

Based on Standard Methods 4500-Cl E for drinking water and wastewater

This application note covers the following application:

Method	Range	Titrant	Buffer, KI and Acid	Sample volume
Total Chlorine Forward Titration— Diluted Titrant	3 to 100 µg/L as Cl ₂	0.000564N PAO	pH 4 Acetate 0.1g KI	200 mL

1. Important information

- This is a method of analysis for an unstable analyte. Care in the use of the method is required.
- The AT1000 is factory programmed to use the 10-mL syringe. The method uses a 5-mL syringe. Before analysis, make sure to change the syringe volume on the instrument. Refer to [10.1 Changing the syringe volume on the AT1000](#).
- Use a 2 3/8-in. stir bar and a stirring speed of 1% for the analysis.
- Regular cleaning of the electrode is necessary. Clean and correctly maintained electrodes are necessary for sharp amperometric endpoints. Clean the electrode when the noise in the titration curve interferes with detection of the endpoint. The electrode cleaning duration is approximately 10 minutes. Always clean new electrodes before the analysis. The manufacturer strongly recommends a daily cleaning procedure. Refer to [10.2 Cleaning the Electrode](#).
- The electrode orientation is very important. The noise that occurs when the electrode is not correctly oriented can interfere with accurate detection of the equivalence point.
- Potassium iodide purity is critical for trace total chlorine determinations. The iodide should be free of iodine or iodate, which can react directly with chlorine or chloramines in the sample (even solid potassium iodide can be oxidized with enough exposure to oxygen and UV light).
- ASTM type III water is strongly recommended for use in the preparation of any check standards as well as dilution of samples (should dilution be required). Organics can leach from plastics into water, and result in chlorine demand. For best results, RO water, 18.2 MΩ (Megohm) and very low TOC is strongly recommended (i.e. Milli-Q water).

2. Introduction

This application note follows *Standard Methods number 4500-Cl E in Standard Methods for the Examination of Water and Wastewater (20th Edition)*, Low Level Amperometric Titration Method for Total Chlorine. The endpoint of the titration is determined automatically by the software instead of using a graphical procedure per the 2007 MUR. The SM 4500 Cl E can be found in Table 1B of 40CFR136 (NPDES), and a comparison table is provided at the end of this document.

Total chlorine corresponds to the chlorine derived from all its possible forms in solution including free elemental chlorine (Cl₂), hypochlorous acid (HOCl), hypochlorite (OCl⁻) ion, and chloramines (NH₂Cl, NHCl₂, etc.) among other types.

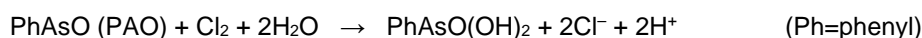
The scope of this application note is to determine the total chlorine concentration (Free Chlorine Conc. + Combined Chlorine Conc.) in water or wastewater samples. In chlorinated wastewater effluents, as well as the waterbodies receiving those effluents, essentially all the chlorine present is combined chlorine. Additionally, it is not possible to differentiate between free and combined chlorine at these low levels. A procedure for preparation of a Monochloramine standard is included in Section [10.4.2 Preparation of a monochloramine standard, 10 mg Cl₂ /L as NH₂Cl \(OPTIONAL\)](#). Support data using both monochloramine, and chlorine is provided in the comparison table at the back of this method. This method uses a more dilute, 0.000564N PAO titrant. This very low range method complies with SM 4500-Cl E for labs that are not able to use a modified version of the method.

Ultra-Low Range (0.000564N PAO titrant): for sample concentrations between 3 and 100 µg/L.

3. Principle

In this procedure for **total chlorine**, an excess of potassium iodide (KI) is added to a water sample. The sample pH is adjusted to pH 4 by the addition of an acetate buffer. The sample solution is then titrated amperometrically using **0.000564N** phenylarsine oxide (PAO) solution. Phenylarsine oxide is used in this forward titration for total chlorine because it provides sharper endpoints than thiosulfate titrant at pH 4.

The chemical reaction is:



4. Electrode and reagents

Electrode:	Pt-Pt electrode with temperature sensor, IntelliCAL MTC695
Titrant:	Phenyl Arsine Oxide (PAO) 0.000564 eq/L solution)
Reagents:	Acetate Buffer Solution, pH 4 Potassium Iodide, ACS or better*
Deionized water	Nitric acid (for electrode cleaning)

5. Range and settings

5.1. Working ranges

The applications for determining chlorine in water cover a range of concentrations up to 5 mg/L as Cl₂ with the choice of multiple methods. It is possible to measure samples with a higher concentration by using a smaller amount of sample and diluting it to 200 mL. Using 0.000564N PAO as titrant (for this method), 1 mL of titrant corresponds to 0.1 mg/L (100 µL) of chlorine.

Note: The other amperometric total chlorine method for low level analysis (0.005-0.100 mg Cl₂-/L) uses a 0.00564N titrant and complies with SM4500 Cl-E for laboratories that are allowed to use a modified method for NPEDS reporting).

5.2. Titration settings (default parameters)

The settings below have been defined with:

- Sample volume: 200 mL.
- Syringe volume: 5 mL. The default syringe volume for the AT1000 is set to 10 mL.
*Note: This application uses a 5-mL syringe. When loading an application, if the message SYRINGE TO REPLACE shows, change the syringe volume in the **Syringe management** option of the **Maintenance** menu. Refer to [10 Appendix](#) for details.*
- Titrant concentration: Phenylarsine Oxide (PAO) Titrant, 0.000564 N
- Continuous imposed voltage: 100 mV (reversed at each analysis)
- Only analyze blanks as samples, not as blanks. Do not use the BLANK designation. If the blank designation is used, it will cause problems with the analysis.

