Determination of Chlorine Dioxide, Chlorite and Chlorine

DOC316.52.93097

Based on Standard Methods 4500-ClO_2 E
for drinking water and wastewater

This application note covers the following application:

Method	Range	Titrant	Buffer, KI and Acid	Sample volume
Chlorine Dioxide (H)	0.100 to 5.00 mg ClO_2 and ClO_2^-/L Cl_2 more than 0.100 mg/L	0.00564N PAO	pH 7 1g KI x 2 2 mL 2.5 N HCl x 2	2 x 200 mL
Chlorine Dioxide (L)	0.100 to 5.00 mg ClO_2 and ClO_2^-/L Cl_2 less than 0.100 mg/L			

1. Important information

- The AT1000 is factory programmed to use the 10-mL syringe. This method uses a 5-mL syringe. Before analysis, make sure to change the syringe volume on the instrument. Refer to 10.1 Change the syringe volume on the AT1000.
- Treat glassware for chlorine demand before analysis. Soak glassware in a dilute bleach solution for a minimum of 1 hour. Rinse thoroughly with deionized water. Use the treated glassware for this method only.
- Chlorine dioxide and chlorine dioxide by-products are volatile and are easily lost from aqueous solutions. Collect the sample in an amber glass bottle with minimum headspace to minimize air contact.
- Minimize agitation when measuring sample volumes. Remove sample portions with a volumetric pipette. Always put the tip of the pipette at the bottom of the sample container.
- Always use organic free water for sample dilution.
- Rinse the electrode and anti-diffusion tip with DI water before every titration.
- If the expected equivalent volume for Titration 3 is very low (< 0.1 mL), use the **L** method. If not, use the **H** method. The ranges for Chlorine Dioxide, Chlorite and Chlorine are the same for the two methods.
- Purge the syringe each day before the analysis.
- Clean the electrode periodically. Refer to 10.2 Cleaning the electrode. Clean and correctly maintained electrodes are necessary to get sharp amperometric endpoints. Clean the electrode when 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 electrode orientation is very important. Noise that occurs when the electrode is not correctly oriented can interfere with the accurate detection of the equivalence point. Refer to 4.1 Position of the electrode and injection tips for information on electrode and delivery tip positioning for this method.
- Too fast stirring can pull air into the sample and bubbles can get caught on the electrode tip. Air bubbles on the electrode tip have a negative effect on the analysis results. Adjust the stirring speed during a titration with the up and down arrows on the instrument. Alternatively, change the stirring speed in the method edit window.
- The method is programmed to measure **200 mL** of sample. **To use less than 200 mL of sample, change the sample volume at the method edit window**. Refer to 10.5.2 Procedure for more information.

2. Introduction

Chlorine dioxide is used as a disinfecting agent for water treatment. The chlorine dioxide content is monitored to indicate the treatment quality. This application is based on the Standard Methods 4500-ClO_2 E, which is an amperometric method that distinguishes three different compounds: chlorine dioxide (ClO_2), free chlorine (Cl_2) and chlorite (ClO_2^-). **The table that follows shows the measuring ranges for each analyte in the two methods, the H and the L:**

ClO_2	0.10 mg/L to 5.00 mg/L
ClO_2^-	0.10 mg/L to 5.00 mg/L
Cl_2	0.10 mg/L to 2.00 mg/L

The difference in the **L** and **H** methods is in the range for titration 3. The ranges for Free Chlorine **L** and **H** are as follows:

ClO2 and ClO_2^- (H)	0.100 to 5.00 mg ClO_2 /L	Cl_2 **more than** 0.100 mg (titration 3)
ClO2 and ClO_2^- (L)	0.100 to 5.00 mg ClO_2 /L	Cl_2 **less than** 0.100mg (titration 3)

3. Principle

Four amperometric titrations are done on two titration samples. The results of each titration are stored and at the end of the sequence, the concentrations of each compound are displayed.

In the first sample, an excess of potassium iodide (KI) and pH 7 buffer are added to titrate Cl_2 and a part of ClO_2. Then, concentrated hydrochloric acid is added to the titrated sample and the reaction releases the remaining ClO_2 and ClO_2^-.

Then, the second portion of the sample is adjusted to pH 7 and degassed with a nitrogen flow. Excess KI is added and the third titration is launched to neutralize the Cl_2 not volatized by the degassing. Finally, concentrated hydrochloric acid is added to the beaker to give the ClO_2^- determined during the last titration.

***Note**: To do the analysis faster, degas the second portion of the sample during titrations 1 and 2 on portion one. Select SKIP to bypass the timer when the sample is for titration.*

The abbreviation GWB in this document refers to the Gas Washing Bottle used for sample preparation before titration 3.

