Standard Operating Procedure
(Field Testing)

Chlorine, Free & Total by Colorimetric DPD

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Approved By: *Courtney Diduck*, Analytical Services Branch Head

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N:\Environmental Standards\Analytical Services\SOP (PDFs)
Hyperlinks to external documents and navigation within this document are highlighted and underlined in green font. These links are functional in the electronic version of this document, when the user has permission and the document is viewed within the City of Winnipeg's intranet site from the above mentioned folder. All documents pertaining to this SOP are maintained in subfolders of the following Master Folder; N:\Environmental Standards\Methods\Chlorine-DPD (SOP 30)
Latest revisions are highlighted in blue print.
All hand-written amendments (except for spelling or grammatical errors) must be approved immediately by the Analytical Services Branch Head or Quality Assurance Officer, who shall initial and date the amendments. The procedure shall be formally revised and reissued as soon as practicable.

Table of Contents

All forms, charts, reagent logs located in the workbook; ChlorineForms.xlsx[1]

Control Charts are printed from; ChartGenerator.xlsm[2]

Introduction and Scope

Chlorine is the most widely used drinking water disinfectant to destroy pathogenic organisms in water in order to prevent the spread of waterborne disease and to protect the water from recontamination during storage. In addition, chlorine reacts with iron, ammonia, manganese, sulfide and some organic compounds to help improve the finished water quality.

Chlorine is applied to water in its molecular or hypochlorite form and initially undergoes hydrolysis to form free chlorine. A portion initially reacts with ammonia, iron, manganese, sulfide and some organic materials and is therefore not available for disinfection. This is called the chlorine demand of the water. The remaining chlorine concentration after the chlorine demand is the total residual chlorine. Total residual chlorine is made up of combined chlorine (amount that has reacted with nitrates and ammonia and is unavailable for disinfection) and free chlorine. Free chlorine is chlorine available to deactivate disease-causing organisms, and is thus used as a measure to determine if the water is potable. The pH and temperature of the water affect the balance and ratio of all the chlorine compounds.

The City of Winnipeg's drinking water supply is chlorinated at the source, at the water treatment plant, and at the three pumping stations. Sodium hypochlorite is either generated on-site in the WTP (either from $NaCl^-$ or from chlorine gas), or purchased, and stored in holding containers and used to chlorinate the effluent treated water. Free and total chlorine is measured at numerous locations and throughout the distribution system. Combined chlorines are not measured by this method but can be calculated from the total and free.

Referenced Method

This method is modified from Standard Methods for the Examination of Water and Wastewater[3], 4500 Cl-G. Chlorine Residuals, approved by Standard Methods Committee, 2000, Editorial Revisions, 2011, with the following modifications;

- a portable, single wavelength unit, Hach Pocket Colorimeter II, is used with the wavelength set at 528 nm NOT 515 nm
- no calibration standards are made nor a calibration curve produced as the meter is factory preset
- Monochloramine and Dichloramine are not measured with the PocketColorimeter II
- Based on in-house method validation studies, samples measured in the range of 2 to 3 mg/L are read at the high range, immediately diluted by ½ with DI water then re-read at the low range.

Scope

This method applies to field analysis of Free and Total Chlorine (residuals). Proficiency testing samples are analyzed by the exact same procedure, but the "field" location is the laboratory at 2230 Main St. All other field locations are conducted within enclosed structures and buildings at other sites which are listed in the LIMS Dictionaries, Locations, and in the corresponding projects.

Minimum Detection Limits

The minimum detectable limit, based on the instrument set to the low range, is 0.02 mg/L Cl-.

Range and Bias

The **low range** is from 0.02 to 2.0 mg/L. Any value at or greater than 2 mg/L is re-analyzed in the high range method.

The **high range** is from 1.0 to 8.0 mg/L. In-house studies show a significant positive **bias** in the 2-3 mg/L range. Since there is no bias in the 1-2 mg/L range, any prepared samples measured at 2-3 mg/L are immediately diluted to 10 mL, mixed, and re-measured. This value multiplied by two (due to the dilution) is recorded as the final result. This eliminates the use of a correction factor due to bias.

Fit-For-Use

This method is fit for its intended use for the Determination of Chlorine, Free and Total by Colorimetric DPD, in water in the range of 0.02 to 8 mg/L Cl, when using a HACH Pocket Colorimeter II.

Method Validation[4] by Gerry Levesque, Quality Assurance Officer, July 31, 2009 and updated November 4, 2014.

