

Based on 4500-Cl D in Standard Methods for the Examination of Water and Wastewater

Amperometric Forward Titration
0.003 – 5.00 mg/L as Cl₂

1. Introduction

This application note follows method number 4500-Cl D in “Standard Methods for the Examination of Water and Wastewater” (20th Edition).

The scope of this application note is to determine the total chlorine concentration (= Free Chlorine Conc. + Combined Chlorine Conc.) in water or wastewater samples.

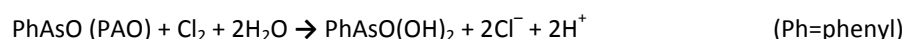
Total chlorine corresponds to the chlorine derived from all its possible forms in solution including free elemental chlorine (Cl₂), hypochlorous acid (HOCl), hypochlorite (OCl⁻) ion, and chloramines (NH₂Cl, NHCl₂, etc.) among other types.

Two applications for total chlorine determination are available with a different increment size to increase accuracy and reduce titration time:

- **High range:** for a sample concentration between 0.05 and 5 mg/L
- **Low range:** for a sample concentration between 0.003 and 0.08 mg/L

2. Principle

In this procedure, 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 with standard phenylarsine oxide solution. The chemical reaction is:



3. Electrode and reagents

Electrodes: PtPt-electrode with temperature sensor, Intellical MTC695

Description	Qty. required per test
Required reagents	
Phenylarsine Oxide (PAO) Titrant, 0.00564 N	varies
Acetate Buffer Solution, pH4, w/dropper	1 mL
Potassium Iodide, SwifTest™ refill	0.1 g
Iodine Standard Solution, 0.0282 N (for the calibration of the PAO)	varies
Required apparatus	
Beaker, Glass, 250 mL	1
Cylinder, Graduated, 250 mL	1
Magnetic Stir Bar, Teflon® coated	1
SwifTest™ dispenser	1
Optional reagents	
Chlorine Standard Solution, Voluette® Ampules	varies
Dilution Water, organic-free	varies
Potassium Iodide, Powder Pillows	varies

4. Ranges and settings

4.1. Default parameters

Using the application note settings described below with the following parameters:

- Sample volume = 200 mL
- Syringe volume = 5 mL
- Titrant concentration: Phenylarsine Oxide (PAO) Titrant, 0.00564 N
- Continuous imposed voltage 100mV (reversed at each analysis)

The default syringe volume for the AT1000 is set to 10 mL. These applications need a 5 mL syringe. When loading an application, if the message **syringe to replace** is displayed, change the syringe volume in the **Syringe management** option of the **Maintenance** menu.

4.2. Working ranges

This procedure for determining chlorine in water has a range of concentration from 0.003 to 5 mg/L as Cl₂. It is possible to measure samples with a higher concentration by using a smaller amount of sample and diluting it to 200 mL.

To measure in samples with a concentration between two applications, select the lower range for better accuracy.

With 0.00564N PAO as titrant, 1 mL of titrant corresponds to 1 mg/L of chlorine.

4.3. Titration settings (default parameters)

4.3.1. Application

	Low range setting (0.003 to 0.08 mg/L)	High range setting (0.05 to 5 mg/L)
Application name	Tot.Cl2 0.003 to 0.08 mg/L	Tot.Cl2 0.05 to 5 mg/L
Advisable syringe	5mL (Hamilton)	5mL (Hamilton)

4.3.2. Sample

	Setting (All ranges)	Unit
Name	Water ? ¹	
Amount	200	[mL]

4.3.3. Titrant settings used for the calculation

	Setting (All ranges)	Unit
Name	PAO	
Real concentration	0.00564	[eq/L]

4.3.4. Manual addition 1 settings:

	Setting (All ranges)	Unit
Active	Yes	
Message	Add 0.1g KI and press OK	
Stirring speed	0	[%]