The table that follows gives details of the sequence:

Titration 1	Cl_2 + 1/5 of ClO_2
Titration 2	4/5 of ClO_2 + ClO_2^-
Titration 3	Cl_2 not volatized by the nitrogen gas purge
Titration 4	ClO_2^-

4. Electrode and reagents

Electrode: Pt-Pt electrode with temperature sensor, IntelliCAL MTC695

Titrant: Phenyl Arsine Oxide (PAO) 0.00564 eq/L solution

Reagents: pH 7 phosphate buffer
Potassium iodide (KI) powder
Hydrochloric acid (HCl) 2.5 N solution

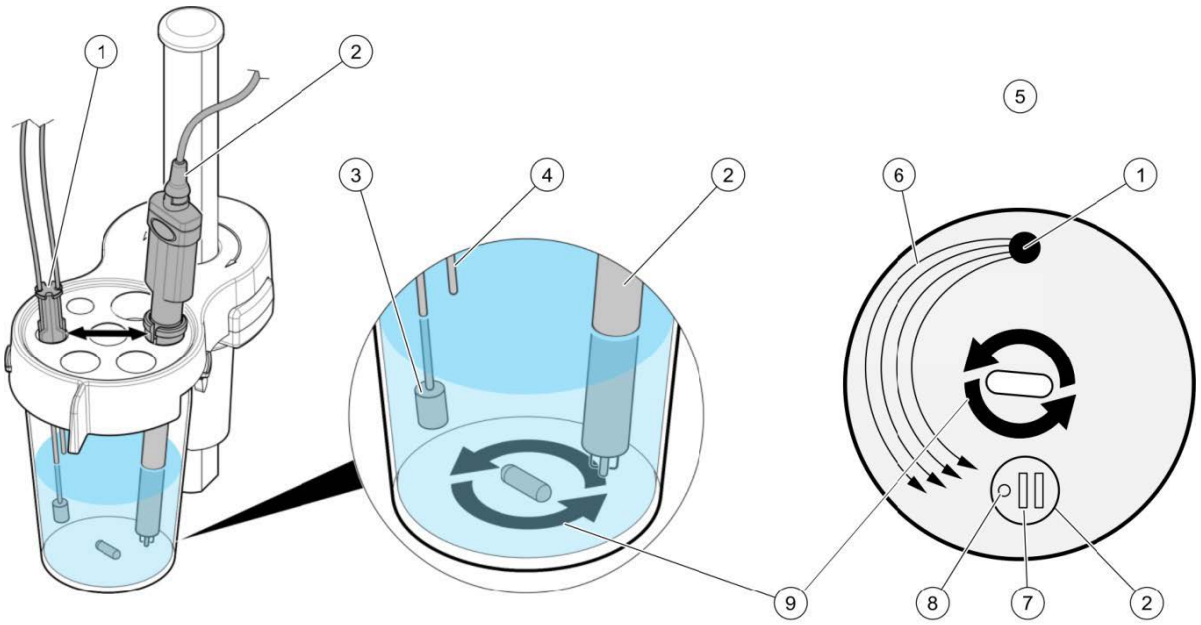
Deionized water

4.1. 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. Settings

5.1. Chlorine Dioxide/Chlorite determination

Two methods, Chlorine Dioxide L and Chlorine Dioxide H, are available. The difference between **L** and **H** are the settings for **titration 3**.

If the expected equivalent volume for titration 3 is very low (< 0.1 mL), use the **L** applications. If not, use the **H** applications. The ranges for Chlorine Dioxide, Chlorite, and Chlorine are the same for the two methods.

The settings have been defined with:

- Sample volume: 200 mL
- Titrant concentration: 0.00564 eq/L Phenyl Arsine Oxide
- Continuous imposed voltage: 100 mV (reversed at each analysis)
- Syringe volume: **5 mL**
  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. Refer to 10 Appendix for more information.
- If a blank is analyzed, analyze the blank as a sample. The BLANK option is not compatible with this method.

Name	**Default parameter**		**Unit**
Application name	**Chlorine Dioxide L**	**Chlorine Dioxide H**	
Syringe			
Advisable	5 mL (Hamilton)		
Sample			
Name	Water ?[1]		
Amount	200		mL
QC			
Name	QC Sample		
Probe			
Recommended electrode	MTC695		
Titrant PAO 0.00564 N			
Real concentration	0.00564		eq/L
Automatic addition 1 (titration 1)			
Active[2]	Yes		

[1] **?** in the name, shows that the sample name will be automatically incremented with a number for each analysis
[2] Only one of these two methods must be active

