flask volume = diluted standard concentration

Example:

The final chlorine standard concentration: 1 mg/L Cl₂

The actual standard ampule concentration (from label): 65.3 mg/L Cl₂

Volumetric flask volume: 50 mL

The calculated volume of standard solution to use:

$$(1 \text{ mg/L} \times 50 \text{ mL}) \div 65.3 \text{ mg/L} = 0.766 \text{ mL}$$

The concentration of the diluted standard solution calculated with the actual pipette volume:

$$(0.75 \text{ mL} \times 65.3 \text{ mg/L}) \div 50 \text{ mL} = 0.98 \text{ mg/L}$$

To make a 0.98 mg/L chlorine standard, use a pipet to add 0.75 mL of a 65.3 mg/L chlorine standard solution to a 50-mL volumetric flask. Fill the volumetric flask to the mark with water that has no chlorine demand.

Table 2 gives more examples of chlorine standard solutions.

Table 2 Examples of volumes used to prepare chlorine standard solutions

Final standard concentration	Standard ampule concentration	Volumetric flask volume	Calculated pipet volume	Actual pipet volume	Actual concentration
0.10 mg/L	65.3 mg/L	100 mL	0.153 mL	0.20 mL	0.13 mg/L
0.20 mg/L	65.3 mg/L	100 mL	0.306 mL	0.30 mL	0.20 mg/L
1.00 mg/L	65.3 mg/L	50 mL	0.766 mL	0.75 mL	0.98 mg/L
2.00 mg/L	65.3 mg/L	50 mL	1.531 mL	1.55 mL	2.02 mg/L
4.00 mg/L	65.3 mg/L	50 mL	3.062 mL	3.05 mL	3.98 mg/L

Compare the measured and calculated values

Compare the measured values to the calculated values for the prepared standard solutions.

If the measured values are ±15% of the calculated values for the prepared standard solutions, the calibration curve is verified. Make sure that the measured value for the method blank is equal to or less than 1/3 the concentration of the lowest standard concentration used.

If the calibration curve is not verified or the measured value of the method blank is not equal to or less than 1/3 the concentration of the lowest standard concentration used, refer to [Troubleshooting](#) on page 7.

Example:

Three standard solutions are prepared and measured. The calculated and measured chlorine concentrations are given in Table 3. The measured concentrations are within ±15% of the acceptable range.

Table 3 Comparisons of calculated and measured standard values (mg/Cl₂)

Standard	Calculated concentration	Acceptable range (±15%)	Measured concentration	Status
Blank	—	0.00–0.06 ¹	0.01 mg/L	Pass
Standard 1	0.20 mg/L	0.17–0.23	0.21 mg/L	Pass
Standard 2	1.60 mg/L	1.36–1.84	1.62 mg/L	Pass
Standard 3	3.50 mg/L	2.98–4.03	3.49 mg/L	Pass

¹ 1/3 or less of the Standard 1 value

Troubleshooting

If the calibration curve is not verified or the measured value of the method blank is not equal to or less than 1/3 the concentration of the lowest standard concentration used, do the steps that follow.

1. Do the verification procedure again to verify the results.
2. Make sure that the glassware and water used have no chlorine demand.
3. Complete the calibration adjust procedure for the grab sample instrument. Refer to the instrument documentation.
Use a chlorine standard concentration that is near the mid-range of the test method.
4. After the calibration adjust procedure is complete, do the verification procedure again.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	4	100/pkg	1407099
Or			
DPD Total Chlorine Reagent Powder Pillow, 25 mL	4	100/pkg	1406499

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite [®] Ampule, 50-75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette [®] Ampule, 50–75 mg/L	16/pkg	1426810
SpecCheck [™] Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549

Required apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette [®] Ampules	each	2196800
PourRite [®] Ampule Breaker, 2 mL	each	2484600
Flask, volumetric, 50 mL	each	1457441
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Gloves, chemical resistant, size 10	pair	2410105
Goggles, safety, standard	each	2927902
Field notebook	each	2091800
Pipette, adjustable volume, 0.1–1.0 mL	each	BBP078
Pipette tips, for 0.1–1.0 mL pipette	100/pkg	BBP079
Pipet, adjustable volume, 1.0–5.0 mL	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	75/pkg	BBP068
Wipes, disposable	70/pkg	2096900
Wipes, disposable	280/pkg	2097000
Water, deionized	4 L	27256

Verification of secondary DPD SpecCheck chlorine standards

EPA Method 334.0 reference: Start-up procedures section—Grab sample method, paragraph 10.1.1.3

Scope and application

USEPA Method 334.0 lets secondary standards be used with the grab sample method. The secondary standards must be verified before they are used. Verify the secondary standards with an instrument that has a calibration curve that was recently verified with grab samples. Refer to [Verification of the chlorine calibration for grab samples](#) on page 1. The Hach DPD Chlorine-MR Spec Check Secondary Standards are used for the grab sample testing requirements in Method 334.0. The secondary standards must be verified for each grab sample instrument used. The chlorine values of each Chlorine Spec Check Secondary Standard are recorded at the time of verification on a verified chlorine grab sample calibration curve. Future measurements of the secondary standards on the same instrument must be $\pm 10\%$ of the recorded value.

Before starting

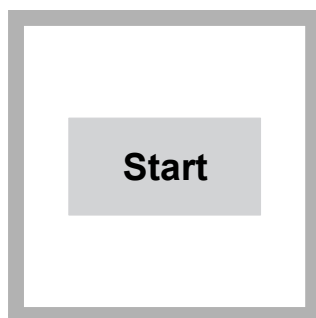
Use the DPD Chlorine-MR SpecCheck Kit with Hach Method 10245 for DPD Free Chlorine and Method 10250 for DPD Total Chlorine.
Read the SpecCheck kit instructions on the kit label and on the certificate of analysis.
Use the SpecCheck blank vial included with the kit.
Record the instrument identification and program number on the Record of Performance Verification supplied in the kit.
One Record of Performance Verification is necessary for each grab sample instrument.
It is recommended that each grab sample instrument has a set of SpecCheck standards to make sure that SpecCheck standards are always available for calibration verification.
Verify the secondary standards each time a grab sample instrument calibration curve is changed.
Do not use a set of secondary standards after the expiration date on the kit label.
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
SpecCheck Secondary Standards kit, Chlorine DPD, MR	1

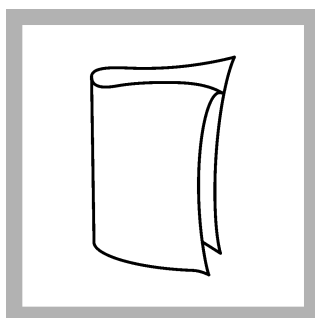
Refer to [Consumables and replacement items](#) on page 9 for order information.

