Determination of Chlorine Dioxide Generator Yield

DOC316.52.93146

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 Generator	100 to 4,500 mg ClO_2 100 to 4,500 mg ClO_2^- 100 to 4,500 mg Cl_2	0.1000N Thiosulfate	2 x 1 mL pH 7 2 x 1g KI 2 x 2 mL 2.5 N HCl	2 mL

1. Important information

- All glassware must be treated for chlorine demand before any analysis. Soak all glassware in a strong chlorine dioxide solution (300 to 500 mg/L) for at least 1 hour. Rinse thoroughly with deionized water. Use the glassware for this method only.
- Chlorine dioxide and its by-products are volatile and can be easily lost from aqueous solution. Collect the sample into 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.
- Purge the syringe each day before 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. Refer to 10.4 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.
- Too fast stirring can pull air into the sample and bubbles may get caught on the electrode tip. Air bubbles on the electrode tip will 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 **2 mL** of effluent from the generator diluted to 200 mL with inorganic free water. Use 1.0 to 5.0 mL sample volume for this method. To use a different sample volume, change the setting at the method edit window. Refer to 10.5.2 Changing the Sample Volume for more information.

2. Introduction

This application is based on the Standard Methods 4500-ClO_2 E, an amperometric method which analyzes three different compounds: chlorine dioxide (ClO_2), free chlorine (Cl_2) and chlorite (ClO_2^-). The table that follow shows the measuring ranges for each element when Generator effluent is analyzed:

ClO_2	100 to 4,500 mg/L
ClO_2^-	100 to 4,500 mg/L
Cl_2	100 to 2,000 mg/L

Chlorine dioxide is used as a disinfection agent for water treatment. This method is used to determine the yield from a chlorine dioxide generator system and to optimize the generator performance.

Yield: Yield is the ratio of chlorine dioxide produced to the theoretical maximum that could be produced. Most modern generators will have yields of 95% or better. Use the formula that follows to calculate the % Yield:

$$\frac{Chlorine\ dioxide\ concentration}{Sum\ of\ the\ total\ chlor-oxy\ species\ concentration} \times 100 = \%\ Yield$$

Ratio: Alternatively, use the ratio of the titrant volumes for Titration 2 and Titration 1 to calculate the ClO_2 generator production. The ratio calculation provides an estimate of any untreated chlorite or chlorine feedstock in the generator effluent.

*Note: **The ratio calculation is only applicable to those generators using chlorite and gaseous chlorine feeds.** Ideally the optimum ratio of Titration 2 to Titration 1 results should fall between 3.9 and 4.05. A ratio of less than 3.75 shows typically a yield of less than 95%. Ratio or Yield result can be excluded from the final display if it is not relevant. Refer to 10 Appendix for more information.*

Less than 3.9	Unreacted Chlorine, possible chlorate contamination
3.9 to 4.05	Optimum
Greater than 4.05	Unreacted Chlorine

This method can be accelerated by purging a sample portion for titrations 3 and 4 with nitrogen while titrations 1 and 2 are underway. Select SKIP to bypass the timer when the sample is degassed before the time is up. Do not hit STOP or the titration series will end. Refer to 10 Appendix for more information.

3. Principle

Four successive amperometric titrations are done on two Chlorine Dioxide Generator effluent sample aliquots. The instrument stores the results of each titration and at the end of the sequence calculates and shows the concentrations of each compound. The software identifies linear segments and detects the equivalence points for the 4 titrations.

In the first sample, an excess of potassium iodide (KI) and buffer 7 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^-.

Afterwards, the second portion of sample is adjusted to pH 7 by the addition of buffer and degassed with nitrogen. Excess KI is added and the third titration is launched to neutralize any Cl_2 not volatized by the degassing. (The result of titration 3 is not used in the calculation; it is done to allow the titration for chlorite to provide an end result of only Chlorite). Finally, concentrated hydrochloric acid is added to the solution to give the ClO_2^- determined during the last titration.

