Method 127: Determination of Monochloramine Concentration in Drinking Water

Questions concerning this document should be addressed to:

Matthew T. Alexander, P.E.
U.S. EPA, Office of Ground Water and Drinking Water, Standards and Risk Management Division, Technical Support Center, 26 W. Martin Luther King Dr. Cincinnati, OH 45268
Phone: (513) 569-7380
alexander.matthew@epa.gov

Office of Water (MS-140)
EPA 815-B-21-004
January 2021
Version 1.0

Authors

Matthew T. Alexander, P.E., U.S. EPA (Cincinnati, OH)

Thomas E. Waters, P.E., U.S. EPA (Cincinnati, OH)

David G. Wahman, PhD, P.E., U.S. EPA (Cincinnati, OH)

Glynda A. Smith, PhD, U.S. EPA (Cincinnati, OH)

Acknowledgements

The following people are acknowledged for their support in development and/or validation of this method:

William A. Adams, PhD, Alison Dugan, Christopher Frebis, and Steven C. Wendelken, PhD, U.S. EPA (Cincinnati, OH)

Lili Wang and Richard Weisman, U.S. EPA (Washington, DC)

Taylor Rosenhagen and Chris Bobay, Louisville Water Company (Louisville, KY)

John Consolvo, Joseph Mockus, Alexandra Rosario-Arocho, and, Philadelphia Water Department (Philadelphia, PA)

Julian Fairey, PhD, University of Arkansas (Fayetteville, AR)

City of Hamilton Water (Hamilton, OH)

Greater Cincinnati Water Works (Cincinnati, OH)

Augusta Regional Water Treatment Plant (Augusta, KY)

City of Falmouth Water and Wastewater Department (Falmouth, KY)

Justin Blashaw and Paul Handke, Pennsylvania DEP (New Stanton, PA)

Kayla Quinter, former U.S. EPA intern, for development of free chlorine and monochloramine stock solution preparation and standardization procedures.

Disclaimer

Publication of the method, in and of itself, does not establish a requirement, although the use of this method may be specified by the EPA or a state through independent actions. Terms such as "must" or "required," as used in this document, refer to procedures that are to be followed to conform with the method.

Contents

1 SCOPE AND APPLICATION

1.1 This method is for the determination of monochloramine (MCA) concentration in drinking water. It requires the use of a bench-top or portable colorimeter, spectrophotometer, or a mesofluidic channel pump colorimeter (also known as a portable parallel analyzer (PPA)). This method is intended for use by analysts skilled in the operation of the instrumentation and interpretation of the associated data. It is primarily intended to be used by drinking water utilities to measure monochloramine disinfectant residual when they are practicing chloramine disinfection.

1.2 The method detection limit (MDL) and application range determined using three different types of instruments are shown in Table 1. The MDL was calculated from analysis of seven aliquots of reagent grade water fortified to 0.1 mg/L monochloramine measured as Cl_2.

Table 1: Method Detection Limit and Application Range

Instrument	MDL (mg/L as Cl_2)	Application Range (mg/L as Cl_2)
Laboratory Spectrophotometer	0.07	0.07 - 4.50
Portable Colorimeter	0.08	0.08 - 4.50
PPA	0.06	0.06 - 4.60

1.3 The laboratory is not allowed to omit any quality control analyses. Each operator that uses this method must demonstrate the ability to generate acceptable results using the initial demonstration of capability (IDC) procedure detailed in Section 9.1.

2 SUMMARY OF METHOD

2.1 An aliquot of a drinking water sample is transferred into a sample cell or cuvette and used to zero the instrument at a wavelength of 610 nm for colorimeters or 655 nm for spectrophotometers. Indophenol Reagent (Hach Cat. No. 2802246 or equivalent) is then added to the aliquot of sample, shaken to mix, and allowed to react for a specified amount of time, depending on the sample temperature. In the presence of a cyanoferrate catalyst, monochloramine in the sample reacts with a substituted phenol in the Indophenol Reagent to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green-colored indophenol, which is proportional to the concentration of monochloramine present in the sample. After the sample reaction is complete, the absorbance of the sample is then measured at wavelengths of 610 nm for colorimeters and 655 nm for spectrophotometers.

2.2 If a PPA is used for analysis, place an unused disposable planar cuvette containing Indophenol Reagent (Hach Cat. No. 9429400 or equivalent) into a planar cuvette port on the bottom of the instrument. Fill the PPA sample cup with sample to the indicated fill line and insert the PPA into the sample cup until sample is drawn into the disposable planar cuvette in the instrument. The PPA will automatically zero, determine the sample reaction time based on temperature, and measure the absorbance of the sample at a wavelength of 655 nm after the reaction is complete.

3 DEFINITIONS

3.1 Continuing Calibration Check (CCC) – A primary calibration standard or secondary calibration standard that is analyzed periodically to verify the accuracy of the existing calibration.

3.2 Laboratory Reagent Blank (LRB) – An aliquot of reagent water or other blank matrix that is processed in the same manner as a sample, including exposure to all glassware, equipment, and reagents that are used with the samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or apparatus.

3.3 Method Detection Limit (MDL) – The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

3.4 Primary Calibration (PCAL) Standards – Solutions of the method analyte that are prepared from the stock standard solutions. The PCAL standards are used to calibrate the instrument response with respect to analyte concentration.

3.5 Safety Data Sheet (SDS) – Written information provided for the chemical reagents concerning a chemical's toxicity health hazards, physical properties, fire, and reactivity data including storage, spill, and handing precautions.

3.6 Secondary Calibration (SCAL) Standards – Commercially prepared, stabilized, and sealed liquid, gel, or solid standards calibrated against properly prepared PCAL standard.

3.7 Quality Control Sample (QCS) – A solution of method analyte of known concentration. The QCS is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal calibration process.

3.8 Reagent Water – Purified water (typically either deionized or distilled) free of analyte and chlorine demand. Reagent water can be purchased from a scientific supply company if it is not available on site.

3.9 Stock Standard Solution (SSS) – A concentrated standard solution that is prepared in the laboratory using assayed reference materials or that is purchased from a commercial source with a certificate of analysis.

4 INTERFERENCES

The substances listed in Table 2 have been individually evaluated up to the listed concentrations and do not cause interference. The cumulative effects and influence of other substances not listed in Table 2 have not been determined. The substances listed Table 3 have been reported by the reagent manufacturer to interfere at the listed concentrations. Interferences with any substance may be verified using sample dilutions or standard additions.

