US Environmental Protection Agency
Office of Pesticide Programs

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Microbiology Laboratory
Environmental Science Center, Ft. Meade, MD

Standard Operating Procedure for
Hach's Digital Titrator for Total Chlorine Titration

SOP Number: EQ-12-02

Date Revised: 12-11-19

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Title	Hach's Digital Titrator for Total Chlorine Titration
Revisions Made	• Application: The SOP is used for determination of total chlorine in products and reference standard solutions of sodium hypochlorite • Removed some definitions and moved them into the text. • Removed which cartridge is to be used and added extra information to section 6. • Added extra information to section 8 • Section 12. Procedure and Analysis had major changes to the subsections and made the titrator accuracy verification more streamline. • Minor editorial changes.

SOP Number	EQ-12-02
Title	Hach's Digital Titrator for Total Chlorine Titration
Scope	This SOP describes the use of the Hach's digital titrator for titration of total chlorine in solutions.
Application	The SOP is used for determination of total chlorine in products and reference standard solutions of sodium hypochlorite.

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1. Definitions	1. Hach's digital titrator = a precision dispensing device fitted with cartridges (concentrated titrants). 2. Titrant = a substance (as a reagent solution of precisely known concentration) that is added in titration. 3. Total chlorine = the concentration of total chlorine is equal to the concentration of the free and the combined forms of chlorine. 4. Additional abbreviations/definitions are provided in the text.
2. Health and Safety	1. Follow procedures specified in SOP MB-01, Laboratory Biosafety. The Study Director and/or lead analyst should consult the Safety Data Sheet for specific hazards associated with chemicals. 2. 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 concentration, sunlight, pH, temperature, and salinity influence the decomposition of chlorine in water.
3. Personnel Qualifications and Training	Refer to SOP ADM-04, OPP Microbiology Laboratory Training. MLB uses proficiency testing exercises, at a frequency as deemed necessary, to determine the proficiency of analysts.
4. Instrument Calibration	Use the standard additions method for accuracy check to validate the test procedure, reagents, apparatus, technique, and to determine if there is an interference in the sample.
5. Sample Handling and Storage	Refer to SOP MB-22, Disinfectant Sample Preparation, and SOP COC-01, Chain of Custody Procedures.
6. Quality Control	1. For quality control purposes, the required information is documented on the appropriate record form(s), see section 14. 2. Perform accuracy verification of each digital titrator used in the laboratory on a semi-annual basis; see section 12.2.
7. Interferences	1. Inaccurate total chlorine results may occur if the digital titrator is not properly used and/or does not meet the manufacturer's requirements for accuracy verification. 2. Inaccurate results will occur if the delivery tube tip is held above the solution rather than in the solution (e.g., under the surface) during sample titration and/or titrator verification procedure. 3. During sample titration and titrator verification procedures, verify that the delivery tube is free of air bubbles and is not misshapen (e.g. bent), which can interfere with the titration process.

	4. During sample titration and titrator verification procedures, conduct the procedure accurately and without urgency to ensure titrant is added consistently. 5. Use clean glass containers for titration; do not use plastic containers. 6. Do not use diluents other than deionized water to avoid interference with titration process. 7. Select the appropriate potassium iodide pillow based on the sodium thiosulfate titration cartridge used.
8. Non-conforming Data	1. Management of non-conforming data will be consistent with SOP ADM-07, Non-Conformance Reports. 2. The acceptable range for total chlorine, expressed as mg/L (ppm) Cl_2, is ±10% of the target concentration. Other ranges of total chlorine may be used as appropriate. If the results are not within acceptable range, the preparation may need to be re-titrated and/or prepared again. If the problem persists, consult with the study director for further guidance.
9. Data Management	Data will be archived consistent with SOP ADM-03, Records and Archives.
10. Cautions	Strict adherence to the protocol is necessary for the validity of the test results.
11. Special Apparatus and Materials	1. Hach digital titrator, cat. #16900-01 and delivery tube, cat. #17205-00 2. Sodium thiosulfate titration cartridges a. 0.02256 N, cat. #24091-01 (for titrating 1-400 mg/L total chlorine) b. 0.113 N, cat. #22673-01 (for titrating 20-2,000 mg/L total chlorine) c. 2.00 N, cat. #14401-01 (for titrating 2,000-70,000 mg/L total chlorine) 3. Dissolved oxygen 3 powder pillow, cat. #987-99 (for use with the 0.113 N and 2.00 N sodium thiosulfate titration cartridges) 4. Acetate buffer solution pH 4, cat. #14909-32 (for use with the 0.02256 N sodium thiosulfate titration cartridge) 5. Potassium iodide powder pillow, cat. #20599-96 (for use with the 2.00 N sodium thiosulfate titration cartridge) 6. Potassium iodide powder pillow, cat #1077-99 (for use with the 0.02256 N and 0.113 N sodium thiosulfate titration cartridges)

