Measuring Total Residual Chlorine
Using the HACH® Pocket Colorimeter™ II Test Kit

1. SCOPE AND APPLICATION

1.1. This method is based on the HACH® Pocket Colorimeter™ II Test Kit instruction manual. As adapted, it is equivalent to SM 4500-Cl G. The method is used for determining total residual chlorine (TRC) in aqueous samples.

1.2. Use of this SOP constitutes acknowledgement that the HACH® Pocket Colorimeter ™ II user manual has been read and understood by the operator.

1.3. This laboratory is not NELAC certified for this analysis. See section 5.1.

2. SUMMARY OF METHOD

2.1. Proper operation of meter is checked. The sample is placed in a vial. Instrument is "blanked" with the sample. DPD (diethyl-p-phenylenediamine) reagent is added to the vial. The timer is started. TRC is read. A duplicate measurement is made. Results are averaged and recorded in LIMS and appropriate logbooks.

2.2. Interferences:

2.2.1. Include: Acidity > 150 mg/L $CaCO_3$; Alkalinity > 250 mg/L as $CaCO_3$; Bromine; Hardness > 1,000 mg/l as $CaCO_3$; Iodine; Oxidized manganese; Oxidized chromium; Monochloramine; and Ozone.

2.2.2. According to Standard Methods, sunlight or other intense light can deplete chlorine in the samples. **Samples should be kept covered during testing.**

2.2.3. Damage to the meter by water/liquid entering the chamber holder.

3. EQUIPMENT AND SUPPLIES

3.1. HACH® pocket colorimeter™ II chlorine test kit (S/N 05110C042002) containing:

3.1.1. Pocket colorimeter™ II

3.1.1.1. The meter has two modes. The LOW mode resolution is 0.01 mg/L (used). The HIGH mode resolution is 0.1 mg/L.

3.1.2. Two HACH®HACH® Company Sample Cell: 25 mm x 60 mm Round Glass 10mL

3.2. 10 mL volumetric pipette per sample with manual or automatic pipettor

3.3. Computer with access to the Laboratory Information Management System (LIMS)

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3.4. *Bioassay Bench Sheets* Logbook (where applicable)

3.5. *Parameter Check* Logbook

3.6. Laboratory timer (count-down or count-up with alarm)

3.7. Kimwipe®

4. REAGENTS AND STANDARDS

4.1. Chlorine demand free water

4.1.1. Deionized (DI) water for dilution of higher-level samples

4.2. Hach-Specv™ Secondary Standards and if needed potassium permanganate standards (1.0 mg/L and 0.1 mg/L)

4.2.1. The HACH® secondary standards come four to a box and include a blank, a low-range standard, a mid-range standard, and high-range standard. The potassium permanganate standard (1.0 mg/L) is prepared per Standard Methods 20th Edition: SM 4500-Cl G, procedure 4-2, page 4-64. Dilute the 1.0 mg/L standard 9:1 with deionized water to make the 0.1 mg/L standard. Record the preparation in LIMS as batch # (batch # = date prepared: ex. 1/05/14), date, expiration (date prepared + 7 days). Make fresh potassium permanganate standards whenever the standard(s) are > ± 10% from nominal even if "unexpired". (This presumes that the secondary standards are within specified ranges and there is not a problem with the meter).

4.3. DPD total chlorine reagent powder pillows

5. METHODS

5.1. Results of chlorine measurements performed on samples in the Bioassay laboratory **are not reportable for compliance purposes.** The results are used to determine potential causes of observed toxicity and as a measure of the success of dechlorination efforts.

5.2. The following methods apply to the Colorimeter™ II when referring to the instrument.

5.2.1. This meter has the low range (0 – 2.00 mg/l) for a total residual chlorine measurement.

5.3. Use Specv™ Secondary Standards and if needed Potassium Permanganate Standards for calibration. Total Residual Chlorine PT samples can be used in lieu of Potassium Permanganate. Ensure that the standards have not expired.

5.4. Sample preparation

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5.4.1. Bring the sample to between 20-25 ºC.

6. COLORIMETER CALIBRATION

6.1. Lab Colorimeters are calibrated before their first use, and periodically throughout service. Colorimeters are also calibrated whenever the standard measurements begin to drift outside the acceptable range (The acceptable value for standard measurements is ±10%).

6.2. The colorimeter is turned on by pressing and releasing the [**Power/Backlight Key**] ( ). The display will turn on and show the value of the last reading. If the colorimeter has been calibrated, the [**Calibration Adjusted Icon**] ( ) will display on the right perimeter of the screen.

6.3. To enter calibration mode, press and hold the [**Menu Key**] ( ) until "**USER CAL**" is displayed and press the [**Read/Enter Key**] (✓). "S0" should appear on the display.

6.4. Place the Blank Standard in the chamber holder, cap the colorimeter, and press the [**Read/Enter Key**] (✓). If not already at 00.00, using the [**Zero/Scroll Key**] ( ) manually input the standard value of the blank (00.00). The [**Read/Enter Key**] (✓) to cycle through the digits. Once the value is correctly entered, "A0" should appear on the display.