Test procedure

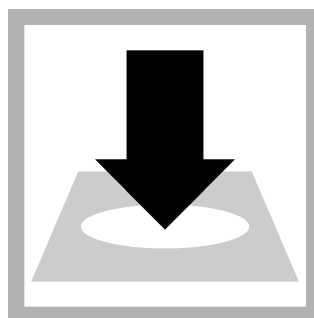


1. Start the program number for Method 10245 (free chlorine) or Method 10250 (total chlorine). For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 2.

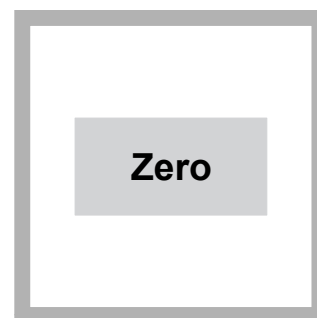
Note: Although the program name can be different between instruments, the program number does not change.



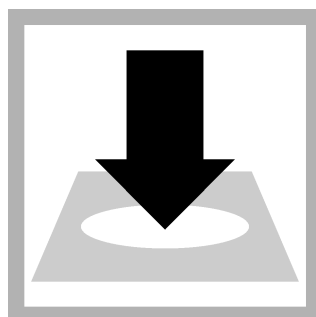
2. Clean each SpecCheck vial.



3. Insert the SpecCheck blank into the cell holder.



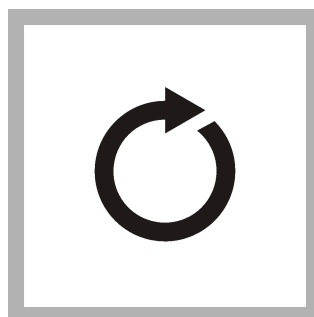
4. Push **ZERO**. The display shows 0.00 mg/L Cl₂.



5. Insert the STD 1 into the cell holder.



6. Push **READ**. Record the results on the Record of Performance Verification label. Results show in mg/L Cl₂.



7. Do steps 5–6 again for STD 2 and STD 3. Attach the completed Record of Performance Verification label to the instrument. Future measurements on the same instrument should be within 10% of the recorded value.

Consumables and replacement items

Required standards

Description	Quantity/test	Unit	Item no.
SpecCheck™ Secondary Standard Kit, Chlorine DPD, MR	1	each	2980500

Initial demonstration of capability (IDC) for field samplers

EPA Method 334.0 reference: Start-up procedures section—Grab sample method, paragraph 10.1.2

Scope and application

Each field sampler or person responsible for verification of online chlorine analyzers must first complete an initial demonstration of capability (IDC) before the grab sample method is used to verify the accuracy of online chlorine analyzers.

An accuracy and precision calculation are necessary for IDC. Measure five copies of a method blank and five copies of a mid-range chlorine standard. The average value of the chlorine standard must be $\pm 15\%$ of the expected chlorine concentration. The average value of the five method blank values must be equal to or less than 1/3 the value of the lowest chlorine concentration used to do the initial verification of the grab sample instrument. The precision or scatter in the concentration values of the five chlorine standard values must have a relative standard deviation (RSD) equal to or less than 15% of the average value.

Before starting

Read the procedure to understand the testing requirements and mathematical calculations necessary to complete the Initial Demonstration of Capability.

Use a spreadsheet application to calculate the statistics as necessary.

Laboratory personnel can prepare the independent reference samples for analyses by the field samplers.

Use only glassware that has no chlorine demand.

Analyze the chlorine standard solutions immediately.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.

Keep a record of the IDC results for each field sampler.

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
Chlorine Standard Solution Ampule, 50–75 mg/L	varies
Water with no organic content	varies
DPD Free Chlorine Reagent Powder Pillow, 25 mL	10
Or	
DPD Total Chlorine Reagent Powder Pillow, 25 mL	10

Refer to [Consumables and replacement items](#) on page 14 for order information.

Prepare the chlorine standard

Items to collect:

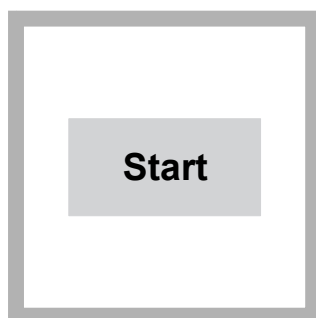
- Chlorine standard solution ampule, 50–75 mg/L Cl_2
- Volumetric flask, 100 mL
- Pipet (0.2–1.0 mL or 1.0–5.0 mL) and pipet tips
- Water that has no organic material

Refer to [Consumables and replacement items](#) on page 17 for order information.

Prepare 100 mL of 2-mg/L Cl_2 chlorine standard solution as follows:

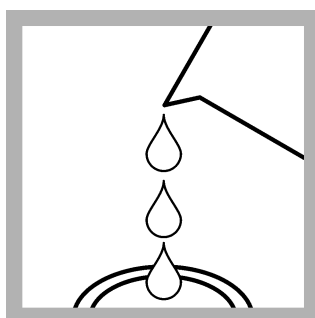
1. Calculate the volume of standard solution and the volumetric flask volume (50 mL or 100 mL) to use to prepare the standard solution. Refer to [Calculate the concentration of the prepared standard solutions](#) on page 5.
2. Add approximately 25 mL of water that has no organic material to a clean 100-mL volumetric flask.
3. Open the standard solution ampule.
4. Use a pipet to add the calculated volume of standard solution to the volumetric flask.
5. Fill the volumetric flask to the mark with water that has no organic material.
6. Put a stopper in the volumetric flask. Invert to mix.