Name	Default parameter	Unit
Application name	Tot.Cl₂ 4500-E, 3 to 100 µg/L	
Syringe		
Advisable	5 mL (Hamilton)	
Titrant	0.000564N PAO ¹	
Sample		
Name	Water? ²	
Amount	200	mL
Probe		
Recommended electrode	MTC695	
Titrant		
Name	PAO	
Real concentration	0.000564N	eq/L
Manual addition 1		

¹ This is 1/10th the typical concentration. Must dilute 0.00564N titrant 1:10 for this method.

² ? in the name, shows that the sample name will be automatically incremented with a number for each analysis.

Name	Default parameter	Unit
Application name	Tot.Cl₂ 4500-E, 3 to 100 µg/L	
Active	Yes	
Message	Add 0.1g KI and press OK	
Stirring speed	0	[%]
Automatic addition 2		
Active	No	
Message	Add 1 mL of buffer and press OK	
Stirring Speed	0	
Automatic addition 2		
Active	Yes ³	
Reagent name	Buffer pH 4	
Pump ID	Pump 1	
Time	0.6	seconds
Stirring speed	0	%
Titration		
Stirring speed	1	%
Measured parameter	µA	
Speed	0.5 mL/min	
Predose Ordinate	0.04	µA
Delay	10	seconds
Max. vol. stop point	0.120	mL
Stop on last EQP	Yes	
Increment size	0.0025	mL
EQP min. ordinate	-0.01	µA
EQP max. ordinate	0.01	µA
Results		
Result 1 name	Total Chlorine	
R1 min	2 µg/L	µg/L
R1 max	110 µg/L	µg/L
R1 QC min	2 µg/L	µg/L
R1 QC max	110 µg/L	µg/L
R1 Molar weight	70.906	g/Mole

5.3. Modification of the settings

To manually add the pH 4 buffer, activate the buffer manual addition and deactivate the automatic addition in the application edit window.

Standard Methods recommends a default sample volume of 200 mL and the parameters have been optimized with this volume for the whole range of concentrations covered by all of the amperometric methods for chlorine.

The final results are calculated based on the sample volume. For a more concentrated sample, pipette a smaller amount of sample, adjust the volume to 200 mL with ASTM Type III water and enter the real sample volume in the application edit window.

The titration time has been reduced with an addition of titrant at the start of the titration (predose). Higher concentrations of total chlorine will take longer to titrate than lower concentrations. Titrations in ASTM type III water will take less time than those in actual samples. Entering a value less than 0.04 [µA] for the predose is not recommended because there may not be enough data points for accurate determination. Increasing the speed of the pre-dose is not recommended because the ordinate can be exceeded.

6. Procedure

6.1. Position of the electrode and injection tips

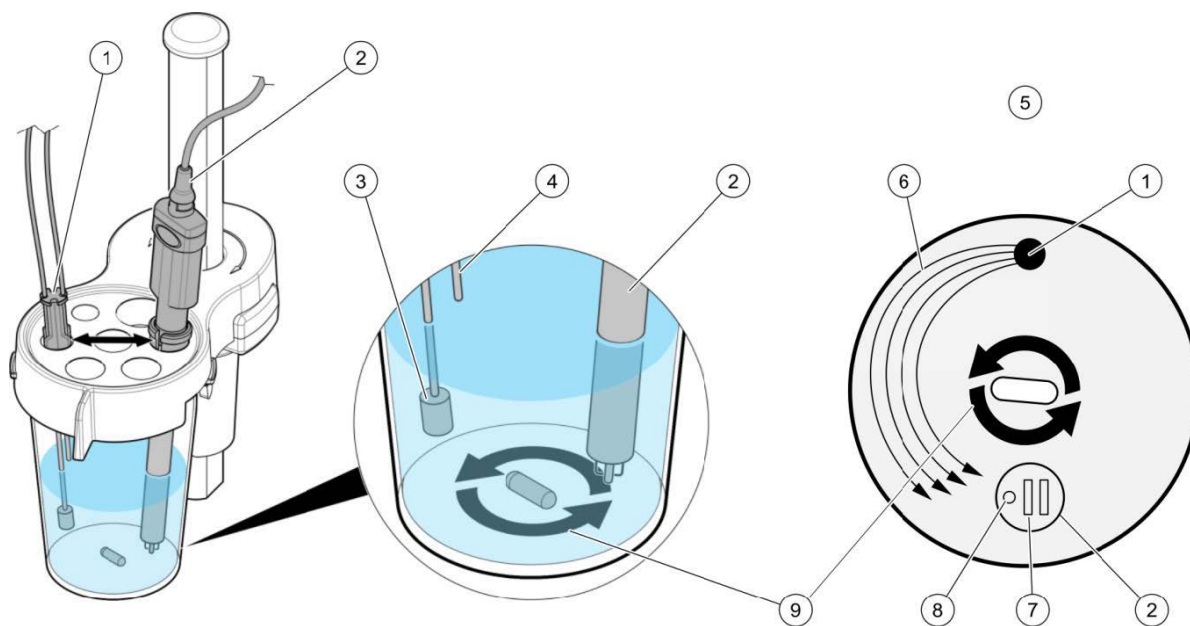
The position of the electrode and injection tips in the titration cell is very important in this application. **If the electrode is incorrectly positioned, noise in the titration curve can adversely affect the results.**

Refer to the steps and the figure that follows to correctly position the electrode and injection tips.

1. Put the electrode in the opposite hole of the tubes in the sensor holder (items 1 and 2 in figure).
2. Turn the electrode so that the platinum wires are perpendicular to the sample flow and the temperature sensor is before the platinum wires (items 6 to 8 in figure) .

³ Only one of these methods must to be active

3. Put the tube from the pump above the sample surface (item 4 in figure).
4. Make sure that the tube with the anti-diffusion tip is fully into the sample (item 3 in figure).