Name	Default parameter		Unit
Application name	**Chlorine Dioxide L**	**Chlorine Dioxide H**	
Reagent	Buffer pH 7, 1.0 mL		
Pump ID	**Pump 1**		
Time	1		seconds
Stirring speed	0		%
Manual addition 1 (titration 1)			
Active[2]	No		
Message	Add 1.0 mL of buffer pH 7 and press OK		
Stirring speed	0		%
Manual addition 2 (titration 1)			
Active	Yes		
Message	Add 1.0 g of KI and press OK		
Stirring speed	0		%
Reagents mixing (titration 1)			
Active	Yes		
Time	5		seconds
Stirring speed	1		%
Message	Reagents mixing. Please wait		
Dip electrode (titration 1)			
Active	Yes		
Message	Dip electrode in sample and press OK		
Stirring speed	1		%
Titration 1			
Active	Yes		
Stirring speed	1		%
Predose ordinate	0.4		µA
Predose speed	2.5		mL/min
Delay	20		seconds
Max. vol. stop point	5		mL
Stop on last EQP	Yes		
Increment size	0.010		mL
EQP min. ordinate	-0.1		µA
EQP max. ordinate	0.2		µA
Result 1 name	Intermediate 1		mL
R1 hide	Yes		
R1 min	0		mL
R1 max	5		mL
R1 QC min	0		mL
R1 QC max	5		mL
Result 2 name	A		
R2 hide	Yes		
R2 min	0		mL/mL
R2 max	0.025		mL/mL
R2 QC min	0		mL/mL
R2 QC max	0.025		mL/mL
R2 equation	FX*(R1/SA) = G1		
R2 user value	1		
Manual addition 3 (titration 2)			
Active	Yes		
Message	Add 2.0 mL of HCl 2.5 N then place the solution in the dark and press OK		
Stirring speed	1		%
Reaction (titration 2)			
Active	Yes		
Time	5		minutes
Stirring speed	0		%
Message	Dark reaction in progress. Please wait		
Dip electrode (titration 2)			
Active	Yes		
Message	Place the sample on the instrument then dip the electrode in the sample and press OK		
Stirring speed	0		%
Titration 2			
Active	Yes		
Stirring speed	1		%

Name	Default parameter		Unit
Application name	**Chlorine Dioxide L**	**Chlorine Dioxide H**	
Predose ordinate	0.4		µA
Predose speed	2.5		mL/minutes
Delay	20		seconds
Max. vol. stop point	25		mL
Stop on last EQP	Yes		
Increment size	0.010		mL
EQP min. ordinate	-0.1		µA
EQP max. ordinate	0.2		µA
Result 1 name	Intermediate 2		mL
R1 hide	Yes		
R1 min	0		mL
R1 max	25		mL
R1 QC min	0		mL
R1 QC max	25		mL
Result 2 name	B		
R2 hide	Yes		
R2 min	0		mL/mL
R2 max	0.125		mL/mL
R2 QC min	0		mL/mL
R2 QC max	0.125		mL/mL
R2 equation	FX*(R1/SA) = G2		
R2 user value	1		
Sample preparation 1 (titration 3)			
Active	Yes		
Message	Renew Sample–Sample amount: 200 mL in GWB and press OK		
Stirring speed	0		%
Sample preparation 2 (titration 3)			
Active	Yes		
Message	Add 1.0 mL of buffer pH 7 then start purge with N_2 and press OK		
Stirring speed	0		%
Purge (titration 3)			
Active	Yes		
Time	15		minutes
Stirring speed	0		%
Message	Purge in progress. Please wait		
Sample preparation 3 (titration 3)			
Active	Yes		
Message	Pour the purged sample into a titration beaker – Add a stir bar and press OK		
Stirring speed	0		%
Manual addition 4 (titration 3)			
Active	Yes		
Message	Place the sample on the instrument - Add 1.0 g of KI and press OK		
Stirring speed	0		%
Reagents mixing (titration 3)			
Active	Yes		
Time	5		seconds
Stirring speed	1		%
Message	Reagents mixing. Please wait		
Dip electrode (titration 3)			
Active	Yes		
Message	Dip electrode in sample and press OK		
Stirring speed	1		%
Titration 3	**Chlorine Dioxide L**	**Chlorine Dioxide H**	
Active	Yes		
Stirring speed	1		%
Predose ordinate	0.1	0.4	µA
Predose speed	0.3	2.5	mL/minutes
Delay	20		seconds
Max. vol. stop point	5		mL
Stop on last EQP	Yes		
Increment size	0.001	0.010	mL

