Free Chlorine

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

Amperometric Forward Titration
0.100–5.000 mg/L as Cl_2

This application note covers the following application:

Method	Range	Titrant	Buffer, KI and Acid	Sample volume
Free Chlorine	0.100 to 1.000 mg/L as Cl_2 0.500 to 5.000 mg/L as Cl_2	0.00564N PAO	1 mL pH 7 buffer	200 mL

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 free chlorine in a water sample.

Free chlorine corresponds to that portion of chlorine existing either as elemental chlorine (Cl_2), hypochlorous acid (HOCl), hypochlorite (OCl^-) ion.

Titration curve end points are not as sharp as those for Total Chlorine. Therefore, the determination of Free Chlorine concentrations below 0.1 mg/L becomes problematic. As a result, the lower limit for the TitraLab AT1000 Series has been arbitrarily set to 0.1 mg/L for experimental reasons. Higher ranges can be determined through sample dilution.

2. Principle

In this procedure, the sample pH is adjusted to pH 7 by the addition of a phosphate buffer. The sample solution is then titrated amperometrically with standard phenylarsine oxide solution.

$$PhAsO\ (PAO) + Cl_2 + 2H_2O \rightarrow PhAsO(OH)_2 + 2Cl^- + 2H^+$$

(Ph=phenyl)

3. Electrode and reagents

Pt-electrode with temperature sensor: **Intellical MTC695**

Description	Qty. required per test
Required reagents	
Phenylarsine Oxide (PAO) Titrant, 0.00564 N	varies
Phosphate Buffer Solution, pH7, w/dropper	1 mL
Potassium Iodide, SwifTest™ refill (for the calibration of the PAO)	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 (for the calibration of the PAO)	1
Optional reagents	
Chlorine Standard Solution, Voluette® Ampules	varies
Dilution Water, organic-free	varies

4. Ranges and settings

4.1. Default parameters

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

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- Sample volume = 200 mL
- Syringe volume = 5 mL
- Titrant concentration: Phenylarsine Oxide (PAO) Titrant, 0.00564 N

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 0.1 to 5 mg/L as Cl_2, and is covered by 2 applications. The **Free Chlorine 0.1 to 1 mg/L** application covers the low range of concentration and the **Free Chlorine 0.5 to 5 mg/L** application is used for the higher range concentration. It is possible to measure samples with a concentration higher than 5 mg/L by using a smaller amount of sample and diluting it to 200 mL.

4.3. Titration settings (default parameters)

4.3.1. Sample

	Default parameter	Unit
Name	Water ?[1]	
Amount	200	mL

4.3.2. Titrant settings used for the calculation

	Default parameter	Unit
Name	PAO	
Titer	0.00564	eq/L

4.3.3. Automatic buffer addition settings

	Default parameter	Unit
Active	Yes	
Reagent name	Buffer pH 7	
Pump	Pump 1	
Time	1	seconds
Stirring speed	0	%

4.3.4. Titration parameters settings

	0.1 to 1 mg/L	0.5 to 5 mg/L	Unit
Stirring speed	1	1	%
Measured parameter	µA	µA	
Predose	0.005	0.01	mL
Max. vol. stop point	2	7	mL
Ordinate stop point	-0.1	-0.1	µA
Stop on last EQP	Yes	Yes	
Delay	30	30	seconds
Stability criterion	500	500	µA/min
Stabilization delay	3 to 8	3 to 10	seconds
Min. increment size	0.01	0.05	mL
Max. increment size	0.05	0.1	mL
Curve filter	4	4	point
Curvature filter	8	8	points
Detection threshold	2.6	2.6	
Linearity threshold	2.6	2.6	
EQP min. ordinate	-0.1	-0.1	µA
EQP max. ordinate	0.05	0.1	µA

[1] "?" in the name, indicates that the sample name will be automatically incremented with a number for each analysis