Table 2: Non-Interfering Concentrations of Evaluated Substances

Evaluated Substance	Non-Interfering Level
Free Chlorine	< 4 mg/L as Cl_2
Free Ammonia	< 5 mg/L as N
Phosphate	< 500 mg/L as PO_4
Iron (III)	< 10 mg/L as Fe^{3+}
Nitrite	< 50 mg/L as N
Nitrate	< 100 mg/L as N

Table 3: Interfering Concentrations of Substances Reported by Manufacturer (*Hach Method 10171*)

Evaluated Substance	Effect	Interfering Level
Magnesium	Positive	> 400 mg/L as $CaCO_3$
Manganese (VII)	Negative	> 3 mg/L
Ozone	Negative	> 1 mg/L
Sulfide	Positive	> 0.5 mg/L, a “rust” color develops
Thiocyanate	Negative	> 50 mg/L

5 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely identified; each chemical compound should be treated as a potential health hazard unless otherwise determined, and exposure to these chemicals should be minimized. The laboratory or water system is responsible for maintaining documentation of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. This method does not address all safety issues associated with its use and disposal. A reference file of SDSs should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

6 EQUIPMENT AND SUPPLIES

6.1 **Sample Analysis Equipment:**

6.1.1 Benchtop or portable colorimeter, spectrophotometer, or PPA. Colorimeter (Hach DR-900 or equivalent) and PPA (Hach SL-1000 or equivalent) must be capable of measuring sample absorbance at a wavelength of 610 nm. Spectrophotometer (Hach DR-6000 or equivalent) must be capable of measuring sample absorbance at a wavelength of 655 nm.

6.1.2 Sample cells (1" round plastic 10 mL with 1 cm pathlength for colorimeter, Hach catalog number 4864302 or equivalent), cuvette (1 cm rectangular quartz for spectrophotometer, Fisher Scientific catalog number 14-958-128 or equivalent), or sample cup (for PPA, Hach catalog number 9418100 or equivalent).

6.1.3 Chlorine demand-free glass sample collection container. If glassware needs to be treated to remove chlorine demand, expose to water containing at least 10 mg/L as Cl_2 chlorine for 3 hours or more before use, and rinse with chlorine demand-free water (Standard Methods for the Examination of Water and Wastewater, 2017).

6.1.4 Laboratory wipes (Kimberly-Clark Professional catalog number 34120 or equivalent)

6.1.5 Thermometer to measure ambient temperature that is capable of measuring in 0.5°C increments or less

6.2 **Standard Preparation Equipment (see Appendices A and B)**:

6.2.1 Chlorine demand-free glassware. If glassware needs to be treated to remove chlorine demand, expose to water containing at least 10 mg/L Cl_2 for 3 hours or more before use and rinse with chlorine demand-free water.

6.2.2 Amber glass bottle (1 L)

6.2.3 Beakers (50 mL)

6.2.4 Volumetric flasks (50 mL, 200 mL, 500 mL, 1000 mL)

6.2.5 Pipettes (100-5000 µL, 5-100 µL)

6.2.6 Stir bars

6.2.7 Ultraviolet-visible (UV-Vis) spectrophotometer capable of measuring absorbance at wavelengths of 245 and 292 nm (Hach DR-6000 or equivalent). A UV-Vis spectrophotometer is used in Appendix A and B for the optional preparation of stock solutions of chlorine (292 nm measurement) and monochloramine (245 nm measurement), respectively.

6.2.8 Aluminum foil to cover glassware

7 REAGENTS AND STANDARDS

7.1 **Indophenol Reagent** – Hach Monochlor F reagent powder pillows (Hach Cat. No. 2802246), or equivalent, are for the determination of monochloramine concentration in drinking water.

7.2 **Reagent Water** – Purified water (typically either deionized or distilled) free of analyte and chlorine demand. Reagent water can be purchased from a scientific supply company if it is not generated on site.

7.3 **Stock Standard Solutions (SSS)** – A purchased SSS must be National Institute of Standards and Technology (NIST) traceable or certified in an equivalent manner. The SSS must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (i.e., prior to the expiration date).

7.3.1 **Free Ammonia** – A free ammonia SSS (ammonium solution) can be purchased from a commercial source (Hach Company, product number 2406549; Fisher Scientific, catalog number NC9739494; or equivalent) or prepared using an ACS-grade ammonium salt (Fisher Scientific, catalog number A702-500; or equivalent) in reagent water.

7.3.2 **Free Chlorine** – A free chlorine SSS (hypochlorite solution) can be purchased from commercial sources (Fisher Scientific, catalog number LC246302; Hach Company, product number 1426820; or equivalent). See Appendix A for preparing and standardizing free chlorine SSS.

7.3.3 **Monochloramine** – A monochloramine SSS must be prepared fresh prior to use with free chlorine and free ammonia SSS in reagent water (see paragraph above) because it is inherently unstable and will auto-decompose. The reagent water should be buffered, such as with a 0.8 µM phosphate buffer made from potassium phosphate monobasic (Fisher Scientific, catalog number P285-500, or equivalent) or an equivalent buffer. The pH of the reagent water should be adjusted to 9.0 prior to adding free ammonia and free chlorine SSSs to minimize degradation and ensure that monochloramine is the predominant chloramine species present (i.e., minimizing dichloramine or trichloramine). See Appendix B for preparing and standardizing monochloramine SSS. To minimize degradation of the monochloramine SSS, it should be protected from light (i.e., beakers wrapped and covered with aluminum foil or stored in amber glass bottles) and used within two hours after standardization.

7.4 **Primary Calibration (PCAL) Standards –** A series of monochloramine PCAL standards spanning the range of the instrument (see Table 1) is obtained by diluting the monochloramine SSS with reagent water. For example, preparation of a series of 250-mL PCAL standards using a 1,000 mg/L as Cl_2 monochloramine SSS is summarized in Table 4 below.

Table 4: Preparation of PCAL Standards (250-mL) Using a Monochloramine SSS (1,000 mg/L as Cl_2)

PCAL Standard Concentration (mg/L as Cl_2)	Monochloramine Stock Standard Solution Volume (mL)
0.0	0.000
0.1	0.025
0.5	0.125
1.0	0.250
2.0	0.500
4.0	1.000

Monochloramine PCAL standards should be prepared with a fresh monochloramine SSS before each use. To minimize degradation of the monochloramine SSS, it should be protected from light (i.e., beakers wrapped and covered with aluminum foil or stored in amber glass bottles) and used within two hours.

7.5 **Secondary Calibration (SCAL) Standards** – Commercially prepared, stabilized, and sealed liquid or gel standards calibrated against a PCAL standard, such as Hach SpecCheck Secondary Gel Standards (Hach Company, catalog number 2507500), or equivalent. SCAL standards may not be used to calibrate the colorimeter, PPA, or spectrophotometer. If using pre-prepared SCAL standards, such as sealed gel standards, ensure that they are within the manufacturer's established expiration date.