Summary of Method

Chlorine can be present in water as free chlorine and as combined chlorine. Both forms can coexist in the same solution and can be determined together as total chlorine. Free chlorine is present as hypochlorous acid or hypochlorite ion. Combined chlorine represents a combination of chlorine-containing compounds including but not limited to monochloramine, dichloramine, nitrogen trichloride, and other chlorine derivatives. The combined chlorine oxidizes triiodide ion (I3) to iodine (I2). The iodine and free chlorine reacts with DPD (N, N-diethyl-p-phenylenediamine) to form a red solution. The color intensity is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run a free chlorine test and a total chlorine test. Subtract the results of the free chlorine test from the total chlorine test to obtain the combined chlorine concentration.

LIMS Test Codes

TestCode	Test Name	Unit
Chlorine, Free	Chlorine Residual, Free	mg/L
Chlorine, Total	Chlorine Residual, Total	mg/L

Sample Requirements

Sample History

Holding Time

Chlorine residuals are analyzed immediately after sampling. Do not store samples. Chlorine in water is not stable and will dissipate rapidly, particularly in weak concentrations.

Sample Collection

All chlorine testing must be done in-situ and cannot be "collected" for later analysis. Samples must be collected immediately prior to the conduct of the test, specifically before the addition of the DPD reagents. Taking samples is described in Test Procedure, Taking Aliquots, page 10.

Volume Required

10 mL each for free and total chlorine.

Interferences

i. Exposure to sunlight, other strong light, or agitation will accelerate the reduction of chlorine.

ii. Very low temperatures (as experienced all winters) will slow the response of the colour development. Ensure sufficient time is allowed.

iii. Condensation on the sample cells will cause positive interferences.

iv. Turbidity, from dissolved gases and air bubble cause positive interferences.

Interferences ii, iii, & iv are only noticeable with very low level chlorine or with non-chlorinated, raw water samples. Refer to False Positive Readings, page 11.

Although the following compounds may interfere in the quantities listed, the levels are too low in any of the City of Winnipeg's raw or treated water to cause interferences. They are listed for information only.

- Acidity greater than 150 mg/L CaCO3 may not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N Sodium Hydroxide. Determine amount to be added on a separate 10-mLsample, and then add the same amount to the sample being tested. Correct for the additional volume.
- Alkalinity greater than 250 mg/L CaCO3 may not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N Sulfuric Acid. Determine amount to be added on a separate 10-mL sample, and then add the same amount to the sample being tested. Correct for the additional volume.
- Bromine, Br_2 and Iodine, I_2 interfere at all levels, but they are not present in our water supply.
- Hardness has no effect at less than 1,000 mg/L as CaCO3

Chemicals & Reagents

Both the powder pillows and SwiftTestTM are used in the laboratory and field. All reagents must be purchased through a Hach approved vendor. The following part numbers (from Anachemia Science) have therefore been listed to facilitate re-ordering of these chemicals.

Purchased Reagents

Description	Part No.
Free Chlorine Powder Pillows for 10mL Samples	21055-69
Total Chlorine Powder Pillows for 10mL Samples	21056-69
Free Chlorine Replacement Vials for the SwiftTest Reagent Dispenser	21055-60
Total Chlorine Replacement Vials for the SwiftTest Reagent Dispenser	21056-60
SPEC Secondary Standard for chlorine	26353-00

Total Chlorine Reference Standard, (sealed ampoules) NSI Solutions Inc./VWR Int. NSQCI-123

Deionized (MilliQ™) water, required to dilute samples in the 2-3 mg range. Prepare/fill a small bottle each day in use. Note: there is currently only one routine location in this range.

Reagent Preparation Logs

No reagents are prepared, but all reagents in use are logged into the LIMS Chemicals and Standards Module, and the use of the Secondary standards is recorded on worksheets found in the *ChlorineForms.xlsx*.

Total Chlorine Reference Standard, Accuracy Check[5]

The following instructions were taken from the certificate of analysis. If future instructions differ, then follow the Certificate of Analysis for that specific standard. Instructions may differ if this standard is purchased from another manufacturer/supplier, other than NSI.

1. Fit a 25 mL flask with about 10-15 mL of DI or MilliQ™ water.
2. Take a tube and shake contents to bottom of tube.
3. Snip off the top of the tube with scissors and invert tube into the opening of the cuvette.
4. Squeeze the bottom of the tube.
5. The contents will fully release into the vessel. No rinsing is required. (The plastic contains a high content of "Teflon" or like material specific for that purpose.)
6. Fill the flask to the mark with DI water, cap, and mix by inverting several times then proceed immediately with analysis.