Name	Default parameter		Unit
Application name	**Chlorine Dioxide L**	**Chlorine Dioxide H**	
EQP min. ordinate	-0.1	-0.03	µA
EQP max. ordinate	0.2	0.03	µA
Result 1 name	Intermediate 3		mL
R1 hide	Yes		
R1 min	0		mL
R1 max	5		mL
R1 QC min	0		mL
R1 QC max	5		mL
Result 2 name	C		
R2 hide	Yes		
R2 min	0		mL/mL
R2 max	0.025		mL/mL
R2 QC min	0		mL/mL
R2 QC max	0.025		mL/mL
R2 equation	FX*(R1/SA) = G3		
R2 user value	1		
Manual addition 5 (titration 4)			
Active	Yes		
Message	Add 2.0 mL of HCl 2.5 N then place the solution in the dark and press OK		
Stirring speed	1		%
Reaction (titration 4)			
Active	Yes		
Message	5		minutes
Stirring speed	0		%
Message	Dark reaction in progress. Please wait		
Dip electrode (titration 4)			
Active	Yes		
Message	Place the sample on the instrument then dip the electrode in sample and press OK		
Stirring speed	0		%
Titration 4			
Active	Yes		
Stirring speed	1		%
Predose ordinate	0.4		µA
Predose speed	2.5		mL/minutes
Delay	20		seconds
Max. vol. stop point	15		mL
Stop on last EQP	Yes		
Increment size	0.010		mL
EQP min. ordinate	-0.1		µA
EQP max. ordinate	0.2		µA
Result 1 name	Intermediate 4		mL
R1 hide	Yes		
R1 min	0		mL
R1 max	15		mL
R1 QC min	0		mL
R1 QC max	15		mL
Result 2 name	D		
R2 hide	Yes		
R2 min	0		mL/mL
R2 max	0.075		mL/mL
R2 QC min	0		mL/mL
R2 QC max	0.075		mL/mL
R2 equation	FX*(R1/SA) = G4		
R2 user value	1		
Result 3 name	**Chlorite**		
R3 hide	No		
R3 min	0		mg ClO_2^-/L
R3 max	6		mg ClO_2^-/L
R3 QC min	0		mg ClO_2^-/L
R3 QC max	6		mg ClO_2^-/L
R3 equation	V1/V1*FX*(G4+(F3/SA)-G3)*TC*16863		
R3 user value	1		

Name	Default parameter		Unit
Application name	**Chlorine Dioxide L**	**Chlorine Dioxide H**	
Result 4 name	**Chlorine Dioxide**		
R4 hide	No		
R4 min	0		mg ClO_2/L
R4 max	6		mg ClO_2/L
R4 QC min	0		mg ClO_2/L
R4 QC max	6		mg ClO_2/L
R4 equation	FX*(5/4)*((G2+(F1/SA)-G1)-(G4+(F3/SA)-G3))*TC*13490		
R4 user value	1		
Result 5 name	**Chlorine**		
R5 hide	No		
R5 min	0		mg Cl_2/L
R5 max	3		mg Cl_2/L
R5 QC min	0		mg Cl_2/L
R5 QC max	3		mg Cl_2/L
R5 equation	FX*(G1-(1/4)*((G2+(F1/SA)-G1)-(G4+(F3/SA)-G3)))*TC*35453		
R5 user value	1		

5.2. Recommendations for modification of the settings

Some parameters can be adjusted, but this is mainly done to decrease the analysis time. Any adjustments can cause a loss of precision of the results.

5.2.1. Sample preparation messages

Messages for sample preparation can be removed from the sequence by setting **No** in the **Active** box in the message section. In this way, the instrument will not give information about sample preparation during the analysis sequence. The methods that follow can be deactivated:

- Automatic addition 1 (titration 1)
- Manual addition 1 (titration 1)
- Manual addition 2 (titration 1)
- Manual addition 3 (titration 2)
- Sample preparation 1 (titration 3) / Sample preparation 1 (titration 1)
- Sample preparation 2 (titration 3) / Sample preparation 2 (titration 1)
- Purge (titration 3) / Purge (titration 1)
- Sample preparation 3 (titration 3) / Sample preparation 3 (titration 1)
- Manual addition 4 (titration 3) / Manual addition 1 (titration 1)
- Manual addition 5 (titration 4) /Manual addition 2 (titration 2)
- Reaction (titration 4) / Reaction (titration 2)

A second portion of sample can be prepared during titrations 1 and 2 to save time. Select SKIP to bypass the timer when the nitrogen purged sample portion is ready to be titrated.

If the treatment process is stable and the samples always have the same range of concentrations, it is possible to change the pre-dose.

Note: Changing the increment sizes is not recommended because they have been optimized for the best equivalent point detection.

5.2.2. Pre-doses in ordinate

Predoses in ordinate are used to decrease the titration duration. They have been fixed for all titrations for chlorine dioxide and chlorite applications. Their 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 does not have an impact on the result. The table that follows show some indications.

Observation	Resolution
The titration is still too long (too many points before inflection).	Decrease the predose ordinate in the ordinate section or increase the titrant addition speed (no more than 2.5 mL/min).
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 in the ordinate section or increase the predose ordinate.