Test procedure—Method blank accuracy

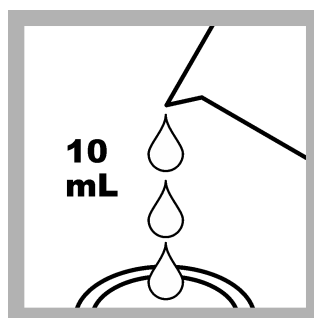


1. Start the program number for Method 10245 (free chlorine) or Method 10250 (total chlorine). For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 2.

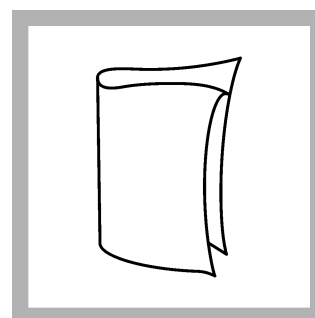
Note: Although the program name can be different between instruments, the program number does not change.



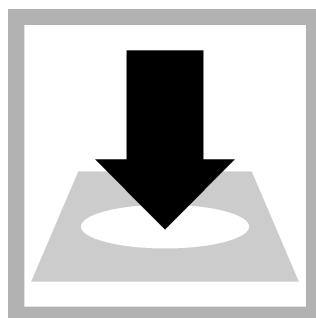
2. Fill the sample cell two times with water that has no organic material. Discard the water.



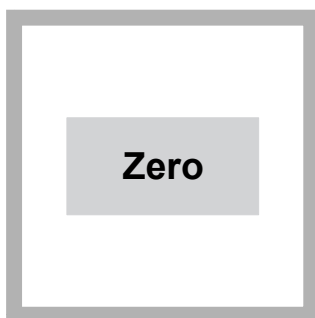
3. Fill the sample cell with 10 mL of water that has no organic material.



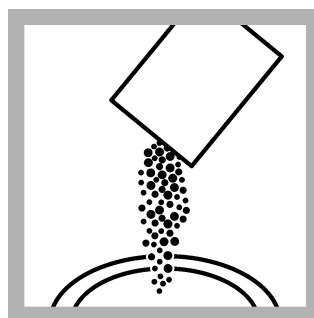
4. Clean the sample cell.



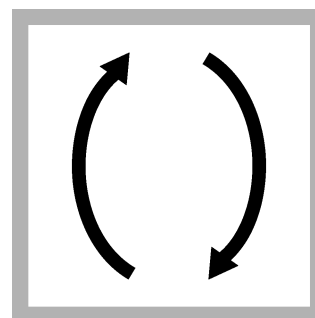
5. Insert the sample cell into the cell holder.



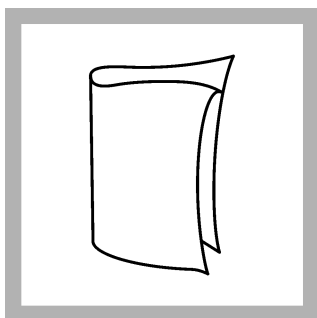
6. Push **ZERO**. The display shows 0.00 mg/L Cl_2 .



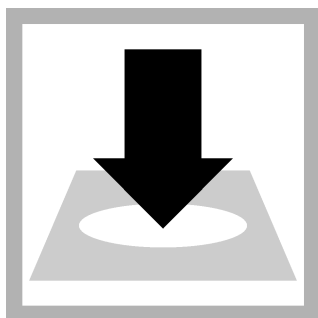
7. **Prepare the method blank:** Add the contents of one DPD Free Chlorine or one DPD Total Chlorine Powder Pillow for 25-mL sample to the sample cell.



8. Put a cap on the sample cell. Invert the sample cell several times to mix. Go to the next step immediately.



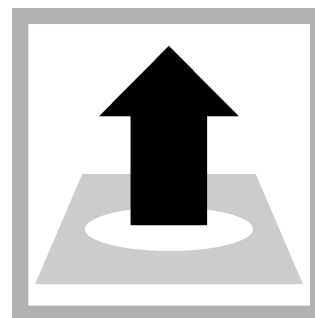
9. Clean the blank sample cell.



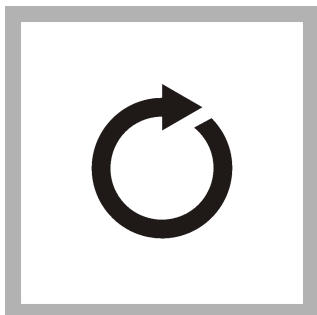
10. Within 1 minute of the reagent addition, insert the sample cell into the cell holder.



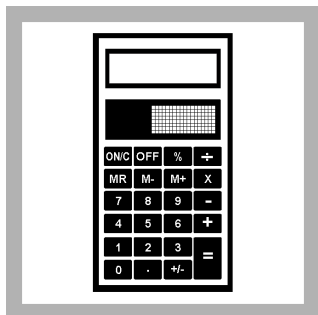
11. Push **READ**. Record the results. Results show in mg/L Cl₂.



12. Remove the sample cell from the cell holder. Discard the contents of the sample cell.

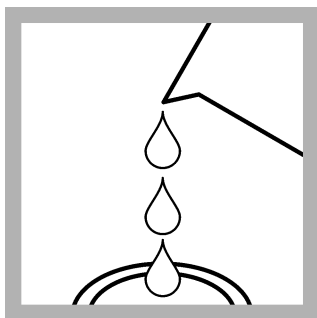


13. Do steps 2–3 and 7–12 four more times. Use the same sample cell for all five measurements.

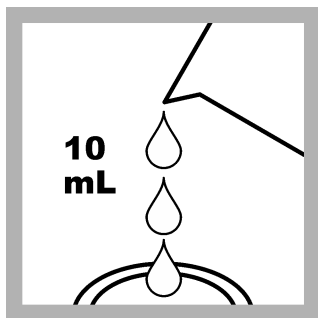


14. Calculate the accuracy and precision. Refer to [Calculate the accuracy and precision](#) on page 13.

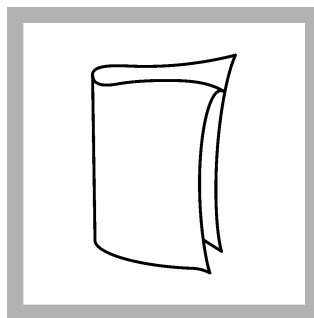
Test procedure—chlorine standard accuracy



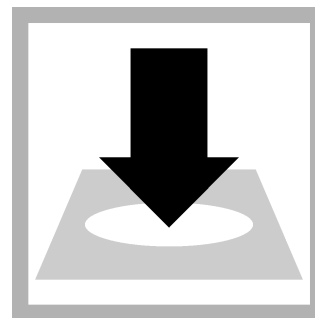
1. Fill the sample cell two times with the standard solution. Discard the standard solution.