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: Sodium Thiosulfate 0.1000 eq/L solution

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

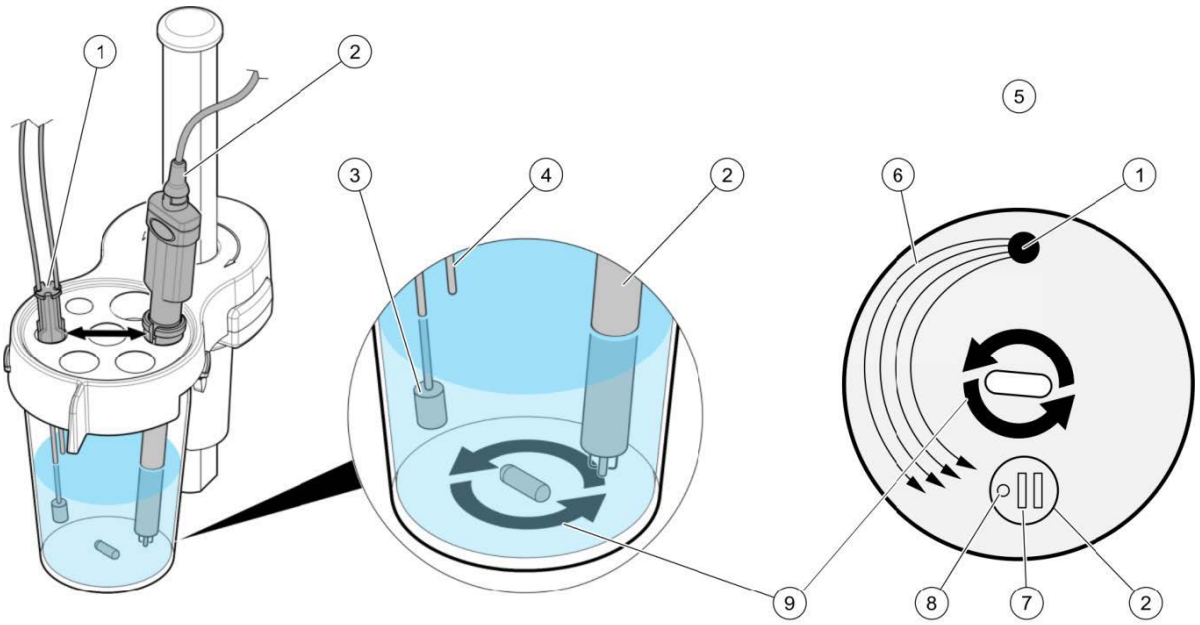
Deionized water

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 Generator Yield determination

One application file for chlorine dioxide generator Yield is available.

The settings below have been defined with:

- Sample volume: 2 mL (diluted to approximately 200 mL with deionized water). If a different volume of sample is used, change the setting in the method edit window. Refer to 10.5.2 Changing the Sample Volume for more information.
- Titrant concentration: 0.1000 eq/L. The titer is most easily entered directly from the manufacturers C.O.A. in the method edit window, or the solution may be titrated.
- Syringe volume: 5 mL. The default syringe volume for the AT1000 is set to 10 mL. 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 10.3 Changing the syringe volume on the AT1000. for more information.
- Continuous imposed voltage: 100 mV (reversed at each analysis)
- If a blank is tested, analyze this as a sample. The BLANK option is not compatible with this method.

Name	Default parameter	Unit
Application name	**ClO_2 Generator Yield**	
Syringe		
Advisable	5 mL (Hamilton)	
Sample		
Name	Sample?[1]	
Amount	2	mL
QC		
Name	QC Sample	
Probe		
Recommended electrode	MTC695	
Titrant Sodium Thiosulfate 0.1000 N		
Real concentration	0.1000	eq/L
Automatic addition 1 (titration 1)		
Active[2]	Yes	
Reagent	Buffer pH 7, 1.0 mL	
Pump ID	Pump 1	

[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	**ClO_2 Generator Yield**	
Time	2	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	1.5	µA
Predose speed	0.5	mL/min
Delay	15	seconds
Max. vol. stop point	10	mL
Stop on last EQP	Yes	
Increment size	0.0075	mL
EQP min. ordinate	-0.03	µA
EQP max. ordinate	0.25	µA
Result 1 name	Intermediate 1	mL
R1 hide	Yes	
R1 min	0	mL
R1 max	10	mL
R1 QC min	0	mL
R1 QC max	10	mL
Titration 1 (continued)		
Result 2 name	A	
R2 hide	Yes	
R2 min	0	mL/mL
R2 max	2	mL/mL
R2 QC min	0	mL/mL
R2 QC max	2	mL/mL
R2 equation	FX*(F1/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 1)		
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	%
Predose ordinate	5	µA
Predose speed	2.0	mL/min