6. Procedure

6.1. Before starting

NOTICE: Treat glassware for chlorine demand before analysis.

- Soak glassware in a dilute bleach solution for at least 1 hour. Rinse thoroughly with deionized water. Use the treated glassware for this method only.
- Chlorine dioxide and its by-products are volatile and can be easily lost from aqueous solution. Minimize air contact by attaching a flexible hose to a tap and placing the end at the bottom of a 1-L amber glass bottle. Turn on the tap and allow several volumes to overflow, then slowly remove the sample line and cap the container with minimum headspace.
- Minimize agitation when measuring sample volumes. Remove sample portions with a volumetric pipette. Always put the tip at the bottom of the sample container. If using 200 mL sample increments, use a 100-mL pipette to withdraw two portions of sample.
- Always use organic free water for sample dilution.
- Rinse the electrode and anti-diffusion tip with deionized water before every titration.
- If a blank is analyzed, analyze the blank as a sample. The BLANK option is not compatible with this method.

6.2. Sample analysis

Titration 1:

1. Measure 200 mL of sample solution with a pipette.
2. Pour the sample into a 250-mL glass beaker.
3. Put the sample in the instrument. Start the application.
4. Add 1.0 mL of phosphate buffer pH 7 (if the instrument does not add with the embedded pump).
5. Add 1.0 g of potassium iodide (KI). The instrument mixes the reagents.
6. Dip the electrode and addition tip into the sample.
   Titration 1 starts.

Titration 2:

7. When titration 1 is complete, raise the electrode holder.
8. Add 2.0 mL of 2.5 N hydrochloric acid (HCl). Stir for a few seconds.
9. Carefully remove the sample from the stirrer and put it in a dark environment.
10. Wait 5 minutes for the reaction.
11. At the end of the 5 minutes, carefully put the sample back in the instrument.
12. Dip the electrode and addition tip into the sample.
    Titration 2 starts.

Titration 3:

13. Use a pipette to add a second 200-mL portion of sample into a Gas Washing Bottle (GWB).
14. Add 1.0 mL of phosphate buffer pH 7. Swirl to mix.
15. Put the purge tube and dispersion tip into the GWB. Connect the GWB inlet to a tank of purified nitrogen.
16. Use a needle valve to adjust the flow of nitrogen to provide a steady stream of bubbles through the sample.
17. Purge the nitrogen gas through the sample for 15 minutes.
18. Pour the purged sample to a 250-mL glass beaker. Add a magnetic stir bar to the beaker. Put the sample in the instrument.
19. Add 1.0 g of KI. The instrument mixes the reagents.
20. Dip the electrode and addition tip into the sample.
    Titration 3 starts.

Titration 4:

21. When titration 3 is complete, raise the electrode holder.
22. Add 2.0 mL of 2.5 N hydrochloric acid (HCl). Stir for a few seconds.
23. Carefully remove the sample from the stirrer and pu it in a dark environment.
24. Wait 5 min for the reaction.
25. At the end of the 5 minutes, carefully put the sample back in the instrument.
26. Dip the electrode and addition tip into the sample.
    Titration 4 starts.
    When titration 4 is complete, the instrument shows the results.

Note: *To make the method faster, purge the sample portion for titrations 3 and 4 during titrations 1 and 2. Select SKIP to bypass the timer when the sample is prepared. If STOP is selected at any point, the entire process is fully stopped. It is not possible to resume a stopped titration..*

7. Results

7.1. Displayed Results

At the end of the analysis sequence, the following results are available:

- Cl_2 in mg/L as Cl_2
- ClO_2 in mg/L as ClO_2
- ClO_2^- in mg/L as ClO_2^-

7.2. Results calculation

Cl_2 calculation: $Cl_2 = \left[A - \frac{1}{4}(B-D)\right] \times N \times 35453$

ClO_2 calculation: $ClO_2 = \frac{5}{4}(B-D) \times N \times 13490$

ClO_2^- calculation: $ClO_2^- = D \times N \times 16863$

Where:

N = Concentration of the titrant (eq/L)

A = Result of titration 1 (mL titrant at equivalent point/mL of sample)

B = Result of titration 2 (mL titrant at equivalent point/mL of sample)

D = Result of titration 4 (mL titrant at equivalent point/mL of sample)

Important: *The instrument calculation can cause an incorrect result if the concentration of one or more of the three measured compounds is less than 0.05 mg/L.*