6.5. Press the [**Read/Enter Key**] (✓) to measure the absorbance value of the blank.

6.6. Press the [**Zero/Scroll Key**] ( ) to move to the next calibration point. S1 should display on the screen.

6.7. Place "**STD 1**" in the chamber holder and cap the colorimeter. Press the [**Read/Enter Key**] (✓) to cycle through the digits and use the [**Zero/Scroll key**] ( ) to manually enter the standard value of "**STD 1**" (Each standard value is written on the inside cap of the Standards box or on the certificate of analysi ✓ at comes with each new box set). Press the [**Read/Enter Key**] ( ), **A1** should appear on the display after the standard value is entered.

6.8. Press the [**Read/Enter Key**] (✓) to measure the absorbance value of "**STD 1**".

6.9. Press the [**Zero/Scroll Key**] ( ) and "**Add**" should appear on the display. Press the [**Read/Enter Key**] (✓) and "**S2**" should appear on the display.

6.10. Place "**STD 2**" in the chamber holder and cap the colorimeter. Press the "Read/Enter Key" (✓) and use the [**Zero/Scroll key**] ( ) to manually enter the standard value of "**STD 2**". **A2** should appear on the display after the standard value is entered.

6.11. Press the [**Read/Enter Key**] (✓) to measure the absorbance value of "**STD 2**".

6.12. Press the [**Zero/Scroll Key**] ( ) and "**Add**" should appear on the display. Press the [**Read/Enter Key**] (✓) and "**S3**" should appear on the display.

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6.13. Place "**STD 3**" in the chamber holder and cap the colorimeter. Press the [**Read/Enter Key**] (✓) and use the [**Zero/Scroll key**] ( ) to manually enter the standard value of "**STD 3**". **A3** should appear on the display after the standard value is entered.

6.14. Press the [**Read/Enter Key**] (✓) to measure the absorbance value of "**STD 3**".

6.15. Once the absorbance value of "**STD 3**" is displayed, press the [**Menu Key**] ( ) twice quickly to return to measurement mode.

6.16. The display will flash the [**Zero/Scroll Key**] symbol ( ). Insert the Blank Standard into the chamber holder and press the [**Zero/Scroll Key**] ( ).

6.17. The display will show 0.00 and the [**Calibration Adjusted Icon**] ( ) will appear on the right perimeter of the display.

6.18. Read Standards 1, 2, and 3 to verify the calibration of the Colorimeter.

7. REMOVE CALIBRATION

7.1. To delete a calibration, turn the colorimeter on, then press and hold the "Menu Key", ( ) until "USER CAL" appears.

7.2. Press the [**Zero/Scroll Key**] ( ) until "**dFL**" appears on the screen. This will return the Colorimeter to the factory default calibration setting.

7.3. The display will flash the [**Zero/Scroll Key**] symbol ( ). Press the Zero button and the display will show 0.00 and the [**Calibration Adjusted Icon**] ( ) will not appear on the right perimeter of the display.

8. VERIFICATION OF INSTRUMENT WITH STANDARDS

8.1. Press the power button on the Colorimeter™II. The display will light up.

8.2. Remove the cap from the instrument. Wipe the SpecV™ blank with a clean Kimwipe® and place into the chamber holder. Ensure that the alignment mark (looks like half of a diamond) is facing the keypad. Securely cover the chamber with the instrument cover.

8.3. Press [**Zero/Scroll Key**] ( ). The display will show "**0.00**".

8.4. Remove the instrument cap. Remove the SpecV™ blank from the chamber holder. Place the **STD 1** chamber into the chamber holder after wiping it with a clean Kimwipe®, aligning the alignment mark with the keypad. Securely cover the chamber with the instrument cover.

8.5. Press [**Read/Enter Key**] (✓) Record the displayed value in the chlorine logbook along with the value of the standard.

8.5.1. If the value is not within ±10 % of the standard value, ensure that the standard chambers are clean and repeat the procedure. If values are still

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out of range, refer to the instrument manual for trouble shooting instructions.

8.5.2. Repeat **STEP 7.4.4.** and **STEP 7.4.5**, first with the SpecV™ chamber labeled **STD 2** and then with the SpecV™ chamber labeled **STD 3**.

8.6. Refer to all steps of the *Sample Reading* procedure using the potassium permanganate standards as the sample. Record the displayed value in LIMS/Laboratory/Technical/Laboratory Logbook/TOX_Chlorine.

8.6.1. In lieu of potassium permanganate standards that can be measured once annually or whenever there appears to be a problem with the secondary standards, semi-annual Total Residual Chlorine proficiency samples can be run. Potassium permanganate standards, if made and used, should read 1.0 mg/L (± 10%) and 0.1mg/L (± 20%). If the values are not within the specified percentage of the standard value, ensure that the standard chambers are clean and repeat the procedure. If values are still out of range, prepare a new standard. Test the new standard, and then if a problem still exists, refer to the instrument manual for trouble shooting instructions.