Name	Default parameter	Unit
Application name	**ClO_2 Generator Yield**	
Delay	20	s
Max. vol. stop point	25	mL
Stop on last EQP	Yes	
Increment size	0.005	mL
EQP min. ordinate	0.0	µA
EQP max. ordinate	0.3	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	5.25	mL/mL
R2 QC min	0	mL/mL
R2 QC max	5.25	mL/mL
R2 equation	FX*(F2/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	Sample amount
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	min
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	s
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		
Active	Yes	
Stirring speed	1	%
Predose ordinate	4	µA
Predose speed	0.4	mL/min
Delay	20	s
Max. vol. stop point	5	mL
Stop on last EQP	Yes	
Increment size	0.0003	mL
EQP min. ordinate	-0.2	µA
EQP max. ordinate	0.03	µA

Name	Default parameter	Unit
Application name	**ClO_2 Generator Yield**	
Result 1 name	Intermediate 3	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	C	
R2 hide	Yes	
R2 min	0	mL/mL
R2 max	5.2	mL/mL
R2 QC min	0	mL/mL
R2 QC max	5.2	mL/mL
R2 equation	FX*(F3/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	1.25	µA
Predose speed	0.25	mL/min
Delay	20	seconds
Max. vol. stop point	15	mL
Stop on last EQP	Yes	
Increment size	0.004	mL
EQP min. ordinate	–0.05	µA
EQP max. ordinate	0.15	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	1.25	mL/mL
R2 QC min	0	mL/mL
R2 QC max	1.25	mL/mL
R2 equation	FX*(F4/SA) = G4	
R2 user value	1	
Displayed Results		
Result 1 Name **(G5)**	**Chlorite**	
R1hide	No	
R1 min	0	mg ClO_2^-/L
R1 max	4500	mg ClO_2^-/L
R1 QC min	0	mg ClO_2^-/L
R1 QC max	4500	mg ClO_2^-/L
R1 equation	V1/V1*FX*(G4+(F3/SA)-G3)*TC*16863	
R1 user value	1	
Result 2 name (G6)	**Chlorine Dioxide**	
R2 hide	No	

Name	Default parameter	Unit
Application name	**ClO_2 Generator Yield**	
R2 min	0	mg ClO_2/L
R2max	4500	mg ClO_2/L
R2 QC min	0	mg ClO_2/L
R2 QC Max	4500	mg ClO_2/L
R4 equation	FX*(5/4)*((G2+(F1/SA)-G1)-(G4+F3/SA)-G3)) *TC*13490	
R4 user value	1	
Result 3 name	**Chlorine**	
R3 hide	No	
R3 min	0	mg Cl_2/L
R3 max	2000	mg Cl_2/L
R3 QC min	0	mg Cl_2/L
R3 QC max	2000	mg Cl_2/L
R3 equation	FX*(G1-1/4)*((G2+(F1/SA)-G1)-(G4+(G4-(F3/SA)-G3))) *TC*35453	
R3 user value	1	
Result 4 Name	**Ratio**	
R4 Hide	No	
R4 Min	0	
R4 Max	5	
R4 QC Min	0	
R4QC Max	5	
R4 Equation	G2/G1	
Result 5 Name	**% Yield**	
R5 Hide	No	
R5 Min	80	
R5 Max	100	
R5 QC Min	80	
R5 QC Max	100	
R5 Equation	100*(G6(G5+G6))	

5.2. Recommendations for modification of the settings

Some parameters can be adjusted, but this is mainly for analysis time reduction. It should be noted that the impact of any adjustments can be a loss of precision on the results.

5.2.1. Sample preparation messages

Messages for sample preparation can be removed from the sequence by setting **No** in the field **Active** in the message section. In this way, the instrument will not give information about sample preparation during the analysis sequence. Methods which can be deactivated are the following:

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

A second portion of sample can be prepared during titrations 1 and 2 to decrease analysis time. If the generation process is stable and the samples always have the same level of concentration, it is also possible to set a different predose.

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

5.2.2. Predoses in ordinate

Predoses in ordinate are used to decrease the titration duration. They have been fixed for all titrations for chlorine dioxide generator yield. 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 typically have an impact on the result.

The table that follows shows some indications.

