US Environmental Protection Agency
Office of Pesticide Programs

Office of Pesticide Programs
Microbiology Laboratory
Environmental Science Center, Ft. Meade, MD

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

SOP Number: EQ-12-01

Date Revised: 10-04-17

SOP Number	EQ-12-01
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. Accuracy check should be done every six months.

	Approval Date
SOP Developer:	_____ Print Name: _____
SOP Reviewer	_____ Print Name: _____
Quality Assurance Unit	_____ Print Name: _____
Branch Chief	_____ Print Name: _____

Date SOP issued:	
Controlled copy number:	
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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. Free chlorine reacts with ammonia to form combined chlorine such as monochloramines. When potassium iodide (in a pillow) is added to a sample that has chlorine at an acidic pH, free iodine is released in direct proportion to the amount of total chlorine in the sample. Then, the iodine is titrated with sodium thiosulfate to a colorless endpoint. 4. Potassium iodide pillows = Powdered potassium iodide (KI) in a pillow is added to a sample being titrated. Two different KI pillows are available. 5. Sodium Thiosulfate Titration Cartridges: Contain either 2.0 N sodium thiosulfate or 0.113 N sodium thiosulfate. 6. 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 find out 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	Perform accuracy check on the digital titrator using the 0.113 N cartridge every six months. Details provided in section 12.3.

7. Interferences	1. The accuracy check provides a way to verify the results and determine if interferences are present. It also provides a method for checking the performance of the reagents, the digital titrator, and operator's technique. 2. Inaccurate results will occur if the delivery tube tip is held out of the solution rather than under the surface. 3. Sample should be in clean glass container; do not use plastic containers. 4. Use of diluents other than deionized water may interfere with titration process. 5. Appropriate potassium iodide pillow should be used based on the sodium thiosulfate titration cartridge. 6. Make sure the delivery tube is free of air bubbles, which can interfere with titration process. 7. The drop wise addition of sodium thiosulfate should be closely monitored.
8. Non-conforming Data	1. Management of non-conforming data will be consistent with SOP ADM-07, Non-Conformance Reports. 2. For the titration cartridges (2.00 N and 0.113 N), acceptable values will be listed on the media preparation sheets. The acceptable values also take into consideration uncertainty associated with the measurement. 3. If the results are not within acceptable limits, it may require re-making and re-titrating the solution.
9. Data Management	Data will be archived consistent with SOP ADM-03, Records and Archives.
10. Cautions	Analyze samples immediately after preparation (within 15-30 minutes).
11. Special Apparatus and Materials	1. Hach digital titrator, Model #16900-01 and delivery tube 2. Sodium Thiosulfate Titration Cartridges, (specified in Table 1) 0.113 N, Cat. # 2267301 2. 00 N, Cat. # 1440101 3. Dissolved Oxygen 3 powder pillow, cat. # 98799 (for the 20–9000 mg/L Cl_2 range) 4. Potassium iodide powder pillow cat. # 20599-96 5. Potassium iodide powder pillow, cat # 107799 6. Starch Indicator Solution 1 dropper full Cat. # 34932. 7. Chlorine standard pourite ampule 50-75 mg/L, 2 mL (1426820) and