4.3.5. Automatic addition 2 settings

	Setting (All ranges)	Unit
Active	Yes	
Reagent name	Buffer pH 4	
Pump ID	Pump 2	
Time	0.3	[s]

¹ “?” in the name, indicates that the sample name will be automatically incremented with a number for each analysis

Stirring speed	0	[%]
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4.3.6. Titration and detection settings

	Low range setting (0.003 to 0.08 mg/L)	High range setting (0.05 to 5 mg/L)	Unit
Stirring speed	45	45	[%]
Measured parameter	μA	μA	
Predose ordinate	0.05	0.8	[μA]
Predose speed	0.05	5	[mL/min]
Delay	40	10	[s]
Max. vol. stop point	0.07	7	[mL]
Stop on last EQP	Yes	Yes	
Increment size	0.0003	0.01	[mL]
Stop on flat signal	Yes	Yes	
EQP min. ordinate	-0.03	-0.1	[μA]
EQP max. ordinate	0.03	0.1	[μA]

4.3.7. Results settings

	Low range setting (0.003 to 0.08 mg/L)	High range setting (0.05 to 5 mg/L)
Result 1 name	Total Chlorine	Total Chlorine
R1 min	0.003 mg/L	0.05 mg/L
R1 max	0.08 mg/L	5 mg/L
R1 QC min	0.003mg/L	0.05 mg/L
R1 QC max	0.08 mg/L	5 mg/L
R1 Molar weight	70.906	70.906

4.4. Modification of the parameters

It is possible to add the pH 4 buffer manually. In this case, activate the buffer manual addition and deactivate the automatic addition in the application edit window

Standard Methods recommends a default volume of 200 mL, and the parameters have been optimized with this volume for the whole range of concentrations (0.003 to 5 mg/L as Cl_2).

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

Predose in ordinate is used to decrease the titration duration in both applications. The parameters (**predose ordinate** and **predose speed**) have been set empirically and are system dependent. A titration starting with an ordinate under the target can happen, but this has no impact on the result provided that the number of points is sufficient to allow detection.

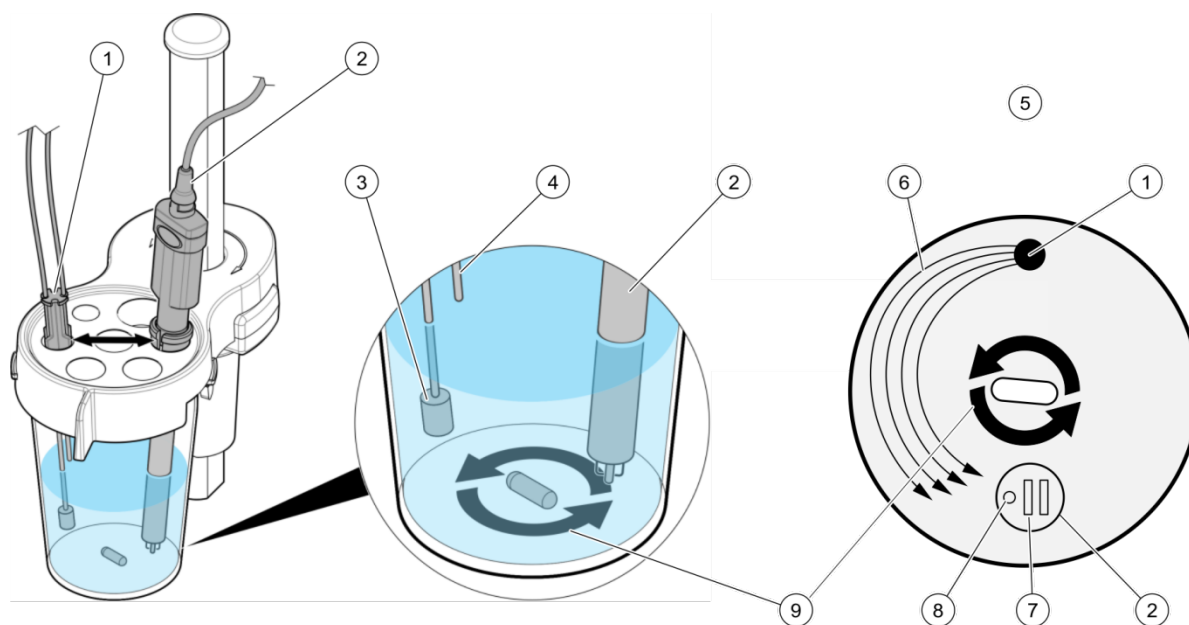
Below is a table giving some indications, if required:

Observation	Resolution
The titration is still too long (too many points during predose)	Increase the predose ordinate and/or increase the titrant addition speed
The titration is still too long (too many points before inflection)	Decrease the predose ordinate and/or increase the titrant addition speed
The initial point of the titration curve is too low (not enough points before inflection) and the EQP is not detected	Decrease the titrant addition speed and/or increase the predose ordinate

5. Titration procedure

5.1. Position of the electrode and injection tips

Place the electrode in the opposite hole of the tubes in the sensor holder. If necessary, turn the electrode to place the platinum wires perpendicular to the sample flow and the temperature sensor before the platinum wires. Place the tube from the pump above the sample surface and make sure that the tube with the anti-diffusion tip is fully into the sample. Refer to the figure that follows.



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

5.2. Sample tips and technique

- To avoid loss of chlorine, be careful not to agitate the sample when measuring or pouring.
- Avoid plastic sample containers with 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 use to reduce the need for pretreatment
- When sampling tap water, let the faucet run for at least 4-5 minutes before collecting the sample.
- Prepare a test sample by diluting Chlorine Standard Solution (Cat. No. 14268-10) with deionized (DI) water
- Always use organic-free reagent water for sample dilution

5.3. Reagent tips and technique

- Download the "Certificate of Analysis" (CAO) to obtain the exact concentration of any unopened bottle of Hach titrant standard solution
- Hach buffer reagents for chlorine titrations are highly recommended for this analysis
- Never substitute buffers designed for calibrating pH meters. They contain dyes that interfere with amperometric titration
- Never use buffers contaminated with mold or bacteria
- Rinse the electrode and tip with deionized water before every titration

5.4. Instrument tips and technique

- A distinction is drawn between running a new test and a new sample (**Exit** or **Next**). Pushing **Next** is a replicate run of the current or previous sample analysis. The titrator automatically tracks the results of a series of tests and automatically calculates the mean and standard deviation for all the results
- Press the Stop key anytime to interrupt instrument operation
- Flush the burette each day before the first sample test or calibration is performed.
- Flush the burette when changing titrants

5.5. Cleaning and storage of electrode MTC 695

- Clean the electrode daily or when necessary (e.g., after a titration when the equivalent point is not detected or before first use).
- Go to the maintenance menu and start the cleaning wizard. Use 10 to 20% Nitric Acid to clean the electrode. Fully rinse with deionized water before analysis, especially for sample analysis at very low concentrations.
- For short term storage or between titrations keep the electrode in tap water with approximately 1% Nitric Acid. Prepare the storage solution with 50 mL of tap water and add 5 mL of 10% Nitric Acid or 2.5 mL of 20% Nitric Acid.
- For long term storage (more than 3 days), rinse the electrode and carefully dry with a soft tissue. Store dry in the electrode protector.