Observation	Resolution
The titration is still too long (too many points before inflection).	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.

5.2.3. Instrument tips and technique

- There is a difference between doing a new test and a new sample. Select **Next** to 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.
- Do not use the BLANK option. Analyze the blank as a sample. If the blank option 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. Procedure

6.1. Before starting

NOTICE: All glassware must be treated for chlorine demand before any analysis.

- Soak all glassware in a strong chlorine dioxide solution (300-500 mg/L) for at least 1 hour. Rinse thoroughly with deionized water. Reserve the glassware for this method only.
- Clean the electrode prior to first use, after storage, and as a part of routine maintenance.
- 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.
- Always use organic free water for sample dilution.
- Rinse the electrode and anti-diffusion tip with deionized water before and after every titration.

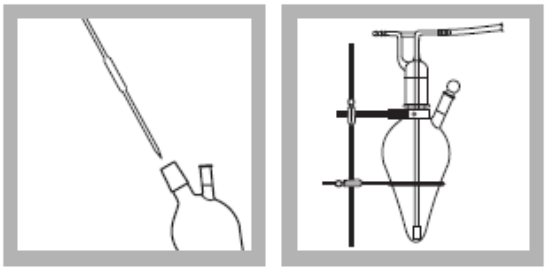
6.2. Sample analysis

1. Measure 2 mL of sample solution with a pipette and transfer to a 250-mL glass beaker.
   1 to 5 mL of sample may be used. If a volume other than 5 mL is used, this must be changed before the test begins through the application edit window.
   The table that follow shows the approximate sample volumes used with this method:

Sample amount (mL)	Max ClO_2 if %Yield is 90	Max ClO_2^-
5	1500	150
4	1800	180
3	2500	250
2	3700	370
1	5600	560

2. Add approximately 195 mL of deionized, organic free water.
3. Put the sample onto the instrument and start the application.
4. Add 1.0 mL of phosphate buffer pH 7 (if it is not added with the embedded pump).
5. Add 1.0 g of potassium iodide (KI). The exact amount is not critical, it is added in excess.
6. The reagents are mixed and the electrode and addition tip are dipped into the sample. Titration 1 is launched.
7. When titration 1 is finished, raise the electrode holder.
8. Add 2.0 mL of 2.5 N hydrochloric acid (HCl) and allow the solution to stir for a few seconds.
9. Carefully remove the sample from the stirrer and put the sample in a dark environment.
10. Wait 5 min for the reaction.

11. At the end of the 5 min, carefully put the sample back onto the instrument.
12. Dip the electrode and addition tip into the sample.
13. Titration 2 is launched.
14. Pipette 5 mL of sample, diluted to approx. 200 mL, into a Gas Washing Bottle (GWB).
15. Add 1.0 mL of phosphate buffer pH 7 and swirl to mix.
16. Insert the purge tube and dispersion tip into the GWB. Connect the GWB inlet to a tank of purified nitrogen.



17. Use a needle valve to adjust the flow of nitrogen to provide a steady stream of bubbles through the sample.
18. Purge the nitrogen gas through the sample for 15 minutes.
19. After the purge, transfer the purged sample to a 250-mL glass beaker, add a magnetic stir bar and put onto the instrument.
20. Add 1.0 g of KI.
21. The reagents are mixed and the electrode and addition tip can now be dipped into the sample.
22. Titration 3 is launched.
23. When titration 3 is finished, raise the electrode holder.
24. Add 2.0 mL of 2.5 N hydrochloric acid (HCl) and stir for a few seconds.
25. Carefully remove the sample from the stirrer and put the sample in a dark environment.
26. Wait 5 min for the reaction.
27. At the end of the 5 min, carefully put the sample back onto the instrument.
28. Dip the electrode and addition tip into the sample.
29. Titration 4 is launched.
30. At the end of titration 4, the results will show as follows:

Chlorite = 105.6 mg ClO_2^-/L

Chlorine Dioxide = 2406.7 mg ClO_2/L

Chlorine = 78 mg Cl_2/L

Ratio = 3.79

% Yield = 95.8 %

***Note**: The ratio value is used for generator systems using chlorite and gaseous chlorine feeds. This result can be disabled in the application edit window if it is not relevant.*