1. Tube holder	4. Tube from the pump	7. Platinum wires
2. Electrode	5. Top view	8. Temperature sensor
3. Anti-diffusion tip	6. Flow direction	9. Stirring direction

6.2. Sample tips and technique

- To avoid loss of chlorine, do not to agitate the sample when measuring or pouring.
- Avoid plastic sample containers, which can have a high chlorine demand
- Pretreat glass sample containers to remove any chlorine demand by soaking in a diluted bleach solution (1 mL commercial bleach solution to 1 liter of water) for at least one hour. After soaking, rinse thoroughly with deionized/distilled water.
- Rinse sample containers thoroughly with deionized/distilled water after each use to reduce the need for additional pretreatment
- When sampling tap water, let the faucet run for at least 4-5 minutes prior to collecting the sample.
- Prepare a test sample by diluting Chlorine Standard Solution with organic-free reagent water.
- A total chlorine standard, as monochloramine, can also be prepared for use with this method. Refer to [10.5 Preparation of a monochloramine standard, 10 mg Cl₂ /L as NH₂Cl \(optional\)](#).
- Only use blanks as samples. If a blank is used as a blank test, it can affect later results

6.3. Reagent tips and technique

- Download the Certificate of Analysis (COA 0.000564N PAO, PN 199849 Purchased from Hach) to obtain the exact concentration of any unopened bottle of Hach titrant standard solution from Hach.com. Enter this value.
- **For this ultra-low level method, the titrant can also be calibrated by the user.** Refer to [10.4.1 Calibration of the titrant with 0.0282N Iodine](#).
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis (pH 4 acetate buffer 1L for automated addition or 100 mL for manual addition)
- Do not substitute buffers made for calibrating pH meters. They contain dyes that interfere with amperometric titration
- Do not use buffers contaminated with mold or bacteria
- Rinse the electrode and tip with deionized water and wipe dry with a lab wipe (such as KimWipe™) before every titration

6.4. Instrument tips and technique

- There is a difference between doing a new test and a new sample (Exit or Next). Pushing Next will bring up two options: REPLICATE SAMPLE and NEW SAMPLE. The titrator automatically tracks the results of a series of tests and automatically calculates the mean and standard deviation for all the results when replicates are analyzed.
- Only analyze blanks as samples, not as blanks. Do not use the BLANK designation. Analyze the blank as a sample. If the blank designation is used, it will cause problems with the analysis.
- Push **STOP** any time to interrupt instrument operation. It is not possible to resume a stopped analysis.

- Clean the MTC695 electrode after a titration when the equivalence point is not detected and after storage. Execute the dedicated routine in the maintenance menu. Use 10 to 20% Nitric Acid as a cleaning medium.
- For short term storage (1 or 2 days) store the electrode in 1% Nitric Acid in Tap water. For longer term storage, the electrode can be stored dry. Always clean using the programmed procedure (Maintenance menu) before use. Multiple cleanings may be required after extended dry storage.
- Purge the burette 1-2 times each day before the first sample test or calibration is started.
- Purge the burette 1-2 times when changing titrant solutions.

6.5. Safety

- Use good safety practices and laboratory techniques throughout the procedure. Refer to the Safety Data Sheet (SDS) for specific reagent(s) information.
- Always use proper PPE (Personal Protective Equipment) such as lab glasses and nitrile gloves.
- When preparing dilute nitric acid, always add acid to water and use proper PPE.

6.6. Sample analysis

1. In the Main menu, select the method based on the expected concentration of the sample, then push **Start**. This method uses **0.000564 N PAO titrant** for very low levels of chlorine. For information of the titrant calibration, refer to [10.4.1 Calibration of the titrant with 0.0282N Iodine](#).
2. Confirm the operator name and the sample name. Modify them as necessary.
3. Measure 200 mL of sample solution with a 250-mL graduated cylinder. Carefully—with as little agitation as possible—pour the solution into a 250-mL glass beaker with the specified magnetic stir bar. Alternatively, weigh 200 g of sample (1 mL= 1 g)
4. Dip the electrode and the anti-diffusion titrant tip into the sample as shown in the figure. Make sure not to hit the electrode on the side of the beaker to avoid damaging the electrode. The anti-diffusion tip must be submerged in the sample.
5. Add the buffer.

Note: The acetate buffer is added only to adjust the sample pH. The amount of acetate buffer used is not crucial for the accuracy or precision of the analysis.

 - **Manual buffer addition:** Add 1 mL of pH 4 acetate buffer with the dropper or a pipette. Push **OK** to confirm
 - **Automatic buffer addition:** The buffer addition starts automatically. If adding the pH 4 buffer automatically, adjust tip from the peristaltic pump to **above** the sample surface and push **Start**.
6. Add approximately 0.1 g of potassium iodide (KI) using the 0.1g scoop. Push **OK** to confirm. The KI is added in excess, but the precise amount used is not crucial for the accuracy or precision of the analysis. (Swiftest™ is not recommended for this very low-level application). A 10-seconds delay starts. The 10-second delay lets the signal stabilize before data collection. During this time, the reagents and sample are stirred. After the signal has stabilized, the titration and data acquisition starts. The titration curve is plotted.
7. During the delay, adjust the stirrer speed to ensure efficient stirring and prevent the formation of bubbles, if necessary. Bubbles that stick to the electrode cause noise in the titration curve. In most cases, the stirring speed, which is set to **1** in this method, will not cause bubbles to stick to the electrode.
8. The titration curve shows on the display. The display auto scales as the titration proceeds. The TitraLab AT1000 Series does the analysis based on the automated selection of linear segments.
9. When the analysis for this test is complete, push **Next**. Then, select REPLICATE SAMPLE to repeat the analysis of the same sample or NEW SAMPLE for analysis of a different sample.

7. Results

7.1. Displayed Results

On the first screen:

- Result expressed as Total Chlorine in $\mu\text{g Cl}_2/\text{L}$
- Temperature of the analysis and duration of the titration

On the second screen:

The titration curve

- Abscissa of the equivalent point in mL (x-axis)
- Ordinate of the equivalent in μA (y-axis)
- Notation of the identified equivalence point
- Temperature of the analysis and duration of the titration

It is good laboratory practice to visually inspect the titration curve to verify the result.