8 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection

Collect samples in a clean, chlorine demand-free glass container (see Section 6.1.3 for a suggested procedure for preparing chlorine demand-free glass sample collection containers). Rinse the sample container three times with the sample prior to filling and capping the container. Minimize sample agitation or aeration and the presence of air bubbles, which can interfere with analysis. Fill the sample container headspace-free by allowing the sample to overflow the container prior to capping. Consider using amber or foil-wrapped glass sample containers to minimize exposure to light, as monochloramine can photodegrade. Analyze the sample immediately after collection (< 15 minutes). Samples cannot be preserved and/or stored for later analysis.

8.1.1 Treatment Process and Distribution System Representative Sampling

To obtain a representative water quality sample from the drinking water system treatment process or distribution system, the analyst should determine an appropriate sample flushing time based on the theoretical detention time in the piping or sample line between the sample tap and desired sample location (e.g., distribution system main). This may be accomplished by estimating the pipe diameter and length between the sample tap and the desired sample location, as well as the flow rate. The objective of flushing a sample line is to ensure that water is representative of the desired sample location (U.S. EPA, 2021).

9 QUALITY CONTROL

Quality control (QC) procedures are incorporated into analytical methods to demonstrate that the results are valid and within the accuracy and precision ranges needed for protection of public health. The following sections detail the QC procedures that are required for monochloramine analysis by colorimeters and spectrophotometers. The IDC and ongoing QC criteria are summarized in Section 17, Tables 9 through 12. Each analyst must complete the Initial Demonstration of Capability (see Section 9.1) demonstrating their ability to generate acceptable results that meet the accuracy and precision criteria of this method. The laboratory is required to maintain performance records that define the quality of data generated, and on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the system of analysis is in control. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs. For regulatory drinking water monitoring applications, additional QC and documentation may be specified by the associated drinking water primacy agency.

9.1 **Initial Demonstration of Capability (IDC) –** The IDC must be successfully performed prior to analyzing any field samples. Prior to conducting the IDC, the analyst must meet the calibration or verification requirements outlined in Section 10.

9.1.1 **Demonstration of Low System Background** – Analyze an LRB following all sample collection and procedure steps outlined in Section 8 and Section 11. The LRB concentration must be less than 0.2 mg/L as Cl_2 or the minimum chlorine residual required by the state. The LRB concentration must be subtracted from future results generated by this method if using a colorimeter or spectrophotometer with a calibration curve programmed by the manufacturer. If a standard curve is independently developed, the LRB concentration may be incorporated into the standard curve development. In that case, it is not necessary to subtract the LRB concentration from future results.

9.1.2 **Initial Precision and Recovery (IPR)** – To demonstrate the ability to generate data of acceptable precision and accuracy, the analyst should prepare and analyze at least five samples ($n \geq 5$) at the same concentration. Prepare the *n* samples at a concentration at or below the middle of the method range as specified in Table 1 in Section 1.2.

a. Determine the average percent recovery for the *n* samples. To determine percent recovery for each sample, R_i, where x_i is the determined individual sample concentration and x_e is the fortified concentration, calculate the following:

$$R_i = \frac{x_i}{x_e}(100)$$

To calculate the average percent recovery, $\bar{R}$, of the *n* (5) replicates:

$$\overline{R} = \frac{\sum R_i}{n}$$

To ensure acceptable accuracy, the average percent recovery should be within 15% of the expected value, x_e, (i.e., 85% to 115%).

b. Determine the relative standard deviation (RSD) for the *n* (5) samples. First determine the sample mean, $\bar{x}$:

$$\bar{x} = \frac{\sum x_i}{n}$$

To calculate the standard deviation, *s*, calculate the following:

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

To calculate the percent relative standard deviation:

$$\%RSD = \frac{s}{\bar{x}} \times 100\%$$

To ensure acceptable precision, the percent RSD should be less than or equal to 10%.

9.1.3 **Method Detection Limit (MDL)** – To establish the ability to detect monochloramine, the analyst shall determine the MDL using the apparatus, reagents, and standards that will be used in the practice of this method. Establish an MDL using reagent water (blank) fortified at a concentration three to five times an estimated detection limit, using the MDLs listed in Section 1.2 as a guide. Over three days, prepare daily replicate aliquots of this low level monochloramine fortified reagent water (triplicate on day 1 and duplicate on days 2 and 3) and process through the entire analytical method, generating a set of seven replicate sample results. Perform all calculations defined in the method and record the concentration measured in the appropriate units. To calculate the MDL, using the results from the set of seven replicate analyses (n = 7), use the following equation:

$$MDL = s \times 3.14$$

where,

S = standard deviation of the replicate analyses for seven replicates, and

3.14 represents the seven replicate student's t-value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

9.2 **Ongoing QC**

9.2.1 **Laboratory Reagent Blank (LRB)** – Analyze an LRB with each reagent lot. The LRB should be processed through all sample collection and procedure steps outlined in Section 8 and Section 11. The LRB should be less than 0.2 mg/L as Cl_2 or the minimum chlorine residual required by the state. If a standard curve is independently developed, the LRB concentration may be incorporated into the standard curve development. In that case, it is not necessary to subtract the LRB concentration from future results. Otherwise, as specified by the Indophenol Reagent manufacturer, the LRB concentration should be subtracted from results generated by this method and reagent lot if using a colorimeter or spectrophotometer with a calibration curve programmed by the manufacturer.

9.2.2 **Quality Control Sample (QCS)** – Independently verify instrument calibration with a QCS analyzed quarterly. The QCS must be freshly prepared before each use. If the analyst calibrated the instrument, the QCS must be prepared from SSSs that are different than the sources used to prepare the calibration standards. If discrepancies arise, depending on the instrument used, either adjust the calibration curve or follow manufacturer's instruction.

9.2.3 **Continuing Calibration Check (CCC)** – Verify instrument calibration with PCAL or SCAL standards to verify calibration each time the instrument is used, or daily if used multiple times per day, prior to any sample analysis.

9.2.4 **Grab Sample Duplicate (GSD)** – Analysis of GSD (i.e., two samples collected at the same time) provides an estimate of the precision of the grab sample analyses. Analyze a GSD at least once per set of samples on an analysis day. To ensure acceptable precision, the relative percent difference between GSD results should be less than 10% (i.e., 90% to 110% of each other). To calculate relative percent difference, %RPD, of the GSD samples:

$$\%RPD = \frac{|M_1 - M_2|}{(M_1 + M_2)/2} \times 100$$

Where, M_1 is measurement 1 and M_2 is measurement 2.