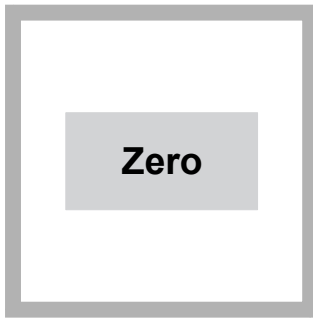
2. Fill the sample cell with 10 mL of the standard solution.



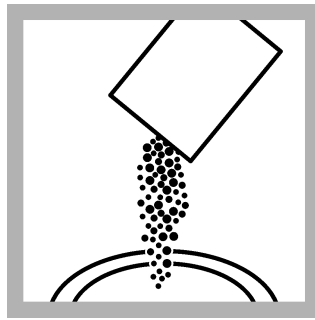
3. Clean the sample cell.



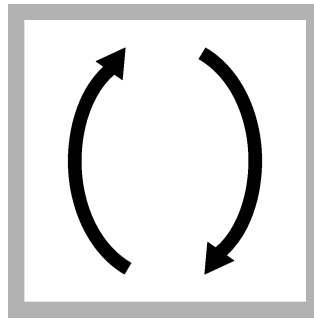
4. Insert the sample cell into the cell holder.



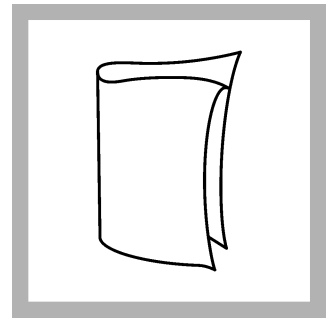
5. Push **ZERO**. The display shows 0.00 mg/L Cl₂.



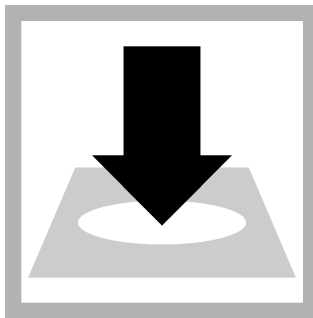
6. **Prepare the standard:** Add the contents of one DPD Free Chlorine or one DPD Total Chlorine Powder Pillow for 25-mL sample to the sample cell.



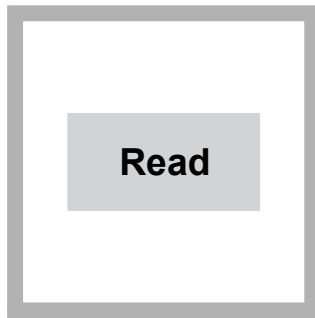
7. Put a cap on the sample cell. Invert the sample cell several times to mix. Go to the next step immediately.



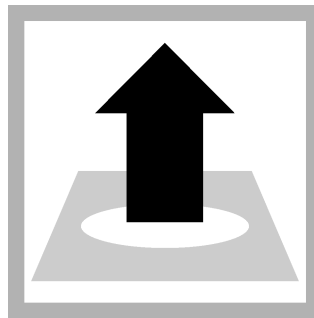
8. Clean the sample cell.



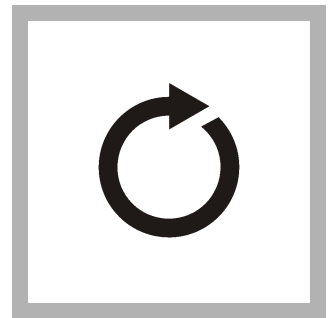
9. Within 1 minute of the reagent addition, insert the sample cell into the cell holder.



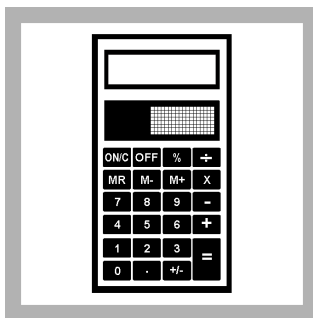
10. Push **READ**. Record the results. Results show in mg/L Cl₂.



11. Remove the sample cell from the cell holder. Discard the contents of the sample cell.



12. Do steps 1–2 and 6–11 four more times. Use the same sample cell for all five measurements.



13. Calculate the accuracy and precision. Refer to [Calculate the accuracy and precision](#) on page 13.

Calculate the accuracy and precision

1. Calculate the accuracy (average) of the method blank values. Add the five method blank values and then divide by 5.
Make sure that the average value of the five method blank values is equal to or less than 1/3 the value of the lowest chlorine concentration used to do the initial verification of the grab sample instrument.
2. Calculate the accuracy (average) of the chlorine standard values. Add the five chlorine standard values and then divide by 5.

Make sure that the average value of the five chlorine standard values is $\pm 15\%$ of the expected chlorine concentration.

3. Calculate the precision of the chlorine standard values as follows:
 - a. Use a spreadsheet application or a calculator function to identify the relative standard deviation (RSD) of the five chlorine standard values.

$$\text{RSD} = (S \div X) \times 100\%$$
 Where:
 S = the standard deviation for the five chlorine standard values
 X = the average value of the five chlorine standard values

Make sure that the precision or scatter in the concentration values of the five chlorine standard values has a relative standard deviation that is 15% or less of the average value.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	10	100/pkg	1407099
Or			
DPD Total Chlorine Reagent Powder Pillow, 25 mL	10	100/pkg	1406499

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite [®] Ampule, 50-75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette [®] Ampule, 50–75 mg/L	16/pkg	1426810
SpecCheck [™] Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549

Required apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette [®] Ampules	each	2196800
PourRite [®] Ampule Breaker, 2 mL	each	2484600
Flask, volumetric, 50 mL	each	1457441
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Gloves, chemical resistant, size 10	pair	2410105
Goggles, safety, standard	each	2927902
Field notebook	each	2091800
Pipette, adjustable volume, 0.1–1.0 mL	each	BBP078
Pipette tips, for 0.1–1.0 mL pipette	100/pkg	BBP079
Pipet, adjustable volume, 1.0–5.0 mL	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	75/pkg	BBP068
Wipes, disposable	70/pkg	2096900
Wipes, disposable	280/pkg	2097000
Water, deionized	4 L	27256

Initial calibration and verification of online chlorine analyzers

EPA Method 334.0 reference: Start-up procedures section—Online analyzer, paragraph 10.2.1

Scope and application

Use this procedure for the initial calibration or verification of the calibration of an online chlorine analyzer. When the online chlorine analyzer has stable values, grab samples are collected and analyzed for chlorine with a DPD chlorine method that was recently verified. The results of the grab sample method are used to verify the analyzer calibration curve.