If series of replicates of a single sample are analyzed, on the fourth screen:

- Average of the series in µg/L and statistics on the series (Standard Deviation (SD) in µg/L and Relative Standard Deviation (RSD) in %)

7.2. Results calculation

The instrument calculates the result R directly in mg/L of chlorine (Cl₂).

One mole of PAO exchanges two equivalents during the chemical reaction.

$$R = \frac{V_{(PAO)} * C_{(PAO)}}{V_{(smp)}} * \frac{MW}{2} * 1000$$

C_(PAO) = Concentration of titrant: Phenylarsine Oxide (PAO) in eq/L, currently 0.00564 eq/L

V_(PAO) = Volume of titrant: Phenylarsine Oxide (PAO) in mL added to reach the equivalent point

V_(smp) = Volume of the sample in mL: currently 200 mL

MW = Molar weight: Chlorine 70.906 g/mol

8. Examples of chlorine determination

The results described below are indicative and obtained for a given water type in optimized conditions using good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent. Additional single lab validation data using standards prepared from Monochloramine (NH₂Cl) is included in the comparison table at the end of this method.

Experimental conditions:

- **Burette volume:** 5 mL
- **Sample:** 200 mL of deionized water with 0.032mL of standard solution of Chlorine Equivalent Standard (Cl₂) at 62.85 mg/L and 0.1 g KI and 1 mL buffer pH4
- **Titrant:** PAO 0.000564 eq/L

Settings:

- **Settings:** Refer to [5.2 Titration settings \(default parameters\)](#)
- **Number of determinations:** 10 samples
- **Temperature of analysis:** Room temperature

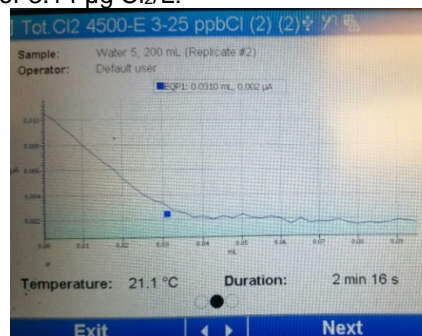
Titration curve: Current [µA] vs. volume of titrant [mL] for 10.46 µg Cl₂/L:



Results for 10 replicates of 10.6 µg/L Cl₂

Average concentration	10.2	µg/L Cl ₂
SD	0.365	µg/L Cl ₂
RSD	3.58	%
% Recovery	94.52	%

Titration curve: Current [µA] vs. volume of titrant [mL] for 3.14 µg Cl₂/L:



Results for 10 replicates of 3.14 µg/L Cl₂ :

Average concentration	3.11	µg/L Cl ₂
SD	0.233	µg/L Cl ₂
RSD	7.49	%
% Recovery	99.04	%

9. Bibliography

- *Standard Methods 4500-ClO₂ E*
- *AutoCAT 9000 Manual 50081 3rd edition*

10. Appendix

10.1. Changing the syringe volume on the AT1000.

The AT1000 instrument is delivered with the syringe volume set to 10 mL. The beverage applications require a 5-mL syringe volume. The syringe volume must be changed before the applications can be started. Complete the steps that follow to change the syringe volume:

1. From the Home screen select MAINTENANCE>SYRINGE MANAGEMENT>SYRINGE VOLUME CHANGE.
Note: If the AT1000 instrument has 2 syringes, select the syringe to edit.
2. Use the arrow keys to select 5 ML (HAMILTON) and push **SELECT**. The display shows APPLYING 5ML (HAMILTON) settings followed by SYRINGE VOLUME UPDATED.

3. Push **OK**.
4. Push **HOME** to go back to the Home screen.

10.2. Cleaning the Electrode

This procedure should be done before first use, after dry storage, and when the electrode response is slowed or equivalence points are missed.

1. Prepare a cleaning solution of 10 to 20-mL HNO₃/100 mL. Always add acid to water! Always wear personal protective equipment!
2. From the HOME screen, select MAINTENANCE > CLEAN PT-PT ELECTRODE
3. Pour enough solution in the beaker to cover the electrode.
4. Select OK
Note: If the stirrer does not start, push the up arrow. As an alternative, use a plastic beaker with a small electrode.
5. After 5 minutes, when prompted, rinse the electrode with DI water and fill the beaker with enough tap water to cover the electrode
6. Put the PtPt electrode in the water and select OK.
7. After five minutes, the cleaning is complete.

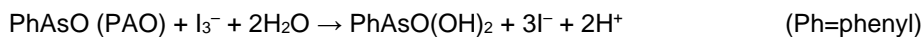
10.3. Hide or Show a Result

1. From the Home screen, select SETTINGS>APPLICATIONS.
2. Select Edit from the list of actions.
3. Highlight the application and push **Edit**.
4. Use the down arrow to go to METHOD>RESULTS.
5. Select YES or NO to show or hide results:
 - **Yes**—the result is not shown (hidden) at the end of the titration
 - **No**—the result is shown at the end of the titration

10.4. Titrant calibration

10.4.1. Calibration of the titrant with 0.0282N Iodine

The 0.000564N PAO titrant is calibrated against a standard solution of 0.0282 N Iodine



The iodine solution can also be calibrated. The procedure is described in the **Total chlorine back titration** or in the **Sulfite** working procedures.

If the standard iodine concentration given in the Certificate of Analysis (or obtained by calibration) is different from the default concentration of 0.0282 N, the real value has to be manually entered as the concentration of the standard.

10.4.1.1. Procedure

To prepare the titrant

1. Dilute 100 mL of 0.00564N PAO titrant to 1000 mL.
Note: As an alternative, purchase the 0.000564N titrant at HACH.

To calibrate the titrant,

1. Accurately pipette 0.100 mL of iodine standard solution 0.0282 N and dilute it to 200 mL with deionized water.
2. Calibrate the titrant using the titrant calibration option instead of the sample analysis.
3. Add KI powder and pH 4 buffer when prompted

To determine the frequency of calibration of the titrant, refer to the laboratory S.O.P.