10 CALIBRATION AND VERIFICATION

10.1 **Initial Instrument Calibration** – An initial instrument calibration should be performed for each colorimeter or spectrophotometer, according to the procedure described below. The accuracy of SCAL standards should also be verified at this time. These steps can be performed by laboratory personnel or field samplers. A record of the calibration results should be maintained for each spectrophotometer or colorimeter.

10.1.1 Prepare an LRB and a set of at least three aqueous PCAL standards with concentrations spanning the concentration range of the method for the instrument being used (colorimeter or spectrophotometer). Refer to Section 1.2 (Table 1) for the method application range for each instrument tested.

10.1.2 Analyze the calibration standards and LRB according to the sample collection description in Section 8 and expedited processing through the method procedure outlined in Section 11.

a. For colorimeters or spectrophotometers that use an internal, factory-set calibration curve, compare the measured concentration of each standard to the expected value. If the measured value of any standard is not within ± 15% of its expected value, take corrective action before proceeding. First, re-prepare and re-analyze the PCAL standards. If the recoveries are still not within range, the calibration must be updated by following the manufacturer's instructions for generating or inputting a calibration curve. Otherwise, send the instrument to the vendor for repair or updating.

b. For colorimeters or spectrophotometers that require the preparation of a calibration curve, use the concentration of each PCAL standard versus the instrument response (e.g., absorbance) to calculate the linear regression.

i. Validate the initial calibration by calculating the concentration of each analyte as an unknown against its regression equation. All other calibration points should calculate to be within ±15% of their expected value.

ii. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. In this case, reanalyze the calibration standards or restrict the range of calibration. If the cause for failure to meet the criteria is due to contamination or standard degradation, prepare fresh PCAL standards and repeat the initial calibration.

c. If SCAL standards are available for the colorimeter or spectrophotometer, analyze them to verify calibration immediately after initial calibration. The absorbance or corresponding concentration of the SCAL standards must be within ± 15% of their expected absorbance or corresponding concentrations when compared to the initial calibration curve or within the range specified by the manufacturer. New SCAL standards should be purchased if this criterion cannot be met or contact the manufacturer to determine the appropriate course of action if the calibration curve is internal / factory-set. The SCAL standards must meet the criterion on every colorimeter or spectrophotometer that will be used to conduct this method. SCAL standards must not be used beyond the manufacturer's expiration date.

10.2 **Initial Demonstration of Capability (IDC) –** Each analyst must perform an IDC on each instrument (i.e., colorimeter or spectrophotometer) that will be used to conduct this method. The IDC consists of a demonstration of accuracy and a demonstration of precision using the procedure described in Section 9.1. If the accuracy and precision criteria are not met, determine the source of the problem, take corrective action, and repeat the IDC. Laboratory personnel may prepare the samples for analyses by field samplers. A record of the IDC results must be maintained for each field sampler.

10.3 **Ongoing Calibration Verification –** Instrument calibration should be verified on a quarterly basis with a QCS. Instrument calibration should be verified with a CCC prior to each use of the instrument or daily if the instrument is used multiple times per day, which may be a PCAL or SCAL standard. Results should be within ±15% of the actual value. If discrepancies arise, depending on the type of instrument being used, either adjust the calibration curve or follow the manufacturer's instructions. It is recommended that multiple QCS and CCC standards are prepared and analyzed that span the application range of the instrument (such as 0.5, 2.0, and 3.5 mg/L as Cl_2). Refer to Section 1.2 (Table 1) for the method application range for each instrument tested.

11 PROCEDURE

11.1 **Colorimeters**

11.1.1 Setup the instrument following the instrument manufacturer's instructions for instrument setup, including calibration verification and specify wavelength of 610 nm.

11.1.2 Rinse and fill the sample cell with the prescribed volume of sample based on the reagent and manufacturer's instructions. For example, for Indophenol Reagent Pillows (Hach Company, catalog number 2802299 or equivalent), 10 mL of sample is required.

11.1.3 Clean the outside of the filled sample cell with a lint-free paper fiber optic cleaning wipe or delicate task wipe (Kimberly-Clark Professional catalog number 34120 or equivalent) to remove fingerprints and condensation.

11.1.4 Check the sample cell for air bubbles adhering to the inside of the sample cell that may interfere with the reading. If bubbles are present, gently invert the capped sample cell until the bubbles are eliminated.

11.1.5 Insert the sample cell into the colorimeter cell holder, orient the sample cell based on manufacturer's instructions, place the sample cell cover over the sample cell on the instrument, and zero the colorimeter. The display should show 0.00 mg/L as Cl_2.

11.1.6 Remove the sample cell from the cell holder and measure and record the sample temperature directly in the cell, if possible. Add contents of one Indophenol Reagent Pillow (Hach Company, catalog number 2802299, or equivalent) into the sample cell. Cap the sample cell and shake the sample cell for approximately 20 seconds to dissolve the reagent. Note that the reagent may not completely dissolve.

11.1.7 Method results are influenced by sample temperature. Determine the appropriate reaction time based on the measured sample temperature in Section 11.1.6 and Table 5 below. If the measured sample temperature falls between two listed temperatures in Table 5, use the reagent color development time associated with the lower of the listed temperatures in the range. For example, if the measured sample temperature is 8°C, use the reagent color development time associated with 7°C, which is 22 minutes.

Table 5: Reagent Color Development Time Based on Sample Temperature

Sample Temperature (°C)	Sample Temperature (°F)	Reagent Color Development Time (minutes)
5	41	28
7	45	22
9	47	17
10	50	15
12	54	12
14	57	10
16	61	8
18	64	6
20	68	5
23	73	4
≥25	≥77	3

11.1.8 Some colorimeters have built-in timers for the reagent reaction time; however, these may assume that sample temperature is at room temperature. Be sure to allow reagent color development time based on the actual sample temperature.

11.1.9 Set a timer for the reagent color development time determined in Section 11.1.7 based on the actual sample temperature and start the timer.

11.1.10 While the sample reacts with the reagent, clean the sample cell again with a lint-free paper fiber optic cleaning wipe or delicate task wipe (Kimberly-Clark Professional catalog number 34120 or equivalent). When the timer expires, inspect the sample cell for air bubbles inside the cell. If bubbles are present, gently invert the cell until they are eliminated. Insert the prepared sample into the colorimeter cell holder, place the sample cell cover over the sample cell on the instrument, and analyze the sample. The sample color is stable for a maximum of 15 minutes after the specified reagent color development time in Table 5.

11.2 **Portable Parallel Analyzer**

11.2.1 Setup the instrument following the instrument manufacturer's instructions for instrument setup, including calibration verification and specify wavelength of 610 nm.