	7. Starch indicator solution, cat. #349-32. 8. Chlorine standard PourRite ampules, 50-75 mg/L Cl_2, 2 mL, cat. #14268-20. Ampules are used for accuracy check of the titrator. 9. TenSette Pipet, cat. #19700-01 10. Pipette tips (0.1-1.0 mL) for TenSette Pipet, cat. #21856-96
12. Procedure and Analysis	Solutions of sodium hypochlorite are titrated using the procedures in this SOP to determine their total chlorine concentration.
12.1 Total chlorine titration procedure	a. Analyze samples for total chlorine within 30 minutes of preparation following Attachments 1 and/or 2. b. The Hach Digital Titrator manual (see ref. 1) lists ranges of concentrations that can be evaluated with a given sample volume and titration cartridge. Refer to Tables 1 and 2 in Attachments 1 and 2, respectively. c. Based on the total chlorine sample target, choose the appropriate sodium thiosulfate cartridge. d. Add required sample volumes of sample and deionized water to an Erlenmeyer flask. Ensure each reagent has gone into the solution prior to subsequent additions. e. Based on the sodium thiosulfate cartridge selected, add either acetate buffer or the contents of one dissolved oxygen powder pillow. Ensure each reagent has gone into the solution prior to subsequent additions f. Add a potassium iodide powder pillow. This changes the color of the solution in the flask from colorless to yellow or yellow-orange depending on the concentration of total chlorine present in the sample. g. Titrate the solution to a pale yellow color. i. The amount of sodium thiosulfate necessary to titrate this solution to a pale yellow varies by cartridge concentration. h. Add starch solution. This will turn the solution dark blue. i. The amount of sodium thiosulfate necessary to titrate this solution from dark blue to colorless varies by cartridge concentration.

	ii. When using the 2.00 N cartridge, add titrant slowly because the color change from dark blue to colorless occurs abruptly within a few turns of the titrator knob. iii. When using the 0.113 N or 0.02256 N cartridge, the color change from dark blue to colorless is more gradual. i. The total chlorine should be within ±10% of the target sodium hypochlorite concentration for all samples. For example: i. An acceptable range of total chlorine for a 200 ppm sodium hypochlorite solution is 180-220 ppm. j. Follow the digital titrator instructions to calculate the total chlorine (refer to section 15).
12.2 Titrator accuracy verification	a. On a semi-annual basis, determine the accuracy of the digital titrator using the accuracy verification method found in the Hach kit user's manual for using total chlorine, see section 15. Note: The accuracy verification of the digital titrator may be performed by either the total chlorine method described in this SOP (section 12.2) or by the hard water method described in MB-30: Preparation of Hard Water and Other Diluents for Preparation of Antimicrobial Products, section 12.6b. b. Prepare a sodium hypochlorite sample of a concentration that can be titrated using the 0.113 N sodium thiosulfate titration cartridge (e.g., approximately 50-500 ppm) and determine the total chlorine concentration as described in section 12.1. Use this sample for accuracy verification. c. Open the Chlorine Standard Solution PourRite ampule (50-75 mg/L Cl_2). d. Use a TenSette pipet to add 1.0 mL of the standard solution to the titrated sample (spiked sample). Swirl to mix. e. Titrate the spiked sample to the end point. Record the number of digits on the digital titrator display that was used to reach the end point. f. Repeat steps 12.2d and 12.2e twice more for a total of three 1.0 mL samples of the standard added to the titrated sample g. Each 1.0 mL addition of the standard should require 10-15 digits of the 0.113 N sodium thiosulfate titration cartridge. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

	i. To identify the correct number of digits for each 1.0 mL addition, multiply the actual standard concentration by the spike volume and divide by 5. For example, (50 mg/L × 1.0 mL) ÷ 5 = 10 digits ii. Refer to the certificate with the PourRite ampule for the exact concentration of the standard. h. Record outcome of accuracy verification procedure on the log sheet (see section 14). i. If the verification procedure fails, repeat steps 12.2d-f. After the repeat, if the verification procedure continues to fail, identify the titrator as unusable. Use an alternate titrator or purchase a new one to ensure titration procedures are accurate.
12.3 Cleaning the delivery tube	a. Drain the delivery tube after use. After draining the delivery tube, rinse the tube for a minimum of 5 seconds with deionized water. Make sure the delivery tube does not have air pockets after rinsing.
13. Data Analysis/ Calculations	Digits required × digit multiplier = sample concentration.
14. Forms and Data Sheets	1. Media/Reagent Preparation Sheets. Prep sheets for sodium hypochlorite solutions are stored on G drive. 2. Attachment 1. Hach Digital Titrator Total Chlorine Method (method 8209): Iodometric Method (1 to 400 mg/L as Cl_2 using sodium thiosulfate) 3. Attachment 2. Hach Digital Titrator Total Chlorine Method (method 8209): Iodometric Method (20 to 70,000 mg/L as Cl_2 using sodium thiosulfate) 4. Test Sheets. Test sheets are stored separately from the SOP under the following file names: Accuracy Verification Semi-Annual Log Sheet EQ-12-02_F1.docx
15. References	1. Digital Titrator Manual, Model 16900-08, March 2013.