10.4.1.2. Results

The results described below are indicative and obtained respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

The instrument calculates the titrant concentration directly in eq/L.

$$C_{(PAO)} = \frac{V_{(I_2)} * C_{(I_2)}}{V_{(PAO)}}$$

- $C_{(PAO)}$ (concentration of titrant): Phenylarsine Oxide (PAO) in eq/L,
- $C_{(I_2)}$ (concentration of standard): Iodine (I₂) in eq/L, currently 0.0282 eq/L
- $V_{(I_2)}$ (volume of standard): Iodine (I₂) in mL, currently 0.5 mL
- $V_{(PAO)}$ (volume of titrant): Phenylarsine Oxide (PAO) in mL added to reach the equivalent point

Experimental conditions:

- **Burette volume:** 5 mL
- **Sample:** 200 mL of deionized water with 0.1 mL of standard solution iodine 0.0282 eq/L
- **Addition:** 0.1 g KI and 1 mL buffer pH 4
- **Titration:** PAO 0.000564 eq/L
- **Acceptable Range:** 0.000564N +/- 10% (0.000508-0.000620N)

Results for 5 replicates of the titrant:

Average concentration	0.0005445	eq/L
SD	0.0000078	eq/L
RSD	1.45	%

Settings:

- **Settings:** Refer to [10.4.1.3 Titration calibration settings \(default parameters\)](#)
- **Number of determinations:** 5 samples
- **Temperature of analysis:** Room temperature

10.4.1.3. Titration calibration settings (default parameters)

	Setting	Unit
Titration name	PAO	
Nominal concentration	0.000564	eq/L
Calibration frequency	0	days
Stirring speed (%)	1	%
Predose volume	4.8	mL
Delay	20	seconds
Stop on last EQP	Yes	
Min increment size	0.0075	mL
Max increment size	0.025	mL
EQP min. ordinate	-0.1	µA
EQP max. ordinate	0.2	µA
Titration calibration result		
Min. titration concentration	0.00051	eq/L
Max. titration concentration	0.00062	eq/L
Standard		
Name	Iodine (I ₂) 0.0282N	
Amount	0.100	mL
Min amount	0.090	mL
Max amount	0.110	mL
Concentration	0.0282	eq/L

10.4.1.4. Modification of the parameters for the titration calibration

The titration calibration application has been optimized for an amount of standard higher than 0.49mL, a standard concentration higher than 0.0270 eq/L and a titration concentration between 0.00051 eq/L and 0.00062 eq/L.

Based on the concentration of the standard, the titration volume needed for the equivalence will be affected by an amount or a concentration of the standard different to the default values. The predose volume can be adjusted in relation to this amount, to ensure about 0.2 mL of titration before the equivalence point.

As an example, the table below shows the effect of the standard concentration on the equivalent volume and the optimum predose volume as a function of the equivalent volume expected.

Standard volume and concentration	Titrant concentration	Theoretical equivalent titrant volume	Number of addition points before equivalent point detection with default predose at 2.1 mL	Optimized predose volume
0.10 mL at 0.0270 eq/L	0.00058 eq/L	4.66 mL	11	4.2 mL
0.10 mL at 0.0270 eq/L	0.00055 eq/L	4.9 mL	18	4.4 mL
0.10 mL at 0.0290 eq/L	0.00058 eq/L	5.0 mL	20	4.6 mL
0.10 mL at 0.0290 eq/L	0.00055 eq/L	5.28 mL	27	4.8 mL

10.5. Preparation of a monochloramine standard, 10 mg Cl₂ /L as NH₂Cl (optional)

Principle: Monochloramine can be used as a more stable standard for total chlorine.

Items to collect:

- Beaker, low form Griffin, glass, 250 mL
- Magnetic stir bar, PTFE coated (LZE136)
- Pipettes, variable volume and pipette tips
- 100 mL volumetric flasks
- Nitrogen-Ammonia standard solution, 100 mg/L as NH₃-N
- Stock Chlorine 50-70 mg/L Cl₂ Voluette® Ampule
- Buffer Pillows, pH 8.3

Do the steps that follow to prepare a 10.0 mg Cl₂/L as NH₂Cl standard. The Cl₂ to N ratio to form theoretical amounts of monochloramine should be 5:1 ratio of Cl₂ to N by weight (MW of Cl₂ is 70.906 and MW of N is 14.007, actually 5.062:1). By Volume:

1. Add 50 mL of organic free DI water and the contents of one pH 8.3 Buffer Powder Pillow in a 100-mL volumetric flask. Swirl or sonicate to fully dissolve the powder.
2. Use a pipette to add 4.44 mL of nitrogen-ammonia standard solution (100 mg/L NH₃-N). Dilute to the mark with DI water. The solution is a 4.44 mg/L NH₃-N buffered standard.
3. Use a pipet to add 50.0 mL of the buffered ammonia standard to a 100-mL beaker.
4. Get a recent lot of Chlorine Solution Ampules, 50-70 mg/L Cl₂. Note the actual free chlorine concentration of this lot, listed on the box of ampules.
5. Calculate the amount of Chlorine Solution to add to the 4.44 mg/L NH₃-N standard using the following equation:

$$mL \text{ of chlorine standard required} = \frac{1000}{\text{free chlorine concentration (listed in box)}} \cdot \frac{10 \text{ mg/mL} \cdot 100 \text{ mL}}{\text{concentration of free chlorine used}} = mL \text{ of standard needed}$$

Note: The 1000 factor is derived from the 10.00 mg/L as Cl₂ times 100 mL.

Example:

$$x = \frac{1000}{63.5 \text{ mg/L Cl}_2} = 15.75 \text{ mL of chlorine standard required}$$

Where 63.5 is the chlorine concentration used for support data.

Open ampules, and slowly transfer the calculated amount of chlorine solution to the ammonia standard, while mixing at medium speed on a stir-plate.