	chlorine standard voluette ampule 50-75 mg/L, 10 mL (1426810) Ampules are used for accuracy check of the titrator 8. TenSette Pipet (Cat. # 1970001) 9. Pipette tips (0.1-1.0 mL) (cat. # 2185696) for TenSette Pipet
12. Procedure and Analysis	
12.1 For Solutions containing 20-2000 mg/L and 2001-9000 mg/L Sodium hypochlorite (1mg/L= 1ppm)	a. Prepare sample according to the media/reagent preparation sheet. b. Remove the polyethylene cap and insert a clean delivery tube into the end of cartridge. c. Slide the cartridge into the titrator receptacle and lock in position with a slight turn. d. To start titrant flowing and flush the delivery tube, hold the cartridge up. Turn the delivery knob until air is expelled and several drops of solution flow from the tip. Then use the counter reset knob to turn the digital titrator back to zero and wipe the tip with kimwipes. e. Select a sample volume and titration cartridge corresponding to the expected sample concentration from Table 1, section 12.2. f. Use a pipet to measure the sample volume from Table 1. i. Measure the sample volume from Table 1 into a 125 mL erlenmeyer flask and dilute to 50 mL using deionized water. Swirl to mix. For example, if the sample volume is 5 mL, add approximately 45 mL deionized water to bring the volume to 50 mL. ii. Add contents of one dissolved oxygen 3 powder pillow. Swirl or use magnetic stir bar to mix until dissolved completely. iii. Add contents of one potassium iodide powder pillow, select from below: Use powder pillow #107799 when using the 0.113 N cartridge. Use powder pillow #2059996 when using the 2.00 N cartridge. iv. Immerse the delivery tube tip in the sample solution and swirl the flask constantly using a stir bar while titrating.

Titrate by turning the knob on the titrator.

v. Continue to titrate until the color changes to pale yellow.

vi. Add one dropper full of starch indicator solution. Color of the solution changes to dark blue.

vii. Keep turning the knob and mixing the sample until the color changes from dark blue to colorless (endpoint).

Note: 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. When using the 0.113 N cartridge, the color change from dark blue to colorless is much more gradual.

viii. Record the number of digits that appear in the digital counter window.

g. Use the formula listed in section 13 to calculate the concentration of the sample.

12.2 Table for sample volumes

Table I

Range mg/L	Example target concentration	Sample volume (mL)	Titration cartridge	Digit Multiplier
20-80	~50 ppm	25	0.113N	0.2
50-200	~100ppm	10	0.113N	0.5
100-400	~200-300 ppm	5	0.113N	1.0
250-1000	~400-600 ppm	2	0.113N	2.5
500-2000	~800-2000 ppm	1	0.113N	5
2001-9000	~2500-7000 ppm	4	2.00 N	22.2

12.3 Accuracy check

Perform accuracy check every six months. Use the 0.113 N cartridge to use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is any interference in the sample.

Note: The accuracy check of the digital titrator may be performed by either the total chlorine method described in this SOP (section 12.3) or the $CaCO_3$

	hard water method described in MB-30: Preparation of AOAC or OECD hard water, section 12.5 b. a. Use the test procedure to measure the concentration of the sample, use 300mg/L solution. b. Use a TenSette pipet to add 1.0 mL of the standard solution to the titrated sample (spiked sample). c. Titrate the spiked sample to the endpoint. Record the number of digits on the counter. d. Add one more 1.0 mL addition of the standard solution to the titrated spiked sample. e. Titrate the spiked sample to the endpoint. Record the number of digits on the counter. f. Add one more 1.0 mL addition of the standard solution to the titrated sample. g. Titrate the spiked sample to the endpoint. Record the number of digits on the counter. h. Compare the actual result to the correct result. See " i' below. i. The correct result for this titration is 10-15 digits of the 0.113 N Sodium Thiosulfate Titration Cartridge for each of the three 1.0 mL volumes of the standard solution. A total of (30-45 digits) required. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference. j. 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
12.4 Cleaning the delivery tube	a. Press the plunger release button and manually retract the plunger into the body of the titrator. Remove the cartridge. Remove the delivery tube and reseal the cartridge with the polypropylene cap. b. If it is necessary to clean the delivery tube, immediately after use, force water, then air, into the tube opening with a syringe or narrow hose.
13. Data Analysis/ Calculations	Digits required × Digits multiplier = sample concentration.
14. Forms and Data Sheets	Media prep sheets (Excel) for sodium hypochlorite solutions are stored on G drive.

15. References	1. Digital Titrator Manual, Model 16900-01, 09-01-93 2. Total chlorine: Iodometric methods using sodium thiosulfate, Hach Method 8209, (DOC316.53.01173), 03/2015, Edition 8