Before starting

Review the safety information and the expiration date on the package.
Use only a DR5000 or DR6000 for this test.
Use only 1-cm quartz sample cells for this test.
Fully clean the quartz sample cell between reagent sets. Clean the sample cell with alcohol (isopropyl or pure ethanol), rinse with water, clean with more alcohol and then let air dry.
Use only a glass pipet and pipet filler for this test. Keep the iso-octane phase out of the pipet filler. UV-active substances can cause inconclusive results (e.g., plasticisers).
Set a zero value on the spectrophotometer for each TNTplus [®] reagent set. Changes in the iso-octane quality of the reagent have a direct effect on the measurement result.
Use the same quartz sample cell to set the zero value and to measure the samples. Sample cell differences have a direct effect on the measurement result.
Degas samples that contain carbon dioxide before the test. For example, stir samples with a magnetic stirrer.
Do not filter the sample. The foam contains bitter substances.
Remove the wort and cloudy beer with a centrifuge before the test.
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.

Before starting

Identify a collection point for the grab sample that is as near as possible to where the sample goes in the online chlorine analyzer.
Use only glassware that has no chlorine demand.
For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 2.
Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.
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
SpecCheck Secondary Standards kit, Chlorine DPD, MR	1
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1

Items to collect (continued)

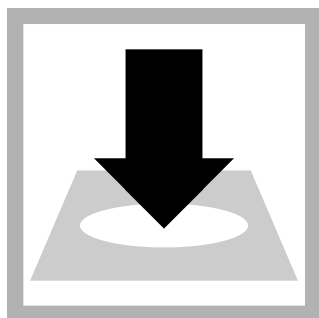
Description	Quantity
Or	
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1

Refer to [Consumables and replacement items](#) on page 17 for order information.

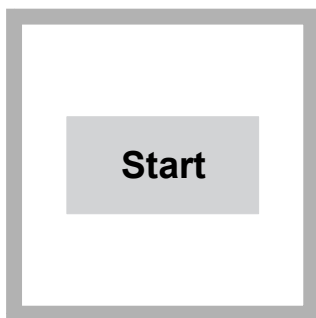
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

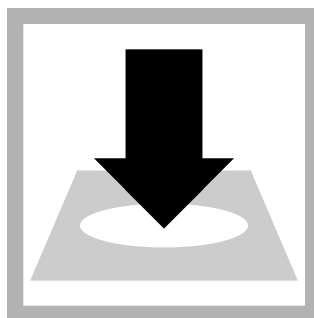
Test procedure



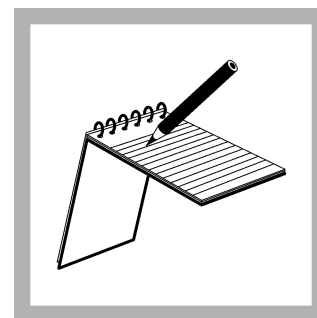
1. Measure the DPD Chlorine-MR SpecCheck standards in the instrument that is used to measure grab samples. Refer to [Verification of secondary DPD SpecCheck chlorine standards](#) on page 8. Acceptable readings confirm that the instrument performance is good and has not changed after the instrument was moved to the analyzer site.



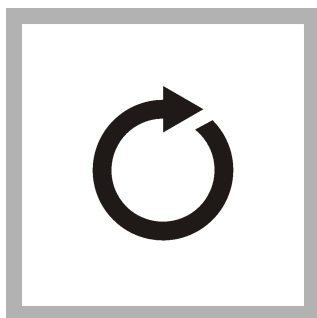
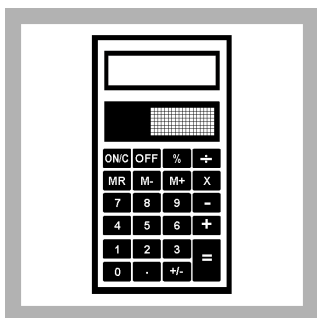
2. Start the program number for Method 10245 (free chlorine) or Method 10250 (total chlorine). For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 2.
Note: *Although the program name can be different between instruments, the program number does not change.*



3. Use the grab sample instrument to measure the sample. Use the same analysis techniques and precautions that were used for the Initial Demonstration of Capability (IDC) grab sample procedure. Refer to [Initial demonstration of capability \(IDC\) for field samplers](#) on page 10.



4. Record the results. Results show in mg/L Cl₂.



5. Compare the results from the grab sample instrument to the results from the online analyzer. The grab sample method can be used for verification of the online analyzer accuracy.

If the results are more than $\pm 15\%$ from the calculated value, adjust the calibration curve of the online analyzer so that it is the same as the result from the grab sample instrument. Refer to the online analyzer documentation to adjust the calibration curve.

Note: During usual operation of the online analyzer, make sure that the readings are ± 0.1 mg/L or $\pm 15\%$ of the results from the grab sample instrument.

6. If the calibration of the online analyzer was adjusted, do steps 3–4 until the measurement from the online analyzer agrees with the results from the grab sample instrument.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1407099
Or			
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1406499

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite [®] Ampule, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette [®] Ampule, 50–75 mg/L	16/pkg	1426810
SpecCheck [™] Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549

Initial demonstration of capability (IDC) for online chlorine analyzers

EPA Method 334.0 reference: Start-up procedures section—Online analyzer, paragraph 10.2.2

Scope and application

Start the initial demonstration of capability (IDC) after the calibration verification is complete. Refer to [Initial calibration and verification of online chlorine analyzers](#) on page 15. The IDC takes a minimum of 14 days. Complete the full IDC before the analyzer is used for compliance monitoring measurements. Record and keep the data collected during the IDC.