6. Let the monochloramine solution to mix for 1 minute after all the chlorine solution is added.
7. **Quantitatively** transfer the monochloramine solution to a 100-mL volumetric flask. Dilute to the mark with organic free DI water and mix thoroughly. **The concentration of this solution is 10 mg Cl₂/L as NH₂Cl**
8. Dilute to the test level. For example, to make a 0.01 mg standard:

$$\frac{0.1 \text{ mg} \cdot 200 \text{ mL}}{10 \text{ mg/mL}} = 0.2 \text{ mL}$$

9. Use this stock standard within 1 hour of preparation. Since NH₂Cl calibration standards are only stable for approximately 1 hour, only make up 100 mLs of the 10 mg Cl₂/L as NH₂Cl. Use this stock standard within 1 hour of preparation. Since NH₂Cl calibration standards are only stable for approximately 1 hour, only make up 100 mLs of the 10 mg Cl₂/L as NH₂Cl.

10. To make a 10, 20 and 30 µg Cl₂/L check standard for example, add the following volume of the 10 mg Cl₂/L standard to 200 mL of chlorine demand free water in a chlorine demand free beaker:

Concentration (µg Cl ₂ /L as NH ₂ Cl)	mL 10 mg Cl ₂ /L as NH ₂ Cl standard added to 200 mL
30	0.6 ml
20	0.4 mL
10	0.2 mL

10.6. Additional Information on Amperometric Chlorine Titrations (with emphasis on very low level Total Chlorine)

Chlorine: Failure to obtain a representative sample is a common source of error in the testing of chlorine in water samples. The decay rate of monochloramine is approximately 10-fold slower than that of free chlorine in natural waters. However, the delay between sample collection and analysis must be minimized.

Container pre-treatment: Avoid plastic sample containers as these may have a high chlorine demand. Pre-treat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL of commercial bleach per liter of water) for at least one hour. Rinse treated containers well with DI water prior to use. Rinsing containers well between uses will reduce the need for additional pre-treatment.

Handling: Use dedicated sample containers for sampling. Avoid excess agitation, and exposure to sunlight. Allow several volumes of the container to overflow and cap the full container to eliminate headspace above the sample.

Interferences:

Other Disinfectants: The common chlorine methods will detect other disinfectants such as chlorine dioxide (ClO₂), ozone (O₃), bromine (Br₂), hydrogen peroxide (H₂O₂) and disinfection by-products such as chlorite and chlorate. These oxidants oxidize iodide to iodine, interfering in the total chlorine determination.

Manganese: Manganese exists in oxidation states of +2 through +7. The higher oxidation states (typically +3 to +7) will interfere with all of the common chlorine methods. Free chlorine reacts to oxidize soluble manganese compounds, for example:



If present, oxidized forms of manganese (+4 to +7) will titrate with PAO in the forward titration procedure for free chlorine. This will cause the free chlorine result to be artificially high.

Iodide (I⁻) can be oxidized by Mn (+4 to +7) to I₂, which also interferes with the titrimetric methods for total chlorine. Oxidized forms of manganese will react at pH 4 producing iodine which then titrates with PAO causing an interference. The interference of manganese in the back titration method appears to be a function of iodide concentration and the test pH.

Nitrite: In the forward titration for total chlorine, nitrites appear to cause positive and negative interferences, depending on the order of reagent addition. If iodide is added to the sample before the pH 4 buffer, the error increases as a function of the nitrite concentration. If the buffer is added before the iodide, a large negative error occurs, which is independent of the nitrite concentration.

Common Errors in Total Chlorine Determinations:

Most of the common total chlorine methods are based on the oxidation of iodide to triiodide (I₃⁻). There are several sources of errors related to the iodide/triiodide reaction. These include:

- oxidation of the iodide (I⁻) reagent
- volatilization of elemental iodine
- iodine or iodate (IO₃⁻) contamination in the iodide reagent
- consumption of triiodide by sample components

Potassium iodide reagent may be oxidized by the following reaction:



The reaction is accelerated by low pH, light, and trace metal ions. Iodide reagent solutions are susceptible to oxidation from exposure to light and oxygen.

Adsorption of the produced iodine on suspended particles can be a serious problem in the case of muddy or highly organic rich waters. A good example of this is the blue complex formed between iodine and starch with is the visual indicator for the starch iodine test. Iodine can also react with organic matter, forming carbon-iodine bonds. This is one reason for the traditional preference for the back titration methods for total chlorine in sewage treatment plant effluents.