Equipment & Supplies

If the colorimeter doesn't turn on or appears to be not working, check or replace the batteries.

For more information on the use of the Pocket Colorimeter II, Error Codes, Battery Replacement, etc, refer to *Equipment Instruction Manuals*[6] listed in References, page 18.

- 10 mL cells, 25 x 60 mm (for low range)
- 1 cm, 10 mL cell (for high range)
- SwiftTestTM Dispenser or packets
- Timer (minutes)

HACH Pocket ColorimeterII

- Lamp: Light emitting diode (LED)
- Detector: Silicon photodiode
- Photometric precision: ± 0.0015 Abs
- Filter bandwidth: 15 nm
- Wavelength: 528 nm
- Absorbance range: 0–2.5 Abs

Operating conditions: 0 to 50 °C (32 to 122 °F); 0 to 90% relative humidity

Power supply: Four AAA alkaline batteries; approximate life is 2000 tests

New & Return to Use

All new instruments or any instrument taken Out-Of-Service (or OUT-OF-USE) must be validated prior to its use. The validation includes the repeated analysis of a Certified Reference Material, and analysis of duplicates, with the latter also analyzed on a valid instrument. After completion, the template "Return-To-Use" used to document is forwarded to the QA Officer for statistical analysis and validation.

Repair Service

Authorization must be obtained from Hach Company before sending any items for repair. Please contact the Hach Service Center serving your location.

Canada:

Mike Demkiw
Senior Field Service Technician – Manitoba and North Western Ontario
Hach Sales and Service Canada Ltd.
Office: 886-223-1793
Fax: 866-806-6797
E-mail: mdemkiw@hach.com
Tech Support: 1-800-665-7635
www.hach.com/servicecanada
Website: www.hach.com

Note: The Pocket Colorimeters are serviced and cleaned annually by HACH personnel. If an instrument is in use outside of the laboratory at the time of service, ensure that it is available for servicing the following year. It should be noted that this is not a calibration service but a general maintenance, cleaning and checks. A full return-to-use validation is not required, but each instrument shall be verified by analyzing the CRM check standard. These instruments are "factory" calibrated and any instrument that is found to be inaccurate or is only suspected as being "off" should be immediately taken out-of-service.

Glassware Preparation

Thoroughly rinse the glass cells with the test water after each use. Check the glassware for cleanliness. Discard samples cells if there are any scratches, pits or marks that could affect the measurement. This is more pronounced with the high range, plastic sample cells.

Perform a manual acid wash weekly by rinsing the sample cell with 50% HCl and rinsing with copious amounts of deionized water. Afterwards, inspect and match the cells as described in Glass Vial Maintenance & Checks. Record the work performed in the worksheet tab "Glass Vials" from the ChlorineForms.xls workbook. The hard copy is maintained on the Chlorine clipboard and filed in the method binder.

Cleaning vials after use with sewage and outfall samples:

Perform a manual acid wash every day that sewage or outfall samples are tested by rinsing the sample cell with 50% HCl and rinsing with copious amounts of deionized water.

Glass Vial Maintenance & Checks

Each kit contains two 10 mL sample cells for the low range method and one or two sample cells for use in the high range. Each time that a sample cell is replaced, both cells must be matched/verified against each other. (Imperfections and variations/stress in the glass can affect the absorbance of the sample or transmittance of the light). Vials must be within 0.02

mg/L of each other. If over this amount, then check against a third vial and reject the outlier that is over the limit. Follow the instructions and use the printed Excel worksheet to record the findings. See *Glass Vials* tab in *ChlorineForms.xlsx*.

Weekly, inspect and match the cells as described in Glass Vial Maintenance & Checks. Record the work performed in the worksheet tab "Glass Vials" from the ChlorineForms.xls workbook. The hard copy is maintained on the Chlorine clipboard and filed in the method binder. Also run the

Quality Control Plan

Batch Creation

Samples are analyzed in batches created using the LIMS "Create Batch" function (see LIMS User Manual). Each batch is assigned a unique identifier, which is recorded with each test assigned to the batch.

Each instrument used shall have its own unique batch ID and set of quality control samples outlined in the next section.

Method Quality Control

Note: a copy of the current QC worksheet and control charts is located in a magazine rack on the WQ laboratory bench.