11.2.2 Insert a monochloramine-specific planar cuvette filled with Indophenol Reagent (Hach Company, catalog number 9429400, or equivalent) into the instrument tray. Ensure that the planar cuvette is inserted all the way into the slot and that the instrument properly recognizes / interfaces with the planar cuvette. If using Hach reagents and instrumentation, the instrument will recognize the barcode on the planar cuvette and will display the monochloramine parameter on the screen if inserted and recognized properly.

11.2.3 Rinse the sample tray container with sample and then fill the sample cup to the fill line marked by the manufacturer or fill with the volume specified by the manufacturer.

11.2.4 Holding the instrument, dip the tip of the planar cuvette into the sample cup until a beep on the instrument acknowledges that the system has drawn the sample into the planar cuvette. The system uses a conductivity detector to determine when the planar cuvette has been dipped into the water. Withdraw the planar cuvette out of the sample once the beep is heard and the test will automatically start. Once the reaction time has finished, the instrument will automatically read the sample, and the results will be stored and displayed on the instrument screen. Remove the planar cuvette out of the instrument port and dispose in accordance with the waste management procedures outlined in Section 14 of this method.

11.3 **Spectrophotometer**

11.3.1 Set up the instrument following the instrument manufacturer's instructions, including calibration verification. If a calibration curve was developed independently based on instrument response (absorbance) at 655 nm wavelength, set the spectrophotometer to single wavelength mode and set the wavelength to 655 nm. Built-in monochloramine programs on spectrophotometers also measure at 655 nm.

11.3.2 The use of sample cell type (10 mL vial versus a 1 cm cuvette) depends on the spectrophotometer being used (i.e., path length) and whether a built-in program with a manufacturer-generated calibration curve is being used versus a calibration curve developed independently. Rinse and fill the appropriate sample cell with sample and zero the spectrophotometer.

11.3.3 Rinse and fill a 10 mL sample cell with the prescribed volume of sample based on the reagent and manufacturer's instructions. For example, for a Indophenol Reagent Pillow (Hach Company, catalog number 2802299 or equivalent), 10 mL of sample is required. If a 1 cm cuvette is being used, the sample may be mixed in a 10 mL cell and transferred to a 1 cm cuvette. Measure and record the sample temperature.

11.3.4 Add contents of one Indophenol Reagent Pillow (Hach Company, catalog number 2802299, or equivalent) into the sample cell. Cap the sample cell and shake the sample cell for approximately 20 seconds to dissolve the reagent. Note that the reagent may not completely dissolve.

11.3.5 Reaction time is strongly influenced by sample temperature. Determine the appropriate reaction time based on the sample temperature (see Table 5) measured in Section 11.3.3.

11.3.6 Set a timer for the reagent color development time determined in Section 11.3.5 based on the actual sample temperature and start the timer.

11.3.7 While the sample reacts with the reagent, clean the sample cell again with a lint-free paper fiber optic cleaning wipe or delicate task wipe (Kimberly-Clark Professional catalog number 34120 or equivalent).

11.3.8 When the timer expires, if using the built-in program on the spectrophotometer, insert the prepared sample into the spectrophotometer cell holder, close the cover, and press the read button on the spectrophotometer. If using an independently-generated calibration curve, pour a few mL of the prepared sample into a 1 cm cuvette to rinse, clean the cuvette with a lint-free paper fiber optic cleaning wipe or delicate task wipe (Kimberly-Clark Professional catalog number 34120 or equivalent), and place the cuvette into the spectrophotometer cell holder. Read the absorbance of the prepared sample at 655 nm and record.

12 DATA ANALYSIS AND CALCULATION

Monochloramine concentration is calculated automatically and displayed, as mg/L as Cl_2, on the screen for colorimeters, mesofluidic channel pump colorimeters, and built-in spectrophotometer programs. If using an independently generated calibration curve, use the absorbance recorded from Section 11.3.8 in the best-fit linear regression equation determined in Section 10.1.2.b. to determine the corresponding monochloramine concentration in mg/L as Cl_2.

13 METHOD PERFORMANCE

Performance of this method was demonstrated in multi-lab studies comparing the method against SM 4500-Cl G. This method was evaluated with low and high ionic strength reference matrices at three monochloramine concentrations (0.5, 2.0, and 3.5 mg/L MCA as Cl_2); three pH levels (7.0, 8.0, and 9.0); and with multiple, geographically-diverse, finished drinking water samples obtained from both surface water and ground water sources. Performance of EPA Method 127 is summarized in Tables 6, 7, and 8.

Table 6: Method Validation Results for Colorimeters

Method Validation Results	Method Section	Limit
Initial Recovery (%)	9.1.3	89% - 94%
Initial Precision (RSD)	9.1.3	1.6 – 2.6%
Method Detection Limit (mg/L MCA as Cl_2)	9.1.1	0.08

Table 7: Method Validation Results for PPAs

Method Validation Results	Method Section	Limit
Initial Recovery	9.1.3	97% - 101%
Initial Precision (RSD)	9.1.3	1.0 – 3.5%
Method Detection Limit (mg/L MCA as Cl_2)	9.1.1	0.06

Table 8: Method Validation Results for Spectrophotometer[1]

Method Validation Results	Method Section	Limit
Initial Recovery	9.1.3	97% - 101%
Initial Precision (RSD)	9.1.3	0.7 – 4.9%
Method Detection Limit (mg/L MCA as Cl_2)	9.1.1	0.07

14 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the waste management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

Quantity of a chemical purchased should be based on expected usage during its shelf-life, disposal cost, and environmental impact of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

For information about pollution prevention that may be applicable to laboratory and field operations, consult *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards* (National Research Council, 2011).

15 WASTE MANAGEMENT

The analytical procedures described in this method generate relatively small amounts of waste because only small amounts of reagents are used. The matrix of concern is drinking water. However, waste management practices should be conducted consistent with all applicable rules and regulations and that the air, water, and land are protected by minimizing and controlling all releases from bench and field operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

Excess reagents, samples, and method process wastes should be characterized and disposed of in an acceptable manner. The SDS sheet provides details of product composition and may be consulted for guidance

[1] Independently-generated standard curve

on waste disposal.

16 REFERENCES

National Research Council. (2011). *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, Updated Version.* Washington, D.C.: The National Academies Press. doi:10.17226/12654

Standard Methods for the Examination of Water and Wastewater. (2017). *Standard methods for the examination of water and wastewater* (23rd ed.). Washington, D.C.: American Public Health Association.

U.S. EPA. (2016). *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.* Washington, D.C.: Office of Water.