8. Examples of ClO_2 determination

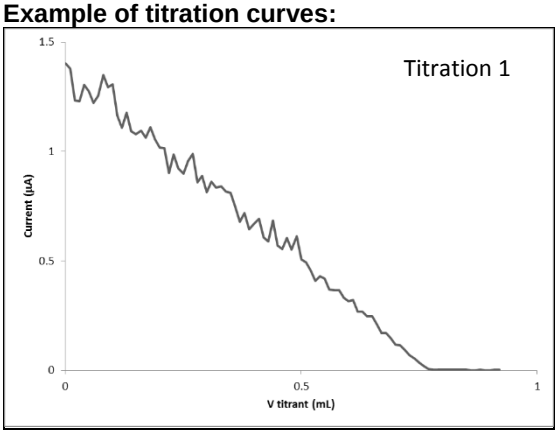
The results described below are indicative and obtained for a given sample in optimized conditions respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

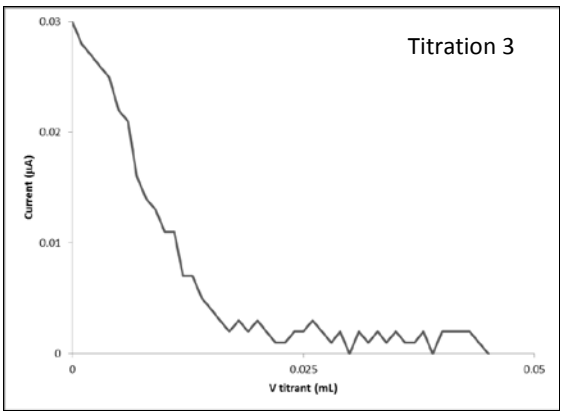
8.1. Case 1: A mixture of a high level of chlorine dioxide and a low level of chlorite

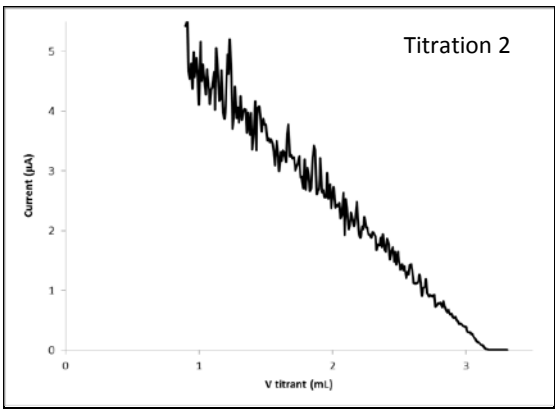
Results for four determinations of a synthetic mixture:

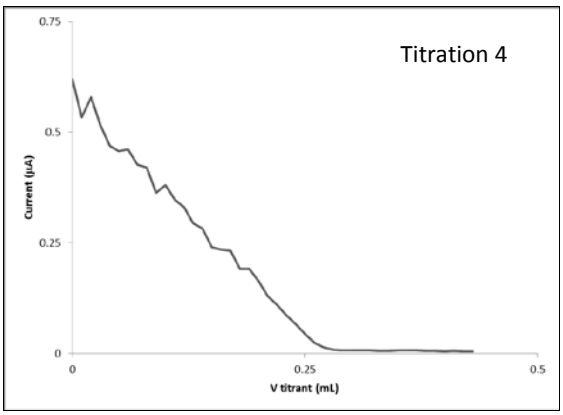
Sample:	2 x 200 mL of solution	**Standard deviation:**	ClO_2: 0.025 mg/L ClO_2^-: 0.008 mg/L Cl_2: -
Application:	Chlorine Dioxide L	**Relative standard deviation:**	ClO_2: 1.76 % ClO_2^-: 5.21% Cl_2: -
Temperature of analysis:	Room temperature		
Mean values:	ClO_2: 1.415 mg/L ClO_2^-: 0.154 mg/L Cl_2: -		

Example of titration curves:







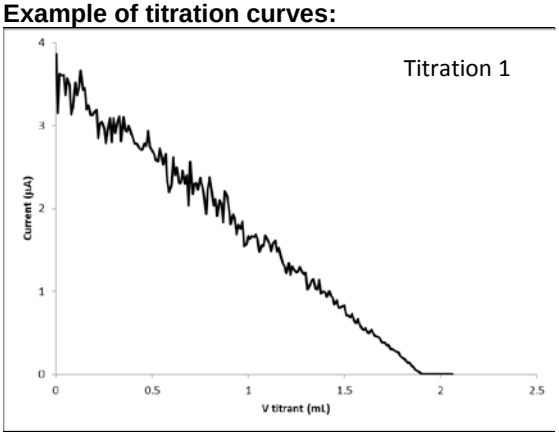


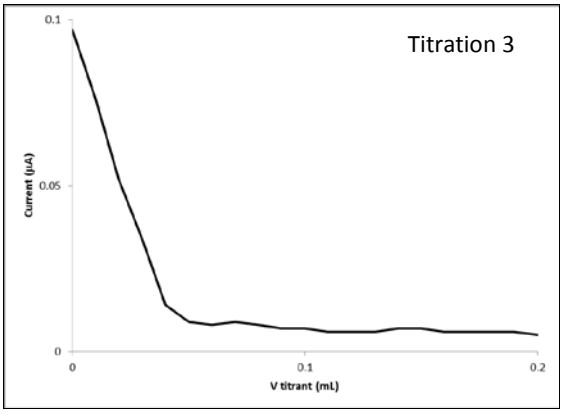
8.2. Case 2: A mixture of a high level of chlorine and a low level of chlorite