The following QC parameters are incorporated into every run:

- For each day in use, measure and record all three secondary standards (CalVer) in the laboratory just prior to the field testing. These secondary standards are not used to calibrate or to calculate the accuracy of the instrument, but they are useful for measuring performance and stability of the instrument and can only be used on the low range. Enter in the LIMS as; No. 3) Calibration Verification Standard.
- Perform the first duplicate using the laboratory tap water, prior to leaving. Perform a second field duplicate in the field, preferably in the second half of the work shift. Record on the Chlorine Residual, Duplicates worksheet. This is useful in determining if there is a problem with the DPD reagent or the reagent dispenser. Enter in the LIMS as QC No. 7) Duplicate Sample (Prep & Analysis).
- Measure and record the mid range secondary standard immediately after returning to the laboratory; this shows your instrument drift. (See worksheet tab name "CRM Check Std & Chart".
- All results are recorded in a notebook and shall include sample information, and date analyzed. Initial each page and record the LIMS Equipment ID of the chlorine kit being used.
- Verify QC data against established upper and lower control limits. If a QC standard is out of control, treat as a non-conformance.

Weekly Vial and Accuracy Checks

Perform once a week for each Pocket Colorimeter II in use.

Prepare the standard as described in *Total Chlorine Reference Standard, Accuracy Check* page 6.

Record the results on the control chart and in the LIMS QC Module as QC No. 8) Sample Reference Material".

Acceptance Criteria

The secondary standards shall be within the tolerance limits as described in the certificate of analysis. A reference value is also given.

The duplicates shall be within the established control limits of ±5.4% for total and free chlorine.

Non-Conformance and Corrective Action

If two or more standards are outside of the control limits, then repeat the verification (page 10, Using the Spec√ Standards), but substitute the Spec√ blank with reagent grade water.

If the duplicate recovery is outside of the control limits then;

- Verify the measurement with another colorimeter. If the colorimeter is determined to be a problem, return it to HACH Instruments for servicing. These instruments cannot be calibrated in-house.
- Run the Total Chlorine Accuracy Check (weekly check)

If the secondary standards are outside of the control limits then;

- Verify the measurement with another colorimeter,
- Run a sample blank (DI & reagents),
- If the standards fail on two instruments, then (one or more) of the standards has degraded and should not be used. Continue to use the "good" standards until replacement is available. (Always replace the set, not one std.)

If the Total Chlorine Accuracy Check (CRM std) fails, then;

- Verify the measurement with another colorimeter. If this other colorimeter passed, then take discontinue the use of the first colorimeter. Place an OUT-OF-USE label on it and investigate further when time permits.
- Run a sample blank (DI & reagents)

If none of the above recommended actions resolve the problem, then further consultation with supervisor and/or quality assurance officer is required including but not limited to;

- Notifying the Branch Head of the non-conformance through an E-Mail identifying the problem.
- Carry out corrective action to resolve the problem. (See Quality Manual for corrective action procedure.)
- Maintain these non-conformance records for audit and review.

Proficiency Testing

The laboratory pursues both accreditation and proficiency for Free and Total Chlorine at the 2230 Main Street laboratory location, through the Canadian Association of Laboratory Accreditation.

Since 2008, the laboratory participates in the CALA Proficiency Testing program for Free and Total Chlorine (in January & June) which are included in the C-32 Chlorine Test Group.

Test Procedure

Documentation Requirements

Chlorine testing of the City of Winnipeg's distribution system is done in conjunction with the bacteriological testing program whereby samples are collected and submitted to a contract lab for analysis. The results of the free and total chlorine are documented on the chain of custody forms that are submitted to the contract lab. A copy of those results, as well as the bacteriological testing, is automatically forwarded to the Manitoba Water Stewardship's Office of Drinking Water. This is applicable to the routine monitoring of the distribution system and water treatment plant effluent.

The list of locations and the template are in the *FORMS*[1] subfolder.

Settings

Switching Ranges

1. Press the MENU key. The display will show "SEL". A flashing arrow indicates the current range.
2. Press the READ/ENTER key to toggle between ranges.
3. Press MENU again to accept and exit back to the measurement screen.

Setting the Time

1. Press the MENU key, then press the ZERO/SCROLL key until the display shows a time in the "00:00" format.
2. Press READ/ENTER. The digit to be edited will flash.
3. Use the ZERO/SCROLL key to change the entry, then press READ/ENTER to accept and advance to the next digit. The time is entered in 24-hour format.