Before starting

The IDC is not a requirement for chlorine analyzers already installed if historical data shows agreement with grab sample analyses. Agreement is within ± 0.1 mg/L or $\pm 15\%$ (the larger value) of the grab sample data. Historical data must show agreement for 14 continuous days without analyzer maintenance or calibration.

For installations with multiple analyzers, the first analyzer must successfully complete the 14-day IDC. Agreement criterion for multiple analyzers is within ± 0.1 mg/L or $\pm 15\%$ (the larger value) of the grab sample data.

When the same model of analyzer is installed at each location, the IDC for the installation of multiple analyzers can be decreased to 7 days with no missed days. The water properties and treatment procedure must be the same at each location.

Make sure that the verification of calibration for grab sample measurements is complete before the IDC procedure is started. Refer to [Initial calibration and verification of online chlorine analyzers](#) on page 15.

Make sure that the IDC for grab sample measurements with the field sampler procedure is completed before the IDC procedure is started. Refer to [Initial demonstration of capability \(IDC\) for field samplers](#) on page 10.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

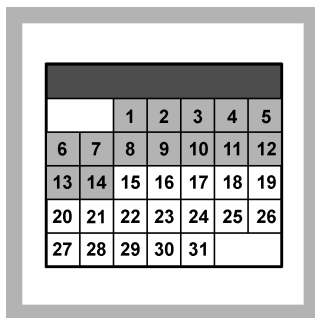
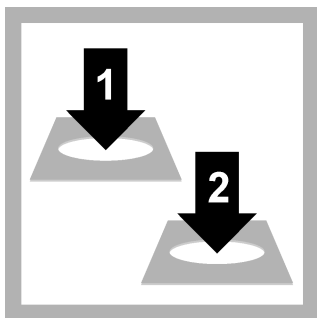
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Description	Quantity
DPD Free Chlorine Reagent Powder Pillow, 25 mL	2
Or	
DPD Total Chlorine Reagent Powder Pillow, 25 mL	2

Refer to [Consumables and replacement items](#) on page 17 for order information.

Test procedure



1. Measure two grab samples for chlorine with the program, instrument and procedures of a recently verified measurement system. Refer to [Initial calibration and verification of online chlorine analyzers](#) on page 15.

The measurements of the two grab samples must be within the ± 0.1 mg/L or $\pm 15\%$ acceptance criteria of the analyzer values.

2. Do step 1 for 14 days with no missed days. When 14 days of data pairs agree with the acceptance criteria, the analyzer can be used for compliance monitoring.

Note: When operation is stopped for analyzer maintenance, do a verification of the online analyzer with a grab sample. Refer to [Initial calibration and verification of online chlorine analyzers](#) on page 15 Do a verification again after one day of operation.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1407099
Or			
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1406499

Routine monitoring procedures

Routine verification of the calibration for grab samples

EPA Method 334.0 reference: Routine procedures section—Grab sample method, paragraph 11.1

Scope and application

Use this procedure to verify the grab sample method that is used to monitor the online chlorine analyzer during normal operation. Verify the grab sample method a minimum of one time each 3 months or when a grab sample is used to adjust the calibration of the online analyzer.

Before starting

If the results are more than $\pm 15\%$ from the calculated value, correct the problem before the grab sample method is used for verification of online measurements.

Record and keep the grab sample and online analyzer comparison data in accordance with the requirements of the primacy agency.

As necessary, use the secondary DPD Chlorine-MR Spec Check Standards to make sure that the performance of the grab sample instrument has not changed.

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
Chlorine Standard Solution Ampule, 50–75 mg/L	varies
Water with no organic content	varies
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1
Or	
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1

Refer to [Consumables and replacement items](#) on page 17 for order information.

Prepare the standard solution

Prepare one chlorine standard solution that is approximately the expected concentration.

Items to collect:

- Chlorine standard solution ampule, 50–75 mg/L Cl_2
- Volumetric flask (50 mL or 100 mL)
- Pipet (0.2–1.0 mL or 1.0–5.0 mL) and pipet tips
- Water that has no organic material

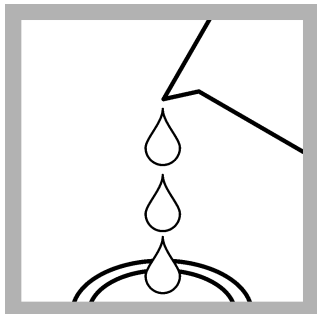
Refer to [Consumables and replacement items](#) on page 17 for order information.

Do the steps that follow to prepare each standard solution.

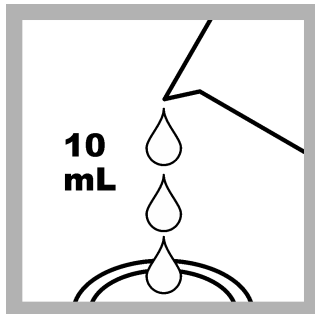
1. Calculate the volume of standard solution and the volumetric flask volume (50 mL or 100 mL) to use to prepare the standard solution. Refer to [Calculate the concentration of the prepared standard solutions](#) on page 5.
2. Add approximately 25 mL of water that has no organic material to a clean 50-mL or 100-mL volumetric flask.
3. Open the standard solution ampule.

4. Use a pipet to add the calculated volume of standard solution to the volumetric flask.
5. Fill the volumetric flask to the mark with water that has no organic material.
6. Put a stopper in the volumetric flask. Invert to mix.

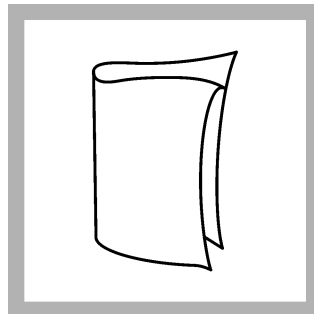
Test procedure



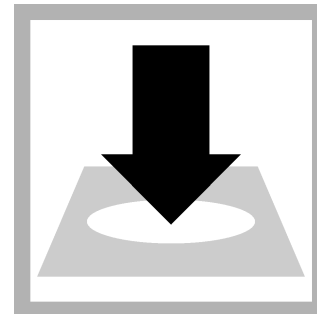
1. Fill the sample cell two times with the standard solution. Discard the standard solution.