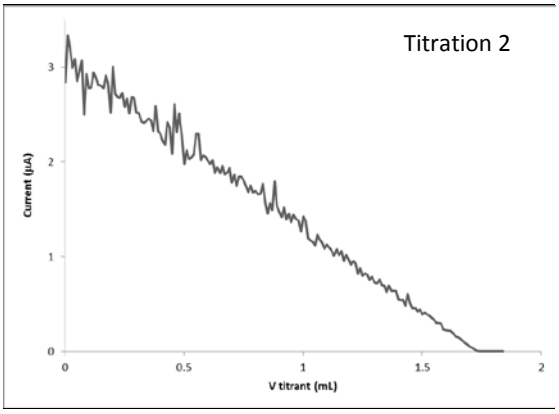
Results for three determinations of a synthetic mixture:

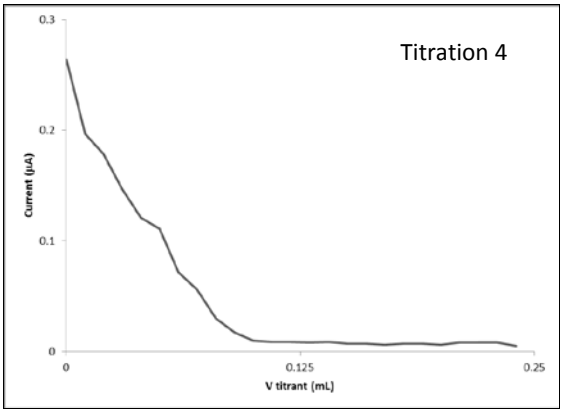
Sample:	2 x 200 mL of solution	**Standard deviation:**	ClO_2: - ClO_2^-: 0.003 mg/L Cl_2: 0.026 mg/L
Application:	Chlorine Dioxide H	**Relative standard deviation:**	ClO_2: - ClO_2^-: 3.48 % Cl_2: 1.40 %
Temperature of analysis:	Room temperature		
Mean values:	ClO_2: - ClO_2^-: 0.089 mg/L Cl_2: 1.874 mg/L		

Example of titration curves:









9. Bibliography

- *Standard Methods 4500-ClO_2 E*
- *AutoCAT 9000 Manual 50081 3rd edition*

10. Appendix

10.1. Change the syringe volume on the AT1000

The AT1000 instrument is delivered with the syringe volume set to 10 mL. The Amperometric 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), then 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 20-mL HNO_3/100 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.*
5. After five 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. Set the titer directly from the C.O.A.

Before the Titer is entered directly from the certificate of analysis (C.O.A.) refer to the customer laboratory standard operation procedure (S.O.P.) to determine if this is acceptable.

1. From the HOME screen, select SETTINGS > APPLICATIONS > EDIT.
2. Select the application for the titer.
3. Scroll down in the application to TITRANT.
4. Select REAL CONCENTRATION.
5. Use the arrow keys or a keyboard to enter the titer value from the C.O.A.
6. Push **OK**.
7. Push **HOME** to go back to the Home screen.
   ***Note**: This step is needed only once for each syringe, even if there is more than one method associated with it.*

10.5. Calibration of the titrant with 0.0282N Iodine

10.5.1. Principle

Alternatively, 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 Sulfite working procedures, which are included on the Amperometric titration method key.

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 must be manually entered as the concentration of the standard.

10.5.2. Procedure

Accurately pipette 0.5 mL of iodine standard solution 0.0282 N. Dilute the solution to 200 mL with deionized water.