Using the Spec√ Standards

Prior to using the field meter, perform the following in the laboratory

1. Place the colorless Spec√ blank into the cell holder with the alignment mark facing the keypad. Tightly cover the cell with the instrument cap.
2. Press **ZERO**. The display will show "0.00".
3. Place the STD 1 cell into the cell holder. Tightly cover the cell with the instrument cap.
4. Press **READ/ENTER**. Record the concentration measurement.
5. Repeat steps 3 and 4 with cells labeled STD 2 and STD 3. Plot Standard 2 on the control chart.

Compare these measurements with previous measurements to verify the instrument is performing consistently. (If these are the first measurements, record them for comparison with later measurements.)

Note: The Spec√ Standards are used to verify that the instrument is functioning correctly. The actual instrument calibration is a factory setting that cannot be changed. Any significant change with these standards indicates a problem with the standard or the instrument.

After the field testing and immediately upon returning to the laboratory, read, record, and plot the result of Standard 2 following the same steps as above.

Taking Aliquots/Test Sample

All chlorine testing must be done in-situ and cannot be "collected" for analysis. This section describes the procedure for collection of the sample/aliquot from a tap, immediately prior to the addition of the DPD reagents. If samples are collected for additional testing (at the laboratory or contract laboratory) then read the corresponding procedure(s), SOP-17 Sampling[7], and/or SOP 18, Bacteriological Monitoring and Sampling Program.

Excerpt from SOP 18, Bacteriological Monitoring, Routine Sampling Procedure, p. 7.

> "1. Open the cold water tap fully and allow the water to run for a minimum of three minutes before collecting the sample. Locations with low flow or larger buildings (such as schools) may require up to five minutes.
>
> 2. Check the water temperature by inserting a thermometer in the flowing stream. When the temperature is stable (usually at its lowest reading) and the minimum time (3 min) has expired, the water is considered to be representative of the distribution system (or of the water that is in the water main). If the temperature is still changing, continue flushing until a stable reading is obtained. Return the thermometer to its protective case/location.
>
> 3. Reduce the water flow to prevent over spilling and splashing.
>
> 4. If the current location is a chlorine residual monitoring location;
>
> a. Record the temperature reading on your worksheet or in your field logbook.
>
> b. Measure and record the chlorine (as described in the next sections).

False Positive Readings

The number of false positive readings from condensation can occur at any time, but are more problematic in summer, in air-conditioned environment, and with very cold water.

The number of false positive readings from Turbidity, caused by dissolved oxygen, is more pronounced during the winter. Cold water has a higher concentration of saturated oxygen. Once the sample comes out of the tap, the pressure is released, causing the dissolved oxygen to dissipate. This increases the Turbidity of the sample and causes positive interference.

To minimize the interference and for all non-chlorinated water showing traces of chlorine, perform the test as normal, then perform these additional steps.

> Remove the sample from the sample compartment, open the cap (~5 seconds) to release any build-up of pressure and air bubbles, close, re-wipe the cell to remove any condensation, invert to mix and take a second reading. (This should only take 10-15 secs.) If the second reading is lower, record this measurement.

Chlorine, Free and Total, Low Range (0.02 to 2.00 mg/L Cl2)

NOTE: If the free chlorine is less than 0.10 mg/L on any distribution system monitoring location, inform the laboratory supervisor immediately.

Read "Taking Aliquots" on page 10.

Note that the steps for the Free and Total Chlorine measurements are the same, except a different reagent is used between the two. Conduct the Free Chlorine First, rinse several times and do the Total Chlorine test.

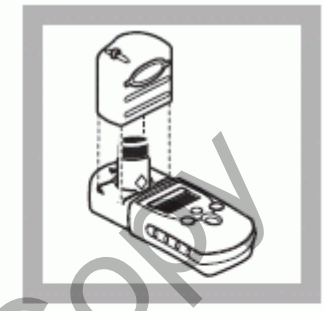
1. Fill a 10-mL cell with sample (the blank). Cap.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

2. Press the **POWER** key to turn the meter on.

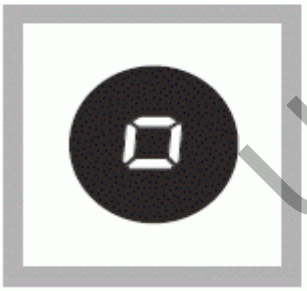
The arrow should indicate the low range channel (LR).