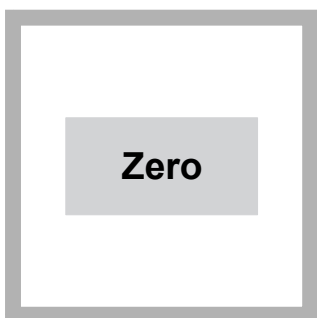
2. Fill the sample cell with 10 mL of the standard solution.



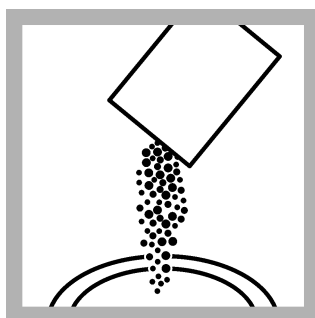
3. Clean the sample cell.



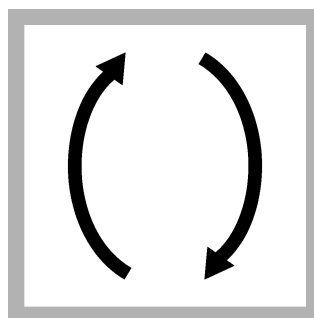
4. Insert the sample cell into the cell holder.



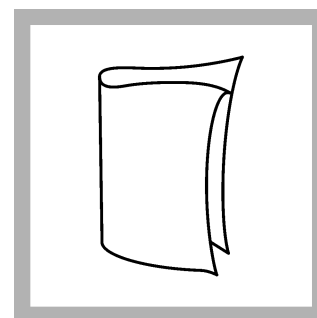
5. Push **ZERO**. The display shows 0.00 mg/L Cl₂.



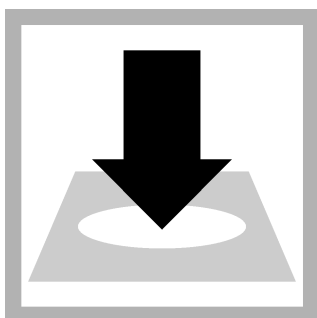
6. **Prepare the standard:** Add the contents of one DPD Free Chlorine or one DPD Total Chlorine Powder Pillow for 25-mL sample to the sample cell.



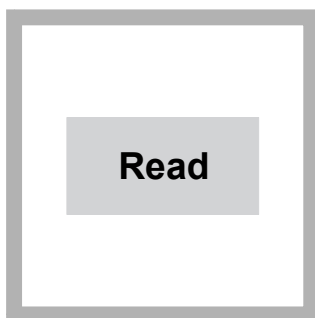
7. Put a cap on the sample cell. Invert the sample cell several times to mix. Go to the next step immediately.



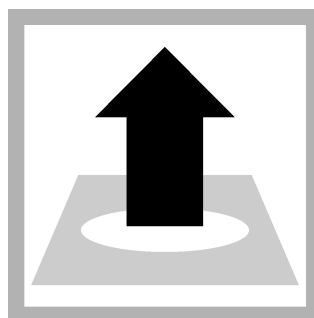
8. Clean the sample cell.



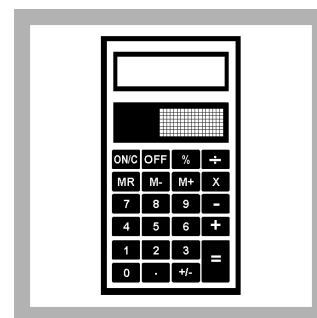
9. Within 1 minute of the reagent addition, insert the sample cell into the cell holder.



10. Push **READ**. Record the results. Results show in mg/L Cl₂.



11. Remove the sample cell from the cell holder. Discard the contents of the sample cell.



12. Compare the measured value to the calculated value. If the measured value is within $\pm 15\%$ of the calculated value, the grab sample method can be used for verification of the online analyzer accuracy.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1407099
Or			
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1406499

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite [®] Ampule, 50-75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette [®] Ampule, 50–75 mg/L	16/pkg	1426810
SpecCheck [™] Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549

Required apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette [®] Ampules	each	2196800
PourRite [®] Ampule Breaker, 2 mL	each	2484600
Flask, volumetric, 50 mL	each	1457441
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Gloves, chemical resistant, size 10	pair	2410105
Goggles, safety, standard	each	2927902
Field notebook	each	2091800
Pipette, adjustable volume, 0.1–1.0 mL	each	BBP078
Pipette tips, for 0.1–1.0 mL pipette	100/pkg	BBP079
Pipet, adjustable volume, 1.0–5.0 mL	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	75/pkg	BBP068
Wipes, disposable	70/pkg	2096900
Wipes, disposable	280/pkg	2097000
Water, deionized	4 L	27256

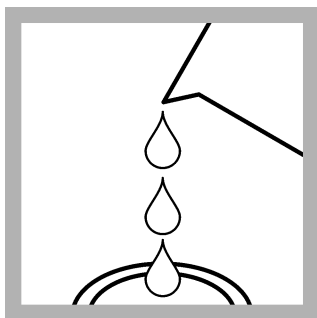
Routine verification of the calibration for online chlorine analyzers

EPA Method 334.0 reference: Routine procedures section—Online analyzers, paragraph 11.2

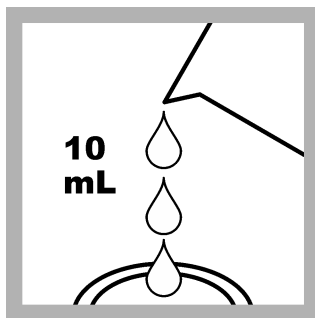
Scope and application

This procedure uses the grab sample method to verify the accuracy of online chlorine analyzers during typical operation. If the results of the grab sample measurements must be within ± 0.1 mg/L or $\pm 15\%$ (the larger value) of the online analyzer value.

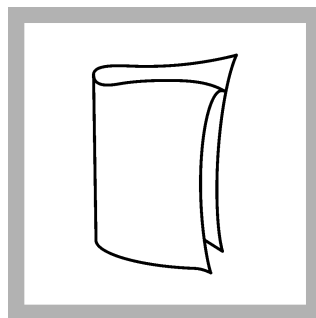
Test procedure



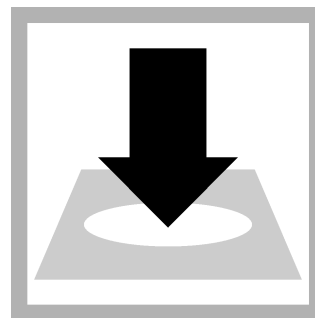
1. Fill the sample cell two times with the standard solution. Discard the standard solution.