U.S. EPA. (2021). *Calculated Flush Time (CFT) or Calculated Flush Volume (CFV) Approach for Representative Distribution System Chlorine and Disinfection Byproduct (DBP) Sample Collection from Building Taps.* Office of Water (140). doi:EPA 815-B-21-001

17 TABLES AND FLOWCHARTS

Table 9: Calibration and Verification Requirements

Method Reference	Requirement	Specification	Acceptance Criteria
10.1	Initial Instrument Calibration	Prepare a method reagent blank and a set of at least three aqueous primary calibration (PCAL) standards with concentrations spanning the concentration range of the method for the instrument being used (colorimeter or spectrophotometer). Meters with pre-installed factory calibrations may be used with proper documentation and must be verified using the same approach as above and comparing each calibration point to its expected value.	If used, secondary calibration (SCAL) standards must be within ± 15% of their expected concentrations or absorbance when compared to the initial calibration curve or within the range specified by the manufacturer. For pre-installed factory calibrations, each calibration point must be within ± 15% of its expected value.
10.3	Calibration Verification	Instrument calibration should be verified on a quarterly basis with a quality control sample (QCS), which must be a PCAL standard. Instrument calibration should be verified with a continuing calibration check (CCC) prior to each use of the instrument or daily if the instrument is used daily, which may be a PCAL or SCAL standard.	Results must be within ± 15% of their expected concentrations or absorbance when compared to the initial calibration curve or within the range specified by the manufacturer.

Table 10: Initial Demonstration of Capability

Method Reference	Requirement	Specification	Acceptance Criteria
9.1.1	Method Detection Limit (MDL)	Determine the MDL using the apparatus, reagents, and standards that will be used in the practice of this method.	Achieve an MDL that meets program data quality objectives, which ideally would be less than or equal to the instrument-specific MDLs reported in Section 1.2.
9.1.2	Demonstration of Low System Background	Analyze a laboratory reagent blank (LRB) after completing all sample collection and procedure steps outlined in Section 8 and 11. If the instrument has an internal, factory-set calibration curve, the LRB concentration should be subtracted from sample results generated by this method.	The LRB concentration must be less than 0.2 mg/L as Cl_2 or the minimum chlorine residual required by the state.
9.1.3	Initial Precision and Recovery (IPR)	Analyze at least five independent reference samples at the same concentration. Prepare the samples at a concentration near the middle of the method application range as specified in Table 1 in Section 1.2. Determine the average percent recovery for the five samples. Determine the percent relative standard deviation (%RSD) for the five samples.	To ensure acceptable accuracy, the average percent recovery should be within 15% of the expected value (i.e., 85% to 115%). To ensure acceptable precision, the %RSD should be less than or equal to 10%.

Table 11. Ongoing Quality Control Requirements

Method Reference	Requirement	Specification	Acceptance Criteria
9.2.1	Demonstration of Low System Background	Analyze an LRB with each reagent lot. The LRB should be processed through all sample collection and procedure steps outlined in Section 8 and 11. The LRB concentration should be subtracted from sample results generated by this method.	The LRB should be less than 0.2 mg/L as Cl_2 or the minimum chlorine residual required by the state.
9.2.2 and 10.3	Quality Control Sample (QCS)	Instrument calibration must be verified with a QCS on a quarterly basis.	Results should be within ±15% of the actual value. If discrepancies arise during primary standard calibration verification and depending on the type of instrument being used, either adjust the calibration curve (if self-generated) or follow the manufacturer's instructions.
9.2.3 and 10.3	Continuing Calibration Check (CCC)	Instrument calibration must be verified with a PCAL or SCAL standard daily or each time the instrument is used, prior to any sample analysis.	Results should be within ±15% of the actual value. If discrepancies arise during primary standard calibration verification and depending on the type of instrument being used, either adjust the calibration curve (if self-generated) or follow the manufacturer's instructions. If secondary gel standards are used, it is recommended that instrument calibration is verified prior to each use. Secondary standards should be within ±15% of their expected concentrations or

			absorbance when compared to the initial calibration curve or within the range specified by the manufacturer.
9.2.4	Grab Sample Duplicate (GSD)	Analysis of duplicate samples (i.e., two samples collected at the same time) provides an estimate of the precision of the grab sample analysis.	To ensure acceptable precision, the relative percent difference (RPD) between duplicate sample results should be less than 10% (i.e., 90% to 110% of each other).

Appendix A: Optional Free Chlorine Stock Solution Preparation and Standardization Procedure Using Molar Absorptivity by Spectrophotometry

1. Create a free chlorine stock solution of approximately 10,000 mg/L as Cl_2 (0.141 M) by performing the following steps:

    a. Add 200 mL of 5% - 6% sodium hypochlorite stock solution (e.g., Fisher Scientific catalog number LC246302; Hach product number 1426820; or equivalent) to 800 mL reagent water (see Section 3.8) in a 1-L volumetric flask and mix thoroughly.

    b. Transfer the prepared stock solution to a chlorine demand-free 1-L amber glass bottle.

    Store at 4°C protected from light.

    c. Calculate the volume of free chlorine stock solution (from Step 1) needed to prepare a diluted aliquot of stock solution to be used for standardization (i.e., at a concentration low enough to be measured by a UV-Vis spectrophotometer) by performing the following steps:

    d. Determine a target absorbance (*A*) at a wavelength (λ) of 292 nm in the desired range to ensure photometric linearity. For example, to calculate the target absorbance (*A*) between 0.5 and 1.2:

$$A = \frac{0.5 + 1.2}{2} = 0.85$$

e. Determine the target concentration (*c*) of the diluted aliquot of the prepared free chlorine stock solution using the Beer's Law equation. For example, for a spectrophotometer cell path length (*b*) of 1 cm, the known hypochlorite ion (OCl^-) molar absorptivity (ε) of 350 $M^{-1}cm^{-1}$, and a calculated target absorbance (*A*) of 0.85 from Step 2a:

$$c = \frac{A}{\varepsilon b} = \frac{0.85}{(350\ M^{-1}cm^{-1})(1\ cm)} = 2.43\ x\ 10^{-3}\ M$$

f. Determine the volume of free chlorine stock solution required to prepare a diluted solution for standardization. For example, the volume (V_1) of free chlorine stock solution needed to prepare a 50 mL (V_2) diluted solution at the target concentration determined in Step 2b ($c = M_2 = 2.43 \times 10^{-3}$ M), assuming the free chlorine stock solution is approximately 10,000 mg/L as Cl_2 (M_1 = 0.141 M) as prepared in Step 1:

$$M_1V_1 = M_2V_2$$

$$(0.141\ M)V_1 = (2.43\ x\ 10^{-3}\ M)(0.05\ L)$$

$$V_1 = 8.61\ x\ 10^{-4}\ L = 0.861\ mL = 861\ \mu L$$

2. Prepare the UV-Vis spectrophotometer to measure absorbance by performing the following steps:
    a. Turn on the UV-Vis spectrophotometer to allow the instrument to initialize and warm-up.
    b. Set the spectrophotometer to "fixed wavelength".
    c. Set the wavelength (λ) to 292 nm.
    d. Using a 1 cm quartz cuvette, blank/zero the spectrophotometer with reagent water.