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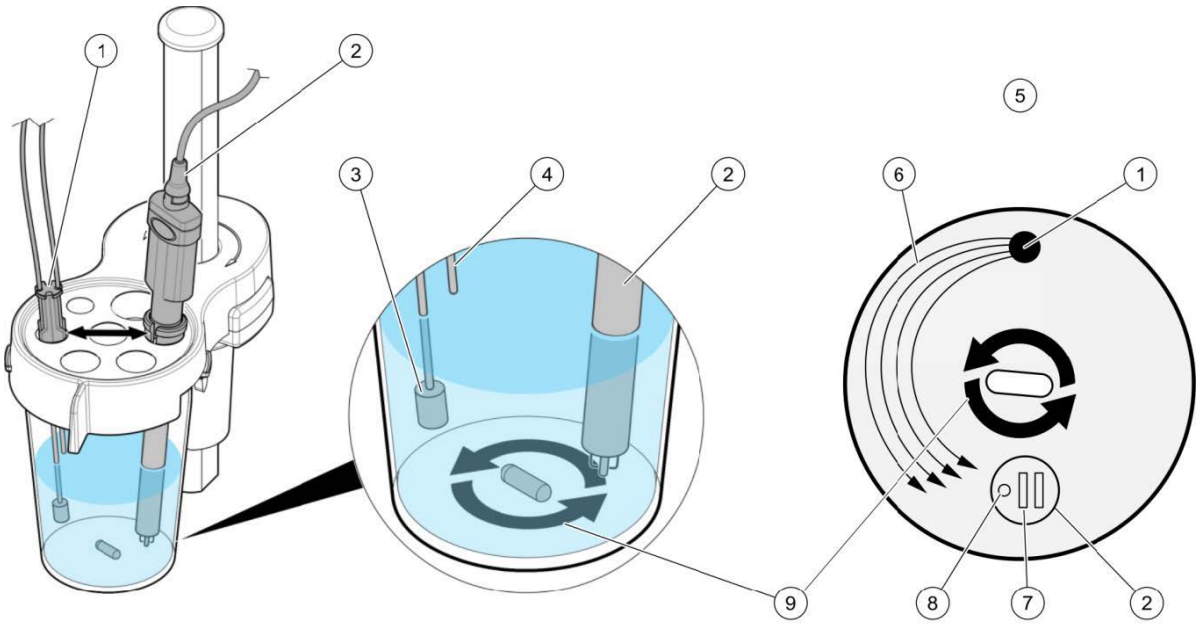
5. Titration procedure

5.1. 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. 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

5.2. Sample tips and technique

- To avoid loss of chlorine, be careful not to agitate the sample when pouring.
- Avoid plastic sample containers which may 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 use to reduce the need for 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 (Cat. No. 14268-10) with deionized (DI) water.
- Always use organic-free 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.

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- Rinse the electrode, temperature probe and injection 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.
- The TitraLab AT1000 Series can accommodate any sample size. *Standard Methods* recommends a default volume of 200 mL. The volume can be adjusted to expand the test range.
- The TitraLab AT1000 Series calculates the chlorine concentration based on the sample volume. Make sure that the sample volume is correct.
- Press the **Stop** key any time to interrupt instrument operation. **You will not be able to restart the test**.
- Purge the burette each day before the first sample test or calibration is performed.
- Flush the burette when changing titrants or putting ona new bottle of titrant.

5.5. Cleaning and storage

- Clean the MTC695 electrode prior to first use, as well as after dry storage.
- Cleaning the MTC695 electrode is also suggested after a titration when the equivalent point is not detected. Refer to the cleaning instructions delivered with the electrode.
- Store the MTC695 electrode overnight in tap water with approximately 1% Nitric Acid. To prepare this solution take 50 mL of tap water and pour in 5 mL of 10% Nitric Acid or 2.5 mL of 20% Nitric Acid (Always add acid to water. Always wear proper PPE). This storage procedure is not needed if doing Total Chlorine titration as well. Dry storage is recommended.
- For long term storage periods (e.g., more than 3 days), rinse the electrode and dry gently with a soft tissue. Store dry in the electrode protector.

5.6. Analysis steps

1. In the Main menu, highlight Free Cl2 and press **Start**.
2. Verify the **Operator Name** and the **Sample Name**. Modify them if necessary.
3. Measure 200 mL of sample solution into a clean 250 mL beaker and insert the specified magnetic stir bar into the sample beaker. Make sure to use only the stir bar provided in order to minimize loss of chlorine.
4. Place the sample onto the TitraLab AT1000 Series stirrer platform.
5. Add 1.0 mL of pH 7.0 Phosphate Buffer Solution. Note that the Phosphate buffer is added only to adjust the sample pH. The precise amount added is not crucial for the accuracy or precision of the analysis. If the buffer addition is done using the pump, keep the dispensing tip for the buffer **above the level of the sample**. **The anti-diffusion tip for dispensing the titrant should be submerged in the sample.**
6. Lower the electrode head onto the beaker rim and press **Start**. Be sure the stir bar does not hit the electrode tip. Follow the instructions on the display.
7. The settling timer begins, allowing the electrode to stabilize before data collection. During this time the reagents are stirred. After the electrode has stabilized, data acquisition begins and the titration curve is plotted.
8. The titration curve will appear on the display. The TitraLab AT1000 Series performs the analysis based on the automatic selection of linear segments.
9. When the analysis for this test is complete, press **Next** for a replicate measurement or a new measurement on a different sample, or press **Exit** to go back to the main menu.
10. If the expected concentration of the sample is known and a reduction in titration time is required, modify the method by increasing the pre-dose at the beginning of the titration. However always leave at least 0.1 to 0.2 mL before the end point when using the **Free Chlorine 0.1 to 1 mg/L** application, and 0.5 to 1 mL for the **Free Chlorine 0.5 to 5 mg/L** application. It has been observed that keeping a small predose volume improved the signal and the stability of the electrode at the beginning of titration (see the default predose value in **4.3.4 Titration parameters settings on page 2**).