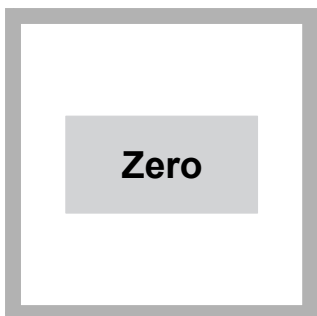
2. Fill the sample cell with 10 mL of the sample water.



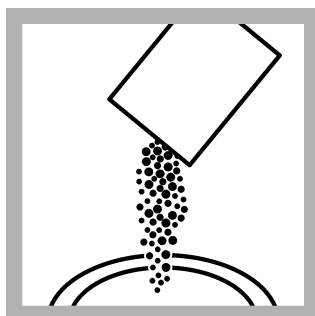
3. Clean the sample cell.



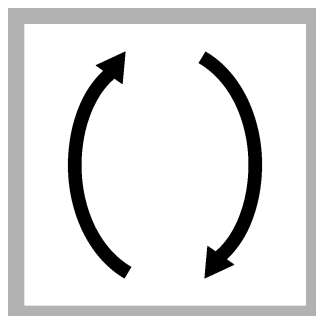
4. Insert the sample cell into the cell holder.



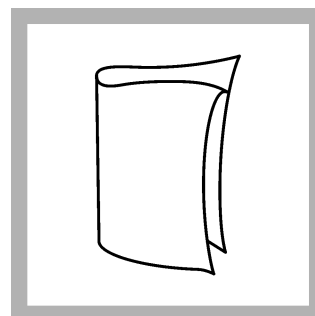
5. Push **ZERO**. The display shows 0.00 mg/L Cl_2 .



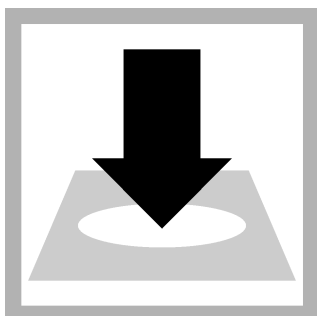
6. **Prepare the sample:** Add the contents of one DPD Free Chlorine or one DPD Total Chlorine Powder Pillow for 25-mL sample to the sample cell.



7. Put a cap on the sample cell. Invert the sample cell several times to mix. Go to the next step immediately.



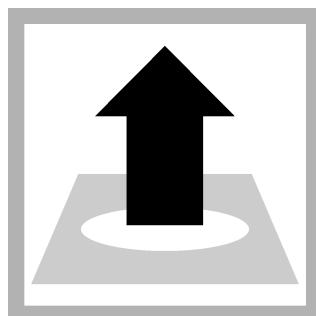
8. Clean the sample cell.



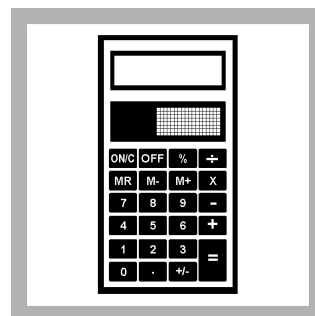
9. Within 1 minute of the reagent addition, insert the sample cell into the cell holder.



10. Push **READ**. Record the results. Results show in mg/L Cl_2 .



11. Remove the sample cell from the cell holder. Discard the contents of the sample cell.



12. Compare the measured value of the grab sample to the online analyzer measurement. If the online analyzer measurement is more than $\pm 15\%$ of the grab sample value, go to [Troubleshooting](#) on page 24.

Troubleshooting

If the online analyzer measurement is more than $\pm 15\%$ of the grab sample value, do the steps that follow:

1. Collect a second grab sample. Do the test procedure again to make sure that the results are the same.
2. Complete analyzer maintenance (e.g., flow adjustment, pH adjustment, cleaning, new membrane or fresh reagents) to make sure that there are no problems with the analyzer.
3. For remote or field sites, use the DPD Chlorine-MR Spec Check Secondary Standards to make sure that the grab sample measurement is accurate. Refer to [Verification of secondary DPD SpecCheck chlorine standards](#) on page 8.
Note: If the secondary standards show that an online analyzer calibration adjustment is necessary, complete the [Routine verification of the calibration for grab samples](#) on page 20 within 24 hours with the same lot of reagents.
4. Use a chlorine check standard solution to verify the accuracy of the grab sample measurement. Refer to [Routine verification of the calibration for grab samples](#) on page 20.
5. If the grab sample measurement is accurate, adjust the calibration curve of the online analyzer so that the online analyzer and the grab sample measurements agree. Refer to the online analyzer documentation to adjust the analyzer calibration.
6. Collect another grab sample. Measure the chlorine concentration to make sure that the online analyzer and the grab sample measurements agree.
7. Do steps 5 and 6 again until the online analyzer and the grab sample measurements agree.
8. After one day of operation, collect and measure an additional grab sample to make sure that the online analyzer measurements are accurate.
9. Follow the routine schedule for grab sample comparisons. Analyze a grab sample at least one time each 7 days.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1407099
Or			
DPD Total Chlorine Reagent Powder Pillow, 25 mL	1	100/pkg	1406499

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite® Ampule, 50-75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
SpecCheck™ Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549

Required apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
PourRite® Ampule Breaker, 2 mL	each	2484600

Required apparatus (continued)

Description	Unit	Item no.
Flask, volumetric, 50 mL	each	1457441
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Gloves, chemical resistant, size 10	pair	2410105
Goggles, safety, standard	each	2927902
Field notebook	each	2091800
Pipette, adjustable volume, 0.1–1.0 mL	each	BBP078
Pipette tips, for 0.1–1.0 mL pipette	100/pkg	BBP079
Pipet, adjustable volume, 1.0–5.0 mL	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	75/pkg	BBP068
Wipes, disposable	70/pkg	2096900
Wipes, disposable	280/pkg	2097000
Water, deionized	4 L	27256



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