3. Prepare a diluted aliquot of free chlorine stock solution by performing the following steps:
    a. Wrap a beaker in foil to minimize photodegradation of the free chlorine solution. The beaker size should hold a volume greater than V_2 used in Step 2c.
    b. Fill the beaker with a volume of reagent water equivalent to the desired volume of diluted stock solution (V_2) used in Step 2c. For example, if a 50 mL diluted solution is being prepared add 50 mL of reagent water to the beaker.
    c. Using a pipette, remove and discard to waste a volume of reagent water from the beaker equivalent to the volume of free chlorine stock solution to be added (V_1) from Step 2c. Then, pipette the same volume of free chlorine stock solution (V_1) into the

beaker. Based on the example in Step 2c, remove 861 µL of the reagent water and then add 861 µL of the free chlorine stock solution.

d. Cover the beaker with foil to minimize photodegradation of the free chlorine and mix thoroughly for about 5 minutes using a stir bar and stir plate.

e. Check the pH of the diluted solution before proceeding. The pH should be above 10 to ensure the solution is predominantly OCl^-. If the pH is below 10, consider the following:

   i. Repeat Step 2 to ensure that the calculations were completed correctly.

   ii. Repeat Step 3 to ensure that the diluted solution was prepared correctly.

   iii. Repeat Steps 1 through 3 using a fresh sodium hypochlorite solution.

4. Measure the absorbance of the diluted free chlorine stock solution by performing the following steps:

   a. After the mixing is complete, rinse the cuvette with the diluted solution once and refill with diluted solution.

   b. Measure the absorbance of the diluted solution at 292 nm and record.

   c. Repeat Step 4 two more times to generate a total of three diluted solution preparations and corresponding absorbance measurements.

5. Determine the free chlorine stock solution concentration by performing the following steps:

   a. Average the three absorbance readings of the diluted free chlorine stock solution from Step 5.

   b. Determine the actual concentration (X_{Cl}) of the free chlorine stock solution in mg/L as Cl_2, using the average absorbance (A) from Step 6a based on the formula derivation below:

$$M_2 = \frac{A}{\varepsilon b} = \frac{A}{(350\ M^{-1}cm^{-1})(1\ cm)}$$

$$M_1V_1 = M_2V_2$$

$$M_1 = \frac{M_2V_2}{V_1} = \frac{M_2(0.05\ L)}{(8.61\ x\ 10^{-4}\ L)} = \frac{A\ (0.05\ L)}{(8.61\ x\ 10^{-4}\ L)(350\ M^{-1}cm^{-1})(1\ cm)} = 0.166(A)\ M$$

Molar conversion to determine concentration in units of mg/L as Cl_2:

$$X_{Cl_2} = M_1 \times \frac{71{,}000\ mg\ Cl_2}{mol\ Cl_2} = \frac{A\ (0.05\ L)(71{,}000\ mg\ Cl_2)}{(8.61\ x\ 10^{-4}\ L)(350\ L \cdot mol^{-1}cm^{-1})(1\ cm)(mol\ Cl_2)}$$

$$X_{Cl_2} = (A)\ 11{,}780\ \left[\frac{mg}{L} as\ Cl_2\right]$$

Appendix B: Monochloramine Stock Solution Preparation and Standardization Procedure Using Molar Absorptivity by Spectrophotometry

1. Create a free chlorine stock solution (C_{Cl}) of approximately 10,000 mg/L as Cl_2 (0.141 M) and standardize as described in Appendix A. Use the actual concentration for the free chlorine stock solution determined in Appendix A in the following calculations to create a monochloramine stock solution.

2. Create a free ammonia-nitrogen stock solution (C_A) of approximately 10,000 mg/L as N by performing the following steps:
    a. Add 23.6 g $(NH_4)_2SO_4$ (e.g., Fisher Scientific catalog number A702-500; or equivalent) to a 500 mL volumetric flask partially filled with reagent water (see Section 3.8). Add the remaining reagent water to the 500 mL fill line on the flask.
    b. Add a stir bar to the volumetric flask and place on a stir plate and stir until the solids are dissolved.
    c. Once the solids are dissolved, pour the solution into an amber glass bottle.
    d. Adjust the pH of this solution to 8.3. Approximately 1.1 mL of 10 N sodium hydroxide (NaOH) is required to raise the pH to 8.3. This can vary slightly, depending on the starting solution pH.

3. Determine the following values needed to prepare a monochloramine stock solution (see Table A for example values):

    C_M = Target monochloramine stock solution concentration (mg/L as Cl_2)

    C_{Cl} = Free chlorine stock solution concentration from Step 1 (mg/L as Cl_2)

    C_A = Free ammonia stock solution concentration from Step 2 (10,000 mg/L as N)

    R = Desired chlorine-to-ammonia-nitrogen mass ratio (Cl_2:N); (e.g., R = 4 in a 4:1 Cl_2:N)

    V_M = Desired volume of monochloramine stock solution to be made (mL)

4. Calculate the following volumes and concentrations needed to prepare a monochloramine stock solution (see Table A for example values) based on the values determined in Step 3:
    a. Calculate the required free ammonia concentration, N_R in mg/L as N.

$$N_R \left[\frac{mg}{L} as\ N\right] = \frac{C_M \left[\frac{mg}{L} as\ Cl_2\right]}{R \left[\frac{mg\ Cl_2}{mg\ N}\right]}$$

b. Calculate the required volume of free ammonia stock solution to add, V_N in mL.

$$V_N[mL] = \frac{N_R\left[\frac{mg}{L} as\ N\right] * V_M[mL]}{10{,}000\ \left[\frac{mg}{L} as\ N\right]}$$

c. Calculate the required volume of free chlorine stock solution volume to add, V_{Cl} in mL.

$$V_{Cl}[mL] = \frac{C_M\left[\frac{mg}{L} as\ Cl_2\right] * V_M[mL]}{C_{Cl}\left[\frac{mg}{L} as\ Cl_2\right]}$$

d. Calculate the required reagent water volume to add, V_W in mL.

$$V_W[mL] = V_M[mL] - V_N[mL] - V_{Cl}[mL]$$

5. Prepare the UV-Vis spectrophotometer to measure absorbance by performing the following steps:
    a. Turn on the UV-Vis spectrophotometer to allow the instrument to initialize and warm-up.
    b. Set the spectrophotometer to “fixed wavelength”.
    c. Set the wavelength (λ) to 245 nm.
    d. Using a 1 cm quartz cuvette, blank/zero the spectrophotometer with reagent water.