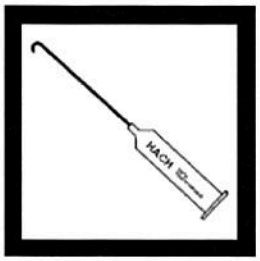
Attachment 1 (excerpt from ref. 1)

Method 8209

CHLORINE, TOTAL

Iodometric Method (1 to 400 mg/L as Cl_2 Using Sodium Thiosulfate)

1. Select the sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected chlorine concentration from *Table 1*.



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.

3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

4. Use a clean graduated cylinder to take a water sample. Pour sample into a clean 125- or 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water.

Note: *See Sampling and Storage following these steps.*

Table 1

Range (mg/L Cl_2)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
1-4	100	0.02256	24091-01	0.01
2-8	50	0.02256	24091-01	0.02
5-20	20	0.02256	24091-01	0.05
10-40	10	0.02256	24091-01	0.10
20-80	5	0.02256	24091-01	0.20
50-200	2	0.02256	24091-01	0.50
100-400	1	0.02256	24091-01	1.00

CHLORINE, TOTAL, continued

5. Add 2 Droppers (2 mL) Acetate Buffer Solution, pH 4 and swirl to mix.

6. Clip open the end of one Potassium Iodide Powder Pillow. Add the contents to the flask. Swirl to mix.

7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate until the solution is a pale yellow.

8. Add one dropper of starch indicator solution and swirl to mix. A dark blue color will develop.

9. Continue the titration until the solution changes from dark blue to colorless. Record the number of digits required.

10. Calculate:

Digits Required x Digit Multiplier = mg/L Total Chlorine (Cl2)

Note: These procedures can be used to check iodine and bromine concentrations if chlorine is not present. Multiply the test result (in mg/L chlorine) by 3.58 or 2.25, respectively, to accurately express the iodine or bromine content of your sample.

Attachment 2 (excerpt from ref. 1)

CHLORINE, TOTAL, continued

Iodometric Method (20 to 70,000 mg/L as Cl_2 Using Sodium Thiosulfate)

1. Select the sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected chlorine concentration from *Table 2*.

2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.

3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: For added convenience use the TirtaStir® stirring apparatus. See General Description, Step 3 of Step-by-Step.

4. Use a pipet or graduated cylinder to measure the sample volume from *Table 2*. Transfer the sample into a 125-mL Erlenmeyer flask and dilute to about the 50-mL mark with deionized water.

Table 2

Range (mg/L Cl_2)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
20-80	25	0.113	22673-01	0.2
50-200	10	0.113	22673-01	0.5
100-400	5	0.113	22673-01	1
250-1000	2	0.113	22673-01	2.5
500-2000	1	0.113	22673-01	5
2000-9000 (0.2-0.9%)	4	2.00	14401-01	22.2
5000-18,000 (0.5-1.8%)	2	2.00	14401-01	44.3
10,000-35,000 (1.0-3.5%)	1	2.00	14401-01	88.7
20,000-70,000 (2.0-7.0%)	0.5	2.00	14401-01	177

5. Add the contents of one Dissolved Oxygen 3 Powder Pillow.

Note: Normally the addition of the powder pillow will lower the pH to 4 or less. If the sample size is large and highly alkaline, verify the solution pH is 4 or less with a pH meter or pH paper before proceeding.

6. If you are using the 2.00 N titration cartridge, add the contents of one Potassium Iodide Powder Pillow (Cat. No. 20599-96) to the flask and swirl to mix.

If you are using the 0.113 N titration cartridge, add the contents of one Potassium Iodide Powder Pillow (Cat. No. 1077-99) to the flask and swirl to mix.

7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate until the solution is a pale yellow.

8. Add one dropperful of starch indicator solution and swirl to mix. A dark blue color will develop.

9. Continue the titration until the solution changes from dark blue to colorless. Record the number of digits required.

10. Calculate:

Digits Required x Digits Multiplier = mg/L Total Chlorine (Cl2)

To convert the above results to the equivalent percent chlorine (Cl_2), divide by 10,000.