Note: *See page 2–4 for information on selecting the correct range channel.*



3. Remove the meter cap. Place the blank in the cell holder with the diamond mark facing the keypad. Fit the meter cap over the cell compartment to cover the cell.

Note: *Wipe excess liquid and finger prints off sample cells.*



4. Press **ZERO/SCROLL**.

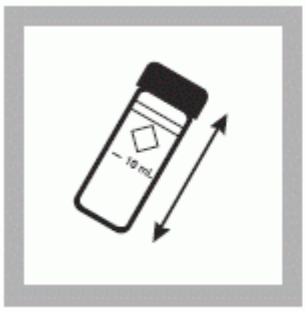
The display will show "- - - -" then "0.00".

Remove the blank from the cell holder.

5. Fill a second 10-mL cell to the 10-mL line with sample.

Note: *Do not use the same sample cells for free and total chlorine analysis without thoroughly rinsing the cells with sample between free and total tests.*

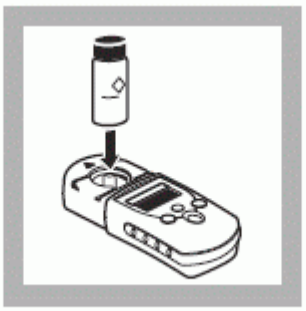
6. Add the contents of one DPD Free Chlorine Powder Pillow (one SwiftTest dispension of DPD Free) or one DPD Total Chlorine Powder Pillow (one SwiftTest dispension of DPD Total.



7. Cap and shake gently for 20 seconds.

Note: *Shaking dissipates bubbles that may form in samples with dissolved gases.*

Note: *A pink color will develop if chlorine is present.*



8. For **free** chlorine, place the prepared sample cell in the cell holder. Cover with the instrument cap and proceed to step 10 within **one** minute after adding the DPD Free Pillow.

Note: *Accuracy is not affected by undissolved powder.*

Note: *Wipe off sample cells.*

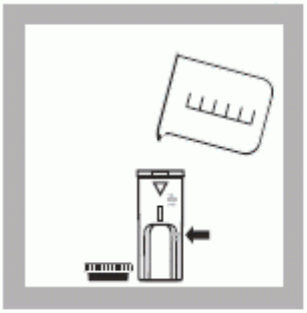
9. For **total** chlorine, place the prepared sample in the cell holder and cover the cell with the instrument cap. Wait **three to six** minutes after adding the DPD Total Pillow.

Proceed to step 10.

10. Press **READ/ENTER**. The instrument will show - - - - followed by the results in mg/L chlorine.

Chlorine, Free and Total, High Range (1.0 to 8.0 mg/L Cl2)

Using Powder Pillows



1. Fill a 1-cm/10-mL cell with sample (the blank). Cap.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

2. Press the **POWER** key to turn the meter on.

The arrow should indicate the high range channel (HR).

Note: *See page 2—4 for information on selecting the correct range channel.*

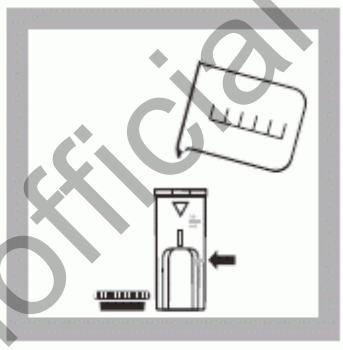
3. Remove the meter cap. Place the blank into the cell holder, with the diamond mark facing the back of the cell holder. Cover the cell with the cap.

Note: *Wipe liquid off sample cells.*

4. Press: **ZERO/SCROLL**

The display will show "- - - -" followed by "0.0".

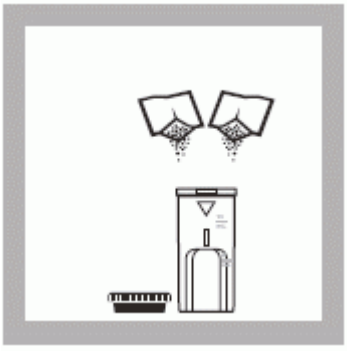
Remove the blank.

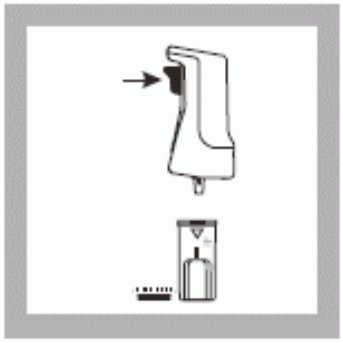


5. Fill another 1-cm/10-mL sample cell to the 5-mL line with sample. Cap.

Note: *Do not use the same sample cells for free and total chlorine without thoroughly rinsing the cells between the free and total tests.*

6. Add two pillows or two dispensations of DPD Free Chlorine reagent or DPD Total Chlorine reagent to the sample cell. Cap the cell and shake gently for 20 seconds.