6. Prepare a monochloramine stock solution by performing the following steps:
    a. Add the required reagent water volume (V_W) to a foil-covered beaker (to minimize photodegradation of monochloramine) and a stir bar.
    b. Add the required free ammonia stock solution volume (V_N) to the beaker.
    c. Begin moderately stirring the solution and add the required free chlorine stock solution volume (V_{Cl}) to the beaker slowly (i.e., dropwise or slow pipetting, adding only 10% of the required free chlorine stock solution volume at a time).
    d. Cover the beaker with foil and allow the solution to mix for 15 minutes.

6. Calculate the volume of monochloramine stock solution (from Step 6) needed to prepare a diluted aliquot of stock solution to be used for standardization (i.e., at a concentration low

enough to be measured by a UV-Vis spectrophotometer) by performing the following steps:

a. Determine a target absorbance (*A*) at a wavelength (λ) of 245 nm in the desired range to ensure photometric linearity. For example, to calculate the target absorbance (*A*) between 0.25 and 1.0:

$$A = \frac{0.25 + 1.0}{2} = 0.625$$

b. Determine the target concentration (*c*) of the diluted aliquot of the prepared monochloramine stock solution using the Beer's Law equation. For example, for a spectrophotometer cell path length (*b*) of 1 cm, the known monochloramine molar absorptivity (ε) of 445 $M^{-1}\,cm^{-1}$, and a calculated target absorbance (*A*) of 0.625 from Step 7a:

$$c = \frac{A}{\varepsilon b} = \frac{0.625}{(445\ M^{-1}cm^{-1})(1\ cm)} = 1.40\ x\ 10^{-3}\ M$$

c. Determine the volume of monochloramine stock solution required to prepare a diluted solution for standardization. For example, the volume (V_M) of monochloramine stock solution needed to prepare a 50 mL (V_D) diluted solution at the target concentration determined in Step 2b ($c = C_D$ = 1.40 x 10^{-3} M), assuming the monochloramine stock solution is approximately 1,000 mg/L as Cl_2 (C_M = 1.40 x 10^{-2} M) as prepared in Table A:

$$C_M V_M = C_D V_D$$

$$(1.40\ x\ 10^{-2}\ M)V_M = (1.40\ x\ 10^{-3}\ M)(0.05\ L)$$

$$V_M = 5\ x\ 10^{-3}\ L = 5\ mL$$

7. Prepare a diluted aliquot of monochloramine stock solution by performing the following steps:

   a. Wrap a beaker in foil to minimize photodegradation of the monochloramine. The beaker size should hold a volume greater than V_D used in Step 7c.

   b. Fill the beaker with a volume of reagent water equivalent to the desired volume of diluted stock solution (V_D) used in Step 7c. For example, if a 50 mL diluted solution is being prepared add 50 mL of reagent water to the beaker.

   c. Using a pipette, remove and discard to waste a volume of reagent water from the beaker equivalent to the volume of monochloramine stock solution to be added (V_M) from Step 7c. Then, pipette the same volume of monochloramine stock

solution (V_M) into the beaker. Based on the example in Step 7c, remove 5 mL of the reagent water and then add 5 mL of the monochloramine stock solution.

d. Cover the beaker with foil to minimize photodegradation of the monochloramine and mix thoroughly for about 5 minutes using a stir bar and stir plate.

e. Check the pH of the diluted solution before proceeding. The pH should be above 8.3 to ensure the solution is predominantly monochloramine. If the pH is below 8.3, consider the following:

   i. Repeat Steps 3 and 4 to ensure that the calculations were completed correctly.

   ii. Repeat Step 7 to ensure that the diluted solution was prepared correctly.

   iii. Verify the pH of the ammonia-nitrogen stock solution is near 8.3. If not, repeat Step 2 using fresh ammonium sulfate and sodium hydroxide

   iv. Repeat Step 1 (see Appendix A) using a fresh sodium hypochlorite solution.

7. Measure the absorbance of the diluted monochloramine stock solution by performing the following steps:

   a. After the mixing is complete, rinse the cuvette with the diluted solution once and refill with diluted solution.

   b. Measure the absorbance of the diluted solution at 245 nm and record.

   c. Repeat Step 7 two more times to generate a total of three diluted solution preparations and corresponding absorbance measurements.

8. Determine the monochloramine stock solution concentration by performing the following steps:

   a. Average the three absorbance readings of the diluted monochloramine stock solution from Step 8.

   b. Determine the actual concentration (X_M) of the monochloramine stock solution in mg/L as Cl_2, using the average absorbance (A) from Step 9a based on the formula derivation below:

$$C_D = \frac{A}{\varepsilon b} = \frac{A}{(445\ M^{-1}cm^{-1})(1\ cm)}$$

$$C_M V_M = C_D V_D$$

$$C_M = \frac{C_D V_D}{V_M} = \frac{C_D(5\ x\ 10^{-3}\ L)}{(0.05\ L)} = \frac{A\ (0.05\ L)}{(5\ x\ 10^{-3}\ L)(445\ M^{-1}cm^{-1})(1\ cm)} = A(2.25\ x\ 10^{-2})\ M$$

Molar conversion to determine concentration in units of mg/L as Cl_2:

$$X_M = C_M \times \frac{71{,}000\ mg\ Cl_2}{mol\ Cl_2} = \frac{A\ (0.05\ L)(71{,}000\ mg\ Cl_2)}{(5\ x\ 10^{-3}\ L)(445\ L \cdot mol^{-1}cm^{-1})(1\ cm)(mol\ Cl_2)}$$

$$X_M = (A)\ \frac{1{,}595\ mg\ Cl_2}{L}$$

Table A: Example Values for Monochloramine Stock Solution Preparation

Parameter	Value	Units
Target Monochloramine Stock Solution Concentration (C_M)	1,000	mg/L as Cl_2
Measured Free Chlorine Working Solution Concentration (C_{Cl})	10,000	mg/L as Cl_2
Created Free Ammonia Stock Solution Concentration (C_A)	10,000	mg/L as N
Target Chlorine to Nitrogen Mass Ratio (R)	4	X:1
Design Monochloramine Stock Solution Volume (V_D)	50.00	mL
Required Free Ammonia Concentration (N_r)	250	mg/L as N
Required Ultra-Pure Water Volume (V_W)	43.75	mL
Required Free Ammonia Stock Solution Volume (V_N)	1.25	mL
Required Free Chlorine Working Solution Volume (V_{Cl})	5.00	mL