Hach Method 10241

Spectrophotometric Measurement of Free Chlorine (Cl_2) in Finished Drinking Water

Hach Company Method 10241

Revision 1.2
November 2015

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1.0 Scope and Application

1.1 This method is for the determination of free chlorine (Cl_2) in finished drinking water.

1.2 The method is applicable in the range from 0.1 to 4.5 mg/L Cl_2.

1.3 This method is equally effective in performance and use to SM 4500-Cl G for the purposes of regulatory compliance reporting of Cl_2.

2.0 Summary of Method

An ammonia solution at a pH of 8.3 is added to a sample that contains free chlorine. The free chlorine is immediately converted into monochloramine (NH2Cl). In the presence of a cyanoferrate catalyst, the monochloramine reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green indophenol compound, which is proportional to the amount of free chlorine in the sample. A sample blank that contains Monochlor F Reagent corrects for background color from the reagent and sample. The measurement wavelength is 655 nm for spectrophotometers or 610 nm for colorimeters.

3.0 Interferences

3.1 The items listed in the *Interfering Substances* table have been individually checked up to the given concentrations and do not cause interference. The cumulative effects and influence of other ions have not been determined. Measurement results can be verified using sample dilutions or standard additions.

Interfering substance	Interference level (mg/L)
Ozone	> 1
Sulfide	> 0.5

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.

4.2 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

4.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of any chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all

personnel involved in these analyses. Additional information on laboratory safety can be found in Sections 16.3 and 16.4.

5.0 Equipment

Note: *Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

5.1 Sampling equipment

5.1.1 Sample collection bottles – Collect samples in chlorine demand-free glass bottles.

6.0 Equipment for sample analysis

6.1 Hach Company DR 6000, DR 3900, DR 1900 spectrophotometer, or equivalent

6.2 Hach Company sample cells

6.3 Equipment for standard preparation

6.3.1 500 mL bottle or flask – Chlorine demand-free glass

6.3.2 Analytical balance.

7.0 Reagents and Standards

7.1 Deionized water – Water in which Cl_2 concentration is below the detection limit of this method. Water prepared by passage of tap water through reverse osmosis and carbon filtration has been shown to be an acceptable source of reagent water.

7.2 Hach Company Monochlor F Reagent Pillows, Cat. No. 2802299, or equivalent

7.3 Hach Company Freechlor F Reagent Solution, Cat. No. 2964926, or equivalent

7.4 Hach Company Cl_2 Ampule: 10 mL, 50-75 mg/L as Cl_2 (Cat. No. 1426810) or equivalent

7.5 Initial precision and recovery (IPR) solution

7.5.1 Prepare 4 or more replicate 1.0-1.5 mg/L Cl_2 IPR solutions by weight. Tare an empty 500 mL bottle. Transfer the contents of a 10 mL standard ampule to the bottle (Sect. 7.4). Record the weight. Identify the concentration of the standard from the label. Using the concentration and the transferred weight of the standard, calculate the final dilution weight as $(W_1)(C_1)/(C_2)=(W_2)$. Dilute to the final weight with DI water. Assuming the concentration in the Standard ampule is 75 mg/L, the calculated final concentration = 1.5 mg/L Cl_2.

7.6 Method detection limit (MDL) solution

7.6.1 Prepare 7 or more replicate Cl_2 MDL solutions by weight (approximately 0.20 mg/L). Tare an empty 500 mL bottle. Transfer 60.00 g of a prepared IPR solution to the bottle. Dilute to 450 g with DI water. Final concentration = 0.20 mg/L Cl_2.

8.0 Sample Collection, Preservation and Storage

8.1 Samples should be collected in clean chlorine demand-free glass bottles.

8.1.1 Pretreat sample containers to remove chlorine demand. Soak containers in a weak bleach solution for at least 1 hr. Rinse fully with DI water.

8.2 Analyze samples immediately.

9.0 Quality Control

9.1 Each laboratory that uses this method is expected to operate a formal quality assurance program (16.1). The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analyses of laboratory prepared water standards as a test of continued performance to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Sections 9.2 and 9.3. The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.2 Accompanying QC for the determination of Cl_2 is required per analytical batch. An analytical batch is a set of samples processed during a contiguous 8-hour period. Each analytical batch must be accompanied by an ongoing precision and recovery sample (OPR), matrix spike sample (MS), and matrix spike duplicate sample (MSD) resulting in a minimum of four analyses (1 OPR, 1 sample, MS, and MSD).

9.2 Initial demonstration of laboratory capability.

9.2.1 To establish the ability to detect Cl_2 the analyst shall determine the MDL using the apparatus, reagents, and standards that will be used in the practice of this method. An achieved MDL less than or equal to the MDL in Section 13.0 is recommended prior to the practice of this method.

9.2.2 Prepare and measure seven replicates of the MDL standard (Sect. 7.6) according to the procedure in Section 11

9.2.3 Using the results of the set of seven analyses, compute the MDL using the following equation:

$$MDL = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}} \times 3.14$$

where:

n = Number of samples (7)
x = measured concentration of each sample

9.3 Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.3.1 Prepare and measure four samples of the IPR standard (Sect. 7.5.1) according to the procedure in Section 11.