7. For **free** chlorine, place the prepared sample cell in the cell holder and cover with the instrument cap within **one** minute after adding the DPD Free Pillow.
Proceed immediately to step 9.

8. For **total** chlorine, place the prepared sample in the cell holder and cover with the instrument cap. Wait **three to six** minutes after adding the DPD Total Pillows. Proceed to step 9.
Note: *Wipe off sample cells.*

9. Press **READ/ENTER**.
The instrument will show "- - - -" followed by the results in mg/L chlorine (Cl_2).

10. Due to a positive bias in the range of 2 to 3 mg/L of Free or Total Chlorine, samples within this range are diluted by half and then re-measured. Immediately open the prepared sample cell and dilute to the 10mL mark using deionized (MilliQ™) water, cap, mix, and re-measure. Multiply this value by two as the final result. (Record the first measurement in the margins or elsewhere.)

Data Analysis & Calculations

Both Free Chlorine and Total Chlorine are direct measurements in mg/L.

Combined Chlorine = Total – Free Cl^-

Calculation of Duplicates or Repeats

%Difference = $(Cl_{dupl} - Cl_{initial}) \times 100/Cl_{initial}$

Duplicate and Initial as final calculated value.

Calculation of %Recovery

Applies to calibration verification standards, calibration checks, and Certified Reference Materials or HRM.

%Recovery = (Result/Certified Value*) x 100
*as listed on the Certificate of Analysis or as prepared (expected) concentration

Safety

Safety glasses must be worn at all times in the laboratory and field, when handling chemicals. Lab coat must be worn in the laboratory at all times.

Wear gloves when handling corrosive chemicals, wastewater, effluent and unknown samples.

Wear plastic aprons and full face shields when acid washing.

Acid wash in "acid washing" fume hoods only.

Refer to each chemical MSDS for detailed hazards and handling instructions, available on the City of Winnipeg's intranet site "Wellness" page[8].

Sewage samples contain pathogenic organisms. Wear gloves, eliminate contact above the chest while working, and thoroughly wash hands with a disinfectant soap after handling.

Refer to Environmental Standards Division, Health and Safety Manual[9], and applicable safe work procedures in the SafeWorkProcedures manual[10].

Read all product labels and the material safety data sheets (MSDS) before using them.

 This symbol, if noted on the instrument, references the instruction manual for operational and/or safety information.

Revision History

Version No.	Issue Date	Author/Reviewers
4.1*		G. Levesque/ J. Jones
5.0	October 28, 2014	J. Jones/G. Levesque
"	December 17, 2014	G. Levesque

*Revision details are documented in these historical versions.
Previous revisions are listed in the obsolete Version 4.1, which is maintained for historical and documentation reasons.

Current Version 5.0

Version 5.0

Reagents, Total Chlorine Reference Standard, preparation of the sealed ampoule std. .....p 6
Equipment and Supplies, updated contact information for HACH .....p 6
Method Quality Control,
Duplicate helps to determines if there is a problem with the DPD reagent/dispenser.....p 8
Weekly Vial Check & Accuracy Check, document the latter in LIMS as the CRM .....p 8
Non-conformance and Corrective Action, substitute the Spec√ blank with reagent grade water if two or more standards are outside of the control limits
Run the Total Chlorine Accuracy Check Standard, Run a sample blank.....p 9
Using the Spec√ Standards, they are used to verify the instrument, not for calibration.
The actual instrument calibration is a factory setting that cannot be changed. ..... p 10
Revision History, includes a table, for better historical documentation (going forward), it's much easier to note when a version number might be skipped and how often the revisions occur.
Appendices, includes a new tab for Tab5 Meter Checks, Tab 6 CRM/Duplicates. ..... p 17
Endnotes, new section referencing the file/folder location of all referenced documents ..... p 18

December 17, 2014 *(reprint pages 5, 11, & 16)*

Interferences, false positive readings caused by condensation and turbidity from DO. .....P. 5
False Positive Readings,.....p. 11
Procedure to use when traces of chlorine (free or total) occur with non-chlorinated water.