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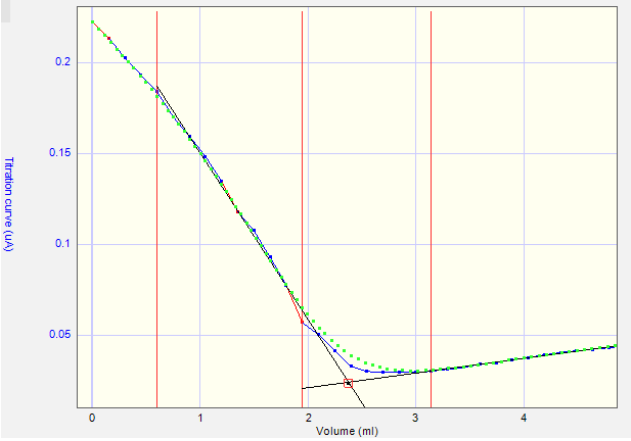
6. Results

6.1. Experimental results

	5 mg/L	0.94 mg/L	0.45 mg/L	0.11 mg/L
Mean result (mg/L)	4.994	0.89	0.41	0.103
Standard deviation (mg/L)	0.048	0.01	0.01	0.0096
Relative standard deviation (%)	0.96	0.6	2.45	9.4
% Recovery	99.88	94.68	90.78	93.18

6.2. Typical titration curve



7. Recommendations

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

If the overnight storage procedure recommended in section **5.4 Cleaning and storage** has been done, the MTC695 should behave correctly for the titration. If there is any loss of performance, perform the cleaning procedure provided by the instrument.

8. Bibliography

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

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9. Appendix: Titrant Calibration

9.1. Principle

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

$$PhAsO\ (PAO) + I_3^- + 2H_2O \rightarrow PhAsO(OH)_2 + 3I^- + 2H^+ \qquad (Ph=phenyl)$$

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

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.

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

- $C_{(PAO)}$ = Concentration of titrant: Phenylarsine Oxide (PAO) in eq/L,
- $C_{(I2)}$ = Concentration of standard: Iodine (I2) in eq/L, currently 0.0282 eq/L
- $V_{(I2)}$ = Volume of standard: Iodine (I2) in mL, currently 0.5 mL
- $V_{(PAO)}$ = 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

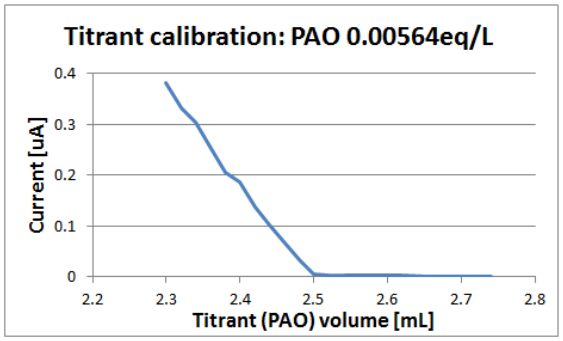
Settings:

- **Settings:** See values by default described in section 9.4
- **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:



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9.4. Titrant calibration settings (default parameters)

	Default parameter	Unit
Titrant name	PAO	
Nominal concentration	0.00564	eq/L
Calibration frequency	0	days
Stirring speed (%)	1	
Predose	2.1	mL
Delay	20	seconds
Stop on last EQP	Yes	
Min increment size	0.02	mL
Max increment size	0.05	mL
EQP1 min ordinate	-0.1	µA
EQP1 max ordinate	0.2	µA
Titrant calibration result		
Resolution	5 decimals	
Min titrant concentration	0.0055	eq/L
Max titrant concentration	0.0058	eq/L
Standard		
Name	Iodine	
Amount	0.500	mL
Min amount	0.49	mL
Max amount	0.51	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.

Because of 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 from the default values.

The predose volume can 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 indicates 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 @2.1 mL	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

HACH COMPANY World Headquarters
P.O. Box 389, Loveland, CO 80539-0389 U.S.A.
Tel. (970) 669-3050
(800) 227-4224 (U.S.A. only)
Fax (970) 669-2932
orders@hach.com
www.hach.com

HACH LANGE GMBH
Willstätterstraße 11
D-40549 Düsseldorf, Germany
Tel. +49 (0) 2 11 52 88-320
Fax +49 (0) 2 11 52 88-210
info-de@hach.com
www.de.hach.com

HACH LANGE Sàrl
6, route de Compois
1222 Vésenaz
SWITZERLAND
Tel. +41 22 594 6400
Fax +41 22 594 6499

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