9.3.2 Using the results of the set of four analyses, compute the average percent recovery (x) and the standard deviation of the percent recovery (s) for Cl_2. Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

where:

n = Number of samples (4)
x = % recovery in each sample

9.3.2.1 Compare s and x with the corresponding limits for initial precision and recovery in Table 1 (Sect. 17). If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4 Ongoing precision and recovery (OPR) - To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:

9.4.1 Prepare a 1.0-1.5 mg/L recovery standard with each analytical batch as described in Sect. 7.5.1 and measure according to the procedure in Section 11. Calculate the percent recovery and compare this value with the limits for ongoing recovery in Table 2 (Sect. 17). If the percent recovery meets the acceptance criteria, system performance is acceptable. If the percent recovery falls outside the acceptance criteria, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.1 Measure a field sample. After measuring the background concentration, spike the sample with a known concentration of Cl_2. The spike concentration should be 1-5 times the background concentration, but still within the reporting range of the method. Prepare a duplicate of this spiked sample.

9.4.1.2 Measure the spike duplicates and calculate the spike recovery for each sample and the relative percent difference (RPD) between the two results.

Use the following equation to calculate the spike recovery:

$$Spike\ Recovery = \frac{[Conc] - [Bkgd]}{[Sp]} \times 100$$

where:

[Conc] = the measured concentration of the spiked sample
[Bkgd] = the measured concentration of the un-spiked sample
[Sp] = the concentration of the spike

$$RPD = \frac{|Conc_1 - Conc_2|}{\left(\frac{Conc_1 + Conc_2}{2}\right)} \times 100$$

where:

$Conc_1$ = the concentration of the first spiked sample
$Conc_2$ = the concentration of the second spiked sample

9.4.1.3 Compare the spike recoveries and RPD with the corresponding limits in Table 2 (Sect. 17). If recoveries and RPD meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If recoveries or RPD fall outside the limits, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.4 The laboratory should add results that pass to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85% to 105%. Control charts are acceptable for evaluating process control, but under no circumstances can the control limits be widened beyond those established in the acceptance criteria defined in Section 13.

10.0 Calibration and Standardization

10.1 The Hach DR series spectrophotometers have a built-in calibration that is automatically initiated when the Indophenol Free Cl_2 procedure is selected through the instrument interface. No further initial calibration is required. However, the instruments have the capability of developing a user-calibration. See manufacturer's manual for instructions.

10.2 Calibration Verification

10.2.1 To verify that the instrument is measuring Cl_2 properly, analyze 0.20 mg/L (Sect. 7.6.1) and 1.5 mg/L (Sect. 7.5.1) Cl_2 standards. Results should be within 15 percent of the actual value. Perform this calibration verification daily while instrument is in use. If the calibration verification standard result is outside the limit, it is unacceptable. In this event, correct the problem, and repeat the test.

11.0 Procedure

11.1 Instrument Setup – follow the instrument manufacturer's instructions for instrument setup.

11.2 Fill two sample cells with 10 mL of sample, one cell will be the sample and one will be the blank.

11.3 Add 5 drops of Freechlor F Reagent to the sample cell.

11.3.1 Stopper the sample cell and invert to mix.

11.4 Add the contents of one Monochlor F Reagent Powder Pillow to both cells.

11.4.1 Stopper the cells and shake for ~20 s to dissolve the reagent.

11.5 Allow the samples to react for 5 min.

11.6 Invert the cells to mix.

11.7 Insert the blank cell into the spectrophotometer and zero.

11.8 Insert the sample cell into the spectrophotometer and read. Results will display in mg/L Cl_2.

12.0 Data Analysis and Calculations

12.1 Cl_2 concentration is calculated automatically against internal instrument calibration.

13.0 Method Performance

Performance of the method was demonstrated in multi-lab studies comparing the method against EPA Reference Method SM 4500-Cl G. The method was evaluated in a low ionic strength reference matrix as well as multiple geographically diverse finished drinking water samples obtained from both surface water and ground water sources.

Validation Results	Section	Limit
Method Detection Limit	9.2	0.05 mg/L Cl_2
Initial Recovery Range	9.3	89.5% - 101%

Initial Precision 95%	9.3	0.02
Matrix Recovery Range	9.4	89.9 – 110%
Matrix Recovery Precision 95%	9.4	0.06

14.0 Pollution Prevention

14.1 Follow guidelines in Section 15.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect air, water, and land by minimizing and control all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 For further information on waste management, consult "The Waste Management manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

16.0 References

16.1 "Protocol for the Evaluation of Alternate Test Procedures for Organic and Inorganic Analytes in Drinking Water," USEPA, EPA-815-R-15-007, February 2015.

16.2 40 CFR 136, Appendix B.

16.3 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976)

16.4 "Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.

16.5 "Water Analysis Handbook," Hach Company, 8th Edition, 2013.

17.0 Tables

17.1 Acceptance Criteria for Performance tests – The QC performance criteria for this method were performed with a Hach Company DR6000 Spectrophotometer and Indophenol Free Cl_2 Reagents.

Table 1. Initial Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Relative Standard Deviation	≤ 10%
Percent Recovery Range	100 ± 15%

Table 2. Ongoing Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Lab Fortified Blank Recovery	100 ± 15%
Sample Matrix Spike Recovery	100 ± 15%
Sample Matrix Spike RPD	≤ 10%

18.0 Glossary of Definitions and Purposes

The definitions and purposes are specified to this method but have been conformed to common usage as much as possible.

18.1 Units of weight and measure and their abbreviations

18.1.1 Symbols
°C: degrees Celsius

18.1.2 Alphabetical characters
mg/L: milligram per liter

18.2 Definitions, acronyms, and abbreviations

18.2.1 MDL: Method detection limit

18.2.2 IPR: Initial precision and recovery

18.2.3 OPR: On-going precision and recovery

18.2.4 MS: Matrix spike

18.2.5 MSD: Matrix spike duplicate

18.2.6 LIS: Low ionic strength, deionized water