Calibrate the titrant using the titrant calibration option instead of the sample analysis. Add KI powder and pH 4 acetate buffer when required. On a titrator with 2 pumps, pH 4 buffer is pumped using **Pump 2.**

10.5.3. 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 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

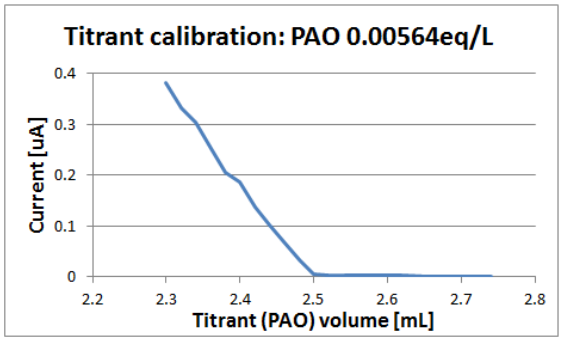
Settings:

- **Settings:** Refer to 10.5.4 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:



10.5.4. Titrant calibration settings (default parameters)

	Setting	Unit
Titrant name	PAO	
Nominal concentration	0.00564	[eq/L]
Calibration frequency	0	[Days]
Stirring speed (%)	1	[%]
Predose volume	2.1	[mL]
Delay	20	[s]

	Setting	Unit
Stop on last EQP	Yes	
Min increment size	0.02	[mL]
Max increment size	0.05	[mL]
EQP min. ordinate	-0.1	[µA]
EQP max. ordinate	0.2	[µA]
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]

10.6. Modification of the parameters

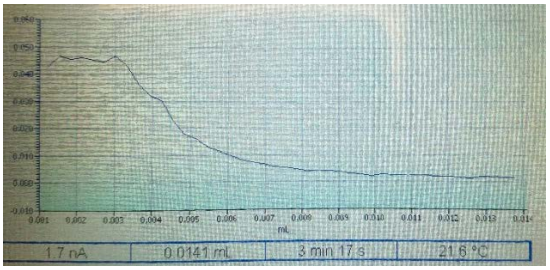
The titrant calibration application has been optimized for an amount of standard higher than 0.49mL, a standard concentration higher than 0.0270 eq/L and a titrant concentration between 0.0055 eq/L and 0.0058 eq/L.

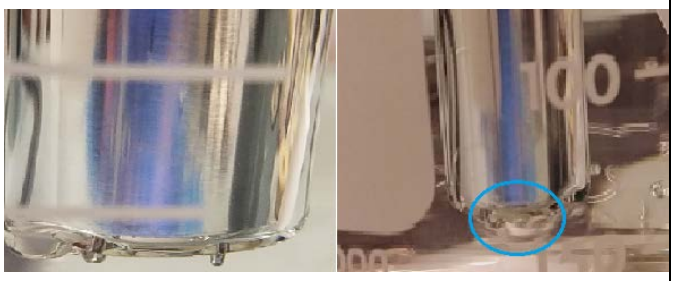
Due to the greater concentration of the standard, the titrant volume needed for the equivalence will be affected by an amount or a concentration of the standard different to the default values. The pre-dose volume must be adjusted in relation to this amount, in order to ensure about 0.2 mL of titrant before the equivalence.

As an example, the table below shows the effect of the standard concentration on the equivalent volume and the optimum pre-dose 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 2.1mL	Optimized predose volume
0.50 mL at 0.0270 eq/L	0.0058 eq/L	2.33 mL	11	2.1 mL
0.50 mL at 0.0270 eq/L	0.0055 eq/L	2.45 mL	18	2.2 mL
0.50 mL at 0.0290 eq/L	0.0058 eq/L	2.50 mL	20	2.3 mL
0.50 mL at 0.0290 eq/L	0.0055 eq/L	2.64 mL	27	2.4 mL

11. Troubleshooting

Symptom	Picture	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.

Symptom	Picture	Solution
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
Predose exceeds the set ordinate. Electrode responds slowly; titration takes longer than usual.	No equivalence point is detected Flat titration curve	Analyte level too low to be detected; Electrode is dirty, slowing response. Clean electrode
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. If analyzing a standard, make sure that the volume of water used is sufficient.
Flat signal Noisy signal Electrode is dirty.		No analyte (blank) No buffer added No KI added Clean the electrode.

11.1. 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.

12. Parts List

Description	Quantity per test	Unit	Part number
Required reagents			
Phenylarsine Oxide (PAO) Titrant, 0.00564 N	varies	1 L	199953
Buffer Solution, pH 7 (automatic addition)	approximately 2 mL	1 L	2155353
Acetate Buffer Solution, pH 7, with dropper (manual addition)	approximately 2 mL	100 mL	2155332
Potassium Iodide, ACS or better*	2.0 g	100 g	16726H
Nitric acid, 1 :1 (for cleaning electrode), 500 mL	20 mL	500 mL	254049
Required apparatus			
1-g scoop for addition of KI to the sample	1	each	2657201
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
Gas washing bottle, 1200 mL	1	each	2662200
Optional reagents			
Dilution Water, ASTM Type III organic-free	varies	500 mL	2641549
Optional Reagents for calibration of the PAO titrant			
0.0282N I_2 (1L)	0.5 mL	1 L	2333353
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
Swiftest, with refill vial	1	each	2834100
Refill for swiftest dispenser	0.1 g	each	2105660

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