9. MEASURING CHLORINE IN SAMPLES

9.1. Use a 10-mL pipet to place 10 mL of sample into a 10-mL sample cell (blank sample).

9.1.1. Use one pipet per sample (do not cross contaminate samples).

9.2. Wipe the exterior of the cell with a Kimwipe® to remove any dirt, smudges, fingerprints, etc. which may reduce the amount of light passing through the chamber, thereby giving an inaccurate reading.

9.3. Place the sample chamber containing the blank sample in the cell holder. Place the instrument cap over the sample chamber.

9.3.1. The diamond mark on the sample chamber (vial) should be facing the front of the instrument (toward the operator).

9.4. Press [**Zero/Scroll Key**] ( ) After the display “zeros,” remove the instrument cap from the cell holder and remove the sample cell.

9.4.1. This step “zeros” the meter while correcting for any color inherent in the sample. The colorimeter will turn on and the display will show "**---**" followed by "**0.00**".

9.5. Open a DPD Total Chlorine powder pillow by tearing the top portion off and add the contents to the sample cell (blank sample). Cap the cell and gently shake for 20 seconds to mix.

9.5.1. A pink color will form if chlorine is present.

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9.5.2. Any undissolved powder does not affect accuracy.

9.6. After shaking, place the prepared sample in the cell holder. Securely place the instrument cap over the sample chamber.

9.6.1. Chlorine is depleted by light; therefore, the sample needs to be covered while developing. Within one minute of mixing the DPD into the sample, the sample cell needs to be blocked from light. This can be accomplished by placing the sample cell in the cell holder and placing the lid over the cell, or by placing the cell within the box that houses the chlorine meter while not in use, or by placing a black towel or other object over the cell.

9.7. Set the timer for 3 minutes.

9.7.1. The sample must be read between 3 and 6 minutes of adding the DPD powder.

9.8. Press [**Read/Enter Key**] (✓). The display will show "**---**" followed by the total chlorine measurement in mg/L.

9.8.1. If the sample temporarily turned yellow or the display is flashing "**2.20**", (indicating an over-range concentration), the chlorine concentration is too high to measure without dilution. The measurement must be repeated with a diluted sample.

9.9. Record the displayed reading in the *Parameter Check* logbook, LIMS/TOX_Chlorine, and the appropriate bench sheets. If an out-of-range indication is displayed, dilute the sample with DI water. Perform **STEPS 9.2-9.9** to measure TRC in both the dilution water (DI water) and diluted sample. Multiply the result by the dilution factor.

9.9.1. Readings that are $\leq$0.07 ppm are recorded as $<$0.07. Readings $>$0.07 are recorded as displayed on the meter.

9.9.2. Dilution water should be chlorine demand free water. If TRC is detected in the dilution water, contact the lab supervisor immediately.

9.10. Repeat STEPS 9.1-9.9 for the replicate sample. If sample readings are <0.07 ppm, two readings are sufficient. If any sample readings are >0.07 and vary by more than 0.02 ppm, or whenever one reading is <0.07 and the other is > 0.07, a third reading must be taken.

9.11. When finished with the instrument, replace the cap, turn off the Colorimeter™ II by pressing the power button, and return the instrument to the carrying case. Rinse all sample chambers (excluding Specv™ Standards) with DI water. Clean up the work area.

10. DATA ARCHIVAL

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10.1. Use a black, waterproof pen for all bench sheets and logbooks.

10.2. Record information in *Bioassay Bench Sheets* logbooks when appropriate.

10.3. To correct raw data entries, place a single line through the incorrect or illegible entry, write the corrected entry near the error and initial and date the correction. Do not overwrite entries.

10.3.1. The corrected entry is written as near as possible to the error or in the comment box on the appropriate bench sheet.

10.3.2. If the correction requires an explanation, write a comment and reference the error with a letter. Initial and date the explanation. Do not attempt to put all information (correction and comments) into a small space.

10.4. Use sequential alphabetical annotation to identify errors and corresponding comments (use A for first error and use A for corresponding explanatory comment; use B for second error, etc.). FDEP Laboratory Information Management System (LIMS).

11. QUALITY CONTROL

11.1. Refer to the Lab Quality Assurance Manual for corrective action and handling out-of-control data.

12. SAFETY/HAZARDOUS WASTE MANAGEMENT

12.1. Proper laboratory protection—including lab hood or ventilation system, lab coat, gloves, and safety glasses—is required when working with chemicals and unprocessed samples.

12.2. Refer to the Laboratory Quality Assurance Manual for sample disposal.

12.3. Refer to the Laboratory Health and Safety Manual and Hazardous Waste Management Plan.

13. REFERENCES

13.1. HACH® Pocket Colorimeter™ II Instruction Manual Method 8021 (free) and 8167 (total)

13.2. SM 4500-Cl G, Standard Methods for the Examination of Water and Wastewater, 20th Edition

13.3. FDEP Laboratory Quality Assurance Manual

13.4. FDEP Laboratory Health and Safety Manual

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APPENDIX OF SIGNIFICANT CHANGES

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