11. Amperometric Chlorine, Total Chlorine Method Comparison Table

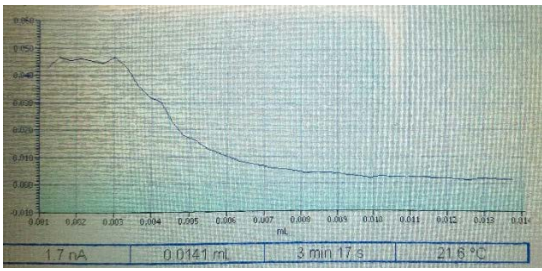



	Method Number SM 4500 Cl E	Hach Low Level Total Chlorine
Scope and Application	0.010-0.200 mg Total chlorine as Cl ₂	3-100 µg (0.003-0.100 mg) total chlorine as Cl ₂
Interferences	Nitrogen Trichloride and Chlorine dioxide Copper and silver can plate out/poison the electrode Too vigorous stirring will lead to losses of chlorine by volatilization	Nitrogen Trichloride and Chlorine dioxide will titrate partially as free chlorine Copper and silver can plate out/poison the electrode Too vigorous stirring will lead to losses of chlorine by volatilization
Equipment	End point detection apparatus consisting of a cell unit connected to a microammeter, with necessary electrical accessories. This cell unit includes a noble-metal electrode of sufficient surface area, a salt bridge to provide an electrical connection without diffusion of electrolyte and a reference electrode of silver-silver chloride in a saturated sodium chloride solution connected with the circuit by means of the salt bridge Glassware, pretreated to eliminate chlorine demand	Hach AT1000 Automated Titration system IntelliCAL™ MTC695 probe which has a double platinum electrode with a glass body and an integrated temperature sensor. The endpoint is determined automatically by the instrument. ⁴ Glassware, pretreated to eliminate chlorine demand 5 mL syringe
Sample Handling and Preservation	Chlorine in aqueous solutions is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly. Exposure to sunlight or other strong light or agitation will accelerate the loss of chlorine. Therefore, start determinations of chlorine immediately after sampling, avoiding excessive light and agitation. Do not store samples to be analyzed for chlorine.	Chlorine in aqueous solutions is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly. Exposure to sunlight or other strong light or agitation will accelerate the loss of chlorine. Therefore, start determinations of chlorine immediately after sampling, avoiding excessive light and agitation. Do not store samples to be analyzed for chlorine.
Reagents and Standards	Phenyl Arsine Titrant, 0.000564N	Phenyl Arsine Titrant, 0.000564N Potassium Iodide

⁴ This is an automated version of a manual titration method. This is allowed for CWA Methods since 2007. EPA has listed acceptable reasons for an analyst to modify a method. Among other justifications, these include analytical practices that lower detection limits and improve precision.

	Method Number SM 4500 Cl E	Hach Low Level Total Chlorine																																																																																																																																																																																				
	Potassium Iodide Acetate buffer, pH 4 Potassium bi-iodate solution (for calibration of the titrant)	Acetate buffer, pH 4 0.0282N I ₂ solution (for calibration of the titrant) ⁵																																																																																																																																																																																				
Method Performance	No precision or recovery data was provided in this method	<p>Single Lab Precision and recovery:</p> <table border="1"> <thead> <tr> <th>Conc. Cl₂ as NH₂Cl → Rep. ↓</th> <th>3 µg</th> <th>10µg</th> <th>20 µg</th> <th>50 µg</th> <th>100 µg</th> </tr> </thead> <tbody> <tr><td>1</td><td>2.85</td><td>9.53</td><td>21.33</td><td>49.44</td><td>97.07</td></tr> <tr><td>2</td><td>2.43</td><td>9.80</td><td>20.83</td><td>49.20</td><td>96.90</td></tr> <tr><td>3</td><td>2.85</td><td>10.01</td><td>21.16</td><td>49.23</td><td>96.77</td></tr> <tr><td>4</td><td>2.69</td><td>9.36</td><td>21.09</td><td>48.53</td><td>96.39</td></tr> <tr><td>5</td><td>2.75</td><td>9.71</td><td>20.54</td><td>47.50</td><td>96.20</td></tr> <tr><td>6</td><td>2.77</td><td>9.93</td><td>20.75</td><td>49.19</td><td>95.02</td></tr> <tr><td>7</td><td>2.84</td><td>10.10</td><td>20.99</td><td>49.56</td><td>94.93</td></tr> <tr><td>8</td><td>2.74</td><td>10.26</td><td>20.57</td><td>49.19</td><td>95.41</td></tr> <tr><td>9</td><td>2.64</td><td>10.44</td><td>20.57</td><td>48.96</td><td>95.23</td></tr> <tr><td>10</td><td>2.51</td><td>10.08</td><td>21.23</td><td>49.12</td><td>95.85</td></tr> <tr><td>AVG</td><td>2.707</td><td>9.92</td><td>20.91</td><td>48.99</td><td>95.98</td></tr> <tr><td>SD</td><td>0.144</td><td>0.329</td><td>0.294</td><td>0.592</td><td>0.803</td></tr> <tr><td>%RSD</td><td>5.32</td><td>3.32</td><td>1.41</td><td>1.21</td><td>0.84</td></tr> <tr><td>%Rec.</td><td>90.23</td><td>99.22</td><td>104.53</td><td>97.98</td><td>95.98</td></tr> </tbody> </table> <p>Single Lab MDL Study using data for 3 µg Cl₂ as NH₂Cl: 0.66 µg Cl₂ as NH₂Cl</p> <p>Single Lab Precision and Recovery for Total Chlorine as Cl₂</p> <table border="1"> <thead> <tr> <th>Conc. Cl₂ → Rep. ↓</th> <th>3.06</th> <th>9.99</th> <th>24.99</th> <th>50.01</th> <th>99.9</th> </tr> </thead> <tbody> <tr><td>1</td><td>3.17</td><td>9.75</td><td>24.14</td><td>48.23</td><td>102.5</td></tr> <tr><td>2</td><td>2.97</td><td>9.67</td><td>25.00</td><td>48.51</td><td>104.43</td></tr> <tr><td>3</td><td>3.04</td><td>9.85</td><td>23.14</td><td>48.63</td><td>101.74</td></tr> <tr><td>4</td><td>3.13</td><td>9.44</td><td>23.20</td><td>48.02</td><td>105.03</td></tr> <tr><td>5</td><td>2.87</td><td>10.31</td><td>24.21</td><td>48.01</td><td>104.37</td></tr> <tr><td>6</td><td>3.01</td><td>9.78</td><td>23.76</td><td>48.02</td><td>103.76</td></tr> <tr><td>7</td><td>3.09</td><td>9.92</td><td>23.92</td><td>48.60</td><td>104.13</td></tr> <tr><td>8</td><td>2.71</td><td>9.93</td><td>23.78</td><td>47.18</td><td>98.26</td></tr> <tr><td>9</td><td>2.84</td><td>10.06</td><td>23.19</td><td>45.04</td><td>100.79</td></tr> <tr><td>10</td><td>3.13</td><td>10.18</td><td>22.43</td><td>46.59</td><td>100.03</td></tr> <tr><td>AVG</td><td>2.996</td><td>9.89</td><td>23.68</td><td>47.68</td><td>102.50</td></tr> <tr><td>SD</td><td>0.15</td><td>0.25</td><td>0.72</td><td>1.13</td><td>2.25</td></tr> <tr><td>%RSD</td><td>5%</td><td>2.56%</td><td>3.04%</td><td>2.37%</td><td>2.20%</td></tr> <tr><td>% Recovery</td><td>98.04</td><td>99%</td><td>95.08</td><td>95.34</td><td>102.64</td></tr> </tbody> </table> <p>Single Lab MDL Study using data for 2.5 µg Cl₂ 1.3 µg Cl₂ as NH₂Cl</p> <p>Spike Recovery: Residual chlorine is not an analyte that can be feasibly spiked into samples</p>	Conc. Cl ₂ as NH ₂ Cl → Rep. ↓	3 µg	10µg	20 µg	50 µg	100 µg	1	2.85	9.53	21.33	49.44	97.07	2	2.43	9.80	20.83	49.20	96.90	3	2.85	10.01	21.16	49.23	96.77	4	2.69	9.36	21.09	48.53	96.39	5	2.75	9.71	20.54	47.50	96.20	6	2.77	9.93	20.75	49.19	95.02	7	2.84	10.10	20.99	49.56	94.93	8	2.74	10.26	20.57	49.19	95.41	9	2.64	10.44	20.57	48.96	95.23	10	2.51	10.08	21.23	49.12	95.85	AVG	2.707	9.92	20.91	48.99	95.98	SD	0.144	0.329	0.294	0.592	0.803	%RSD	5.32	3.32	1.41	1.21	0.84	%Rec.	90.23	99.22	104.53	97.98	95.98	Conc. Cl ₂ → Rep. ↓	3.06	9.99	24.99	50.01	99.9	1	3.17	9.75	24.14	48.23	102.5	2	2.97	9.67	25.00	48.51	104.43	3	3.04	9.85	23.14	48.63	101.74	4	3.13	9.44	23.20	48.02	105.03	5	2.87	10.31	24.21	48.01	104.37	6	3.01	9.78	23.76	48.02	103.76	7	3.09	9.92	23.92	48.60	104.13	8	2.71	9.93	23.78	47.18	98.26	9	2.84	10.06	23.19	45.04	100.79	10	3.13	10.18	22.43	46.59	100.03	AVG	2.996	9.89	23.68	47.68	102.50	SD	0.15	0.25	0.72	1.13	2.25	%RSD	5%	2.56%	3.04%	2.37%	2.20%	% Recovery	98.04	99%	95.08	95.34	102.64
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⁵ A certified iodine solution, 0.0282N I₂, is used to calibrate the titrant in this method. This allows the laboratory to use a known solution to quantify an unknown.