5.6. Safety

- Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information

5.7. Analysis steps

1. In the Main menu, highlight the desired method based on the expected concentration of the sample and press **Start**. Note that these methods use the 0.00564 N PAO titrant.
2. Verify the Operator Name and the Sample Name. Modify them if necessary.
3. Measure 200 mL of sample solution with a 250-mL graduated cylinder and transfer to a 250-mL glass beaker with the specified magnetic stir bar.
4. Dip the electrodes and the titrant tip into the sample.
5. Adjust the tip from the peristaltic pump to above the sample surface and press **Start**.
6. Add 0.1 g of potassium iodide (KI). Press **OK** to confirm. Note that KI is added in excess, but the precise amount used is not crucial for the accuracy or precision of the analysis.
7. Addition of the buffer. Note that the acetate buffer is added to adjust the sample pH, though the amount used is not crucial for the accuracy or precision of the analysis.
 - **Manual buffer addition:** Add 1 mL of pH 4 acetate buffer. Press **OK** to confirm
 - **Automatic buffer addition:** The buffer addition starts automatically
8. The delay begins for a time between 20 and 40 seconds, allowing the signal to stabilize before data collection. During this time the reagents are stirred. After the signal has stabilized, data acquisition begins and the titration curve is plotted.
9. During the delay, if needed, adjust the stirrer speed to ensure an efficient stirring and prevent the formation of bubbles.
10. The titration curve will appear on the display. The TitraLab AT1000 Series performs the analysis based on the automatic selection of linear segments.
11. When the analysis for this test is complete, press **Next** for a replicate measurement or **Exit** to start a new measurement on a different sample.

6. Results

6.1. Displayed results

On the first screen:

- Result expressed as Chlorine in mg/L
- Temperature of the analysis and duration of the titration

On the second and third screens:

- Abscissa of the equivalent point in mL
- Ordinate of the equivalent in μA
- Temperature of the analysis and duration of the titration

If series of samples (with replicate), on the fourth screen:

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

6.2. Results calculation

The instrument calculates the result R directly in mg/L of chlorine (Cl_2).

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

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

- $C_{(\text{PAO})}$ = Concentration of titrant: Phenylarsine Oxide (PAO) in eq/L, currently 0.00564 eq/L
- $V_{(\text{PAO})}$ = Volume of titrant: Phenylarsine Oxide (PAO) in mL added to reach the equivalent point
- $V_{(\text{smp})}$ = Volume of the sample in mL: currently 200 mL
- MW = Molar weight: Chlorine 70.906 g/mol

7. Examples of chlorine determination

The results described below are indicative and obtained for a given water type in optimized conditions respecting Good Laboratory Practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

Experimental conditions:

- **Burette volume:** 5 mL
- **Sample:** 200 mL of deionized water with 0.070mL of standard solution of Chlorine Equivalent Standard (Cl_2) at 28.28 mg/L and 0.1 g KI and 1 mL buffer pH4
- **Titrant:** PAO 0.00564 eq/L

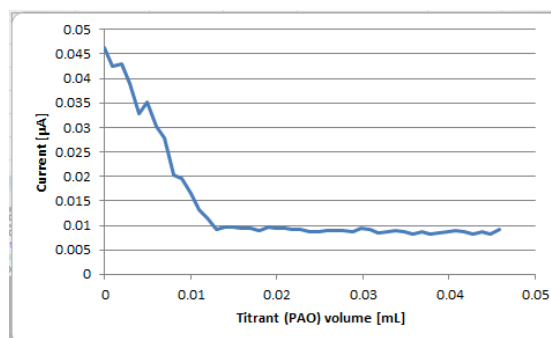
Settings:

- **Settings:** Refer to default values in section [4.3 Titration settings \(default parameters\)](#)
- **Number of determinations:** 10 samples
- **Temperature of analysis:** Room temperature

Results:

Average concentration	0.012	mg/L Cl_2
SD	0.0005	mg/L Cl_2
RSD	4.1	%

Titration curve: Current [μA] vs. volume of titrant [mL]:



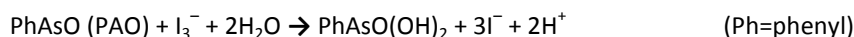
8. Bibliography

- *Standard Methods for the Examination of Water and Wastewater*, Standard 4500-Cl D

9. Appendix: Titrant Calibration

9.1. Principle

The PAO titrant can be calibrated against a standard solution of Iodine 0.0282 N.