Next Review[11]**;** No Later than November 31, 2015

Use the following only if there are no changes required at the next review or there are minor handwritten amendments suitable for continued use, i.e. the SOP does not have to be formally recompiled and distributed.

Annual Review includes verification/ensuring that the laboratory has the most current version of all the referenced methods and manuals.

Appendices (Method Binder Tabs)

Method Binder tabs may appear in different order, but are organized into the following sections.

Tab 1: COA & Logs (Certificate of Analysis and equipment calibration)

Tab 2: COA Total (Certificate of Analysis Total Chlorine)

Tab 3: QC Standards

Tab 4: Vial Cleaning

Tab 5: Meter Checks

Tab 6: CRM/Duplicates

Tab 5: Method Validation

Document Control

Certificates of Analysis; are scanned to PDF in the COA Folder immediately upon receipt. After confirmation of accuracy (no missing or double scanned pages) the hard copy is also destroyed after expiration in accordance with the documented policy in the Quality Manual[12].
Completed QC Records/Charts are moved (from the clip-board) to the method binder tabs noted above.

Batch worksheets, with Free Cl, Total Cl, & Temperature are filed in the Chlorine-Batch Worksheet Binder.

Each calendar year, the QC Records are converted to PDF and filed in the method folder; ….\Methods\Chlorine-DPD\QC RECORDS.

The Glass Vials and any additional maintenance records are combined, converted to PDF and filed in the same QC RECORDS folder.

The batch worksheets are archived (boxed, filed, and stored) according to the policy described in the Quality Manual and documented in the *Box_RecordList.xlsx*[13] worksheet

References

Standard Operating Procedures

SOP-17, Sampling

SOP-18, Bacteriological Monitoring and Sampling Program

Equipment Instruction Manuals

Manual_Pocket Colorimeter II.pdf

Reference Texts

Method 4500 Cl-G, Chlorine Residuals, Standard Methods for the Examination of Water and Waste Water, approved by Standard Methods Committee 2000, Editorial Revisions 2011

Endnotes (file and folder locations)

[1] All forms, worksheets, reagent logs located in
N:\Environmental Standards\Methods\Chlorine-DPD (SOP 30)\FORMS

[2] Control Charts are printed from "ChartGenerator.xlsm" workbook in;
N:\Environmental Standards\Analytical Services\Charts

[3] Standard Method for the Examination of Water and Wastewater are downloaded from the on-line account and maintained as PDF document in a single folder:
N:\Environmental Standards\Analytical Services\SOPs (PDF)

[4] Method Validation Data is located in;
N:\Environmental Standards\Methods\Chlorine-DPD (SOP 30)\METHOD-VALIDATION

[5] For a demonstration of the preparation of this standard, see Chlorine_Check_Standards_Snips.mp4 (or in "flv" format)
N:\Environmental Standards\Methods\Chlorine-DPD (SOP 30)\SOP

[6] Equipment Operation Manuals are available from the following two locations;
N:\Environmental Standards\Methods\Chlorine-DPD (SOP 30)\MANUALS
N:\Environmental Standards\Analytical Services\Instrument & Software\HACH_PocketII_Colorimeters

[7] All Standard Operating Procedure; SOP-17 Sampling, SOP-51 Glassware, SOP-50 LIMS User Manual in; N:\Environmental Standards\Analytical Services\SOP (PDFs)

[8] Access MSDS from the City of Winnipeg, intranet Wellness webpage at;
http://citynet/intrahom/toc/wellness.stm

[9] Safety Manual located in; N:\Environmental Standards\Safety\SafetyManual

[10] Safe Work Procedures in;
N:\Environmental Standards\Safety\Safe Work Procedures\Safe Work Procedures

[11] Perform the review as described in the Method Validation, Method Review section of the Quality Assurance Manual (SOP 16, QAM) in:
N:\Environmental Standards\Methods\Quality Manual (SOP 16)

[12] RECORDS MANAGEMENT BY-LAW NO. 86/2010
http://www.winnipeg.ca/clkdmis/DocExt/ViewDoc.asp?DocumentTypeId=1&DocId=5220&DocType=O

[13] Document using the Excel Workbook, Box_RecordList.xlsx, located in;

N:\Environmental Standards\Analytical Services\Document Control\Archived Records

The official MS Word document of this SOP is maintained in a secure controlled location;
N:\Environmental Standards\Quality Assurance\SourceDocs\Current Word\SOP-30_Cl-DPD_v5.docx