12. Troubleshooting

Symptom	Probable cause	Solution
No clear equivalence point, equivalence point not found.		Concentration too low? Do a cleaning procedure After cleaning, analyze a mid-range standard to verify performance.
Titration curve is noisy. No or incorrect equivalence point found. Electrode responds slowly; titration takes longer than usual.		Concentration too low? Check for bubble caught on electrode Verify electrode is properly oriented Clean electrode
Titration very long; EQP not detected or detected incorrectly.	Dirty or polarized electrode	Clean electrode Analyze a standard
There are bubbles on the electrode tip.		Picture on the left shows no bubbles. Picture on the right shows a bubble caught on the electrode. Adjust the stirring speed to 35-40% which will not normally cause bubbles to occur.
Flat signal Noisy signal Electrode is dirty.		No analyte (blank) No buffer added No KI added Clean the electrode.

12.1. Waste management

The laboratory has the responsibility to follow all of the federal, state, and local regulations governing waste management (particularly the hazardous waste identification rules) and land disposal restrictions. The laboratory must minimize and control all releases from fume hoods and bench operation to protect the air, water and land. Compliance with all sewage discharge permits and regulations is also required.

For more information on waste management refer to the *Waste Management Manual for Laboratory Personnel* guide, available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

13. Parts List

Description	Quantity per test	Unit	Item no.
Required reagents			
Phenylarsine oxide (PAO) titrant, 0.000564 N	varies	500 mL	199849
Acetate buffer solution, pH 4 bottle (automatic addition)	approximately 1 mL	1 L	1490953
Acetate buffer solution, pH 4, with dropper (manual addition)	1 mL	100 mL	1490932
Potassium iodide, ACS or better ⁶	0.1 g	100 g	16726H
Iodine standard solution, 0.0282 N	100 µL	1 L	2333353
Nitric acid, 1 :1	20 mL	500 mL	254049
Required equipment			
0.1-g scoop for addition of KI to the sample	1	each	51100
Tubing with anti-diffusion tip for AT Titrator	1	each	LZE112
Beaker, low form Griffin, glass, 250 mL	1	each	50046H
Beaker, low form Griffin, glass, 250 mL	1	12/pkg	50076H
Cylinder, graduated, 250 mL	1	each	50846
Magnetic stir bar, PTFE coated, 2 x 3/8 in.	1	each	5008500
Magnetic stir bar, PTFE coated, 20 x 6 mm	1	5/pkg	LZE136
Pipette, variable volume, 1.0–5.0 mL	varies	each	BBP065
Pipette tips, 1.0 - 5.0 mL	varies	75/pkg	BBP068
Flask, volumetric, Class A, certified, 100 mL	2	each	2636642
Optional reagents			
Chlorine Standard Solution, Voluette® ampules, 50–75 mg/L 16, 10 mL ampules	varies	16/pkg	1426810
Chlorine standard solution, Pour Rite® ampules, 25–30 mg/L 20, 2 mL ampules	varies	20/pkg	2630020
Buffer Powder Pillows, pH 8.30, 50 mL	1	25/pkg	89868
Nitrogen-Ammonia standard solution, 100 mg/L as NH ₃ -N	4.44 mL	500 mL	2406549
Dilution Water, ASTM Type III organic-free	varies	500 mL	2641549

⁶ Swiftest™ is not recommended for use with this very low level method. The KI granules must be ground with a mortar and pestle for this method.

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