The iodine solution can also be calibrated. The procedure is described in the **Total chlorine back titration** or 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: 0.0282 N, the real value has to be manually entered as the concentration of the standard.

9.2. Procedure

Accurately pipette 0.5 mL of iodine standard solution 0.0282 N and dilute it to 200 mL with deionized water.

Calibrate the titrant using the titrant calibration option instead of the sample analysis. Add KI powder and pH4 when required.

9.3. 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.

$$C_{(\text{PAO})} = \frac{V_{(\text{I2})} * C_{(\text{I2})}}{V_{(\text{PAO})}}$$

- $C_{(\text{PAO})}$ = Concentration of titrant: Phenylarsine Oxide (PAO) in eq/L,
- $C_{(\text{I2})}$ = Concentration of standard: Iodine (I2) in eq/L, currently 0.0282 eq/L
- $V_{(\text{I2})}$ = Volume of standard: Iodine (I2) in mL, currently 0.5 mL
- $V_{(\text{PAO})}$ = Volume of the 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 0.5 mL of standard solution of iodine 0.0282 eq/L.
- **Addition of:** 0.1 g KI and 1 mL buffer pH 4
- **Titrant:** PAO 0.0564 eq/L

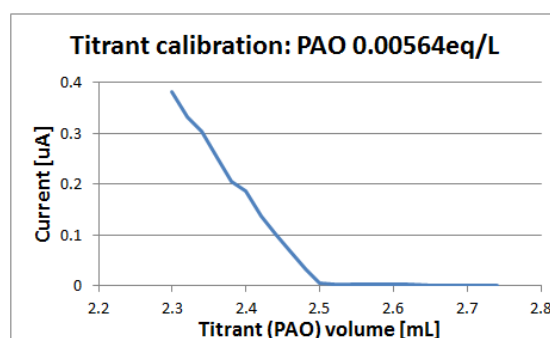
Settings:

- **Settings:** Refer to default values in section [9.4 Titrant calibration settings \(default parameters\)](#)
- **Number of determinations:** 5 samples
- **Temperature of analysis:** Room temperature.

Results:

Average concentration	0.00561	eq/L
SD	0.00002	eq/L
RSD	0.4	%

Titration curve: μA vs. volume of titrant:



9.4. Titrant calibration settings (default parameters)

	Setting	Unit
Titrant name	PAO	
Nominal concentration	0.00564	[eq/L]
Calibration frequency	0	[Days]
Stirring speed (%)	45	[%]
Predose volume	2.1	[mL]
Delay	20	[s]
Stop on last EQP	Yes	
Min increment size	0.02	[mL]
Max increment size	0.05	[mL]
Stop on flat signal	Yes	
EQP min. ordinate	-0.1	[μ A]
EQP max. ordinate	0.2	[μ A]
Titrant calibration result		
Min. titrant concentration	0.0055	[eq/L]
Max. titrant concentration	0.0058	[eq/L]
Standard		
Name	Iodine	
Amount	0.500	[mL]
Min amount	0.490	[mL]
Max amount	0.510	[mL]
Concentration	0.0282	[eq/L]

9.5. Modification of the parameters

The titrant 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 titrant concentration between 0.0055 eq/L and 0.0058 eq/L.

Due to the greater concentration of the standard, the titrant 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 has to be adjusted as a function of this amount, to ensure about 0.2 mL of titrant before the equivalence.

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 @2.1mL	Optimized predose volume
0.50 mL @ 0.0270 eq/L	0.0058 eq/L	2.33 mL	11	2.1 mL
0.50 mL @ 0.0270 eq/L	0.0055 eq/L	2.45 mL	18	2.2 mL
0.50 mL @ 0.0290 eq/L	0.0058 eq/L	2.50 mL	20	2.3 mL
0.50 mL @ 0.0290 eq/L	0.0055 eq/L	2.64 mL	27	2.4 mL