7. Results

7.1. Displayed Results

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

1. Chlorite in mg/L as ClO_2^-
2. Chlorine Dioxide in mg/L as ClO_2
3. Chlorine in mg/L as Cl_2
4. Ratio
5. % Yield

7.2. Results calculation

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

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

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

Ratio: $G2/G1$

%Yield: $G6/G5$

Where:

N = Concentration of the titrant (eq/L)
A = Result of titration 1 (mL titrant at equivalent point/mL of sample; (**G1** in the equation in the instrument))
B = Result of titration 2 (mL titrant at equivalent point/mL of sample (**G2** in the equation in the instrument)
D = Result of titration 4 (mL titrant at equivalent point/mL of sample G4 in the equations in the instrument)
[ClO_2^-] = **G5**
[ClO_2] = **G6**

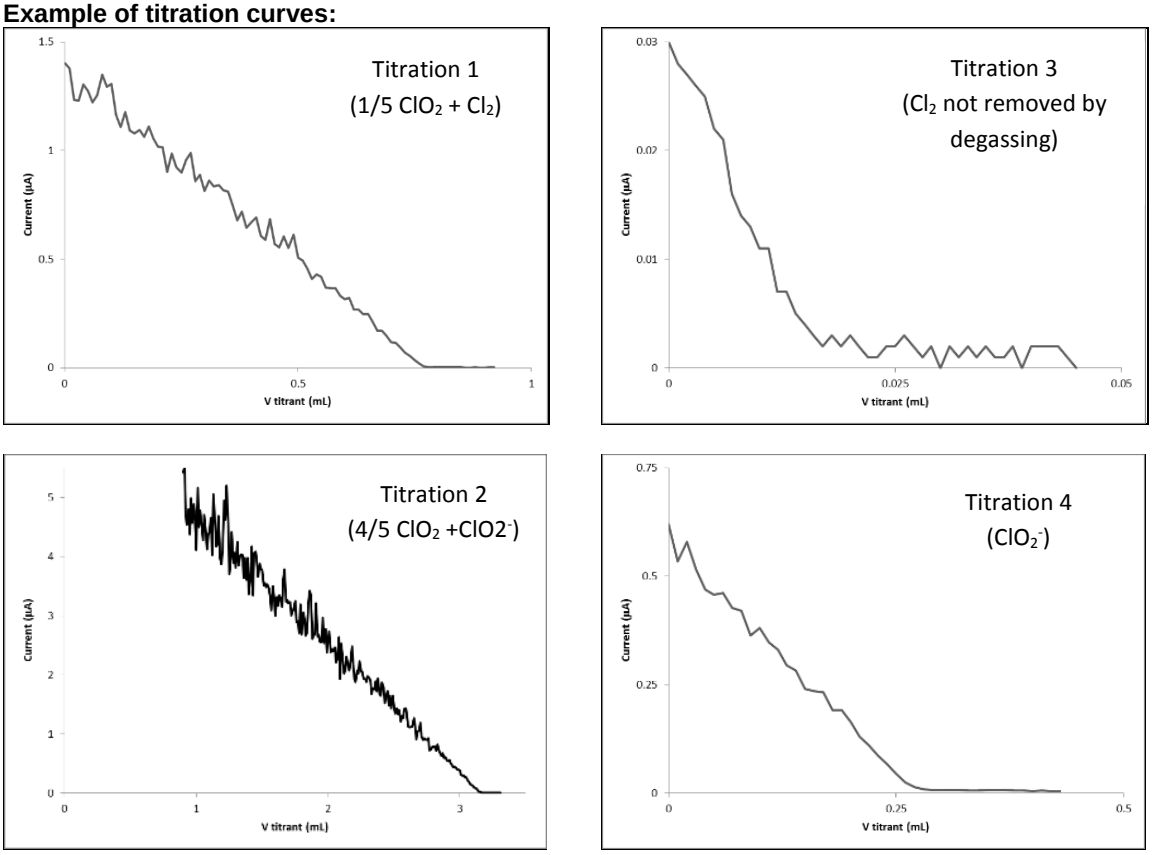
Important: *The instrument calculation may lead to an incorrect result if the concentration of one or more of the three measured compounds is less than 0.05mg/L.*

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: Typical Effluent titration (High CLO_2, Low CLO_2^-)

Example of titration curves:



Analysis of synthetic generator effluent samples

Replicate	ClO_2	ClO_2^-	Cl_2	Yield	Ratio
1	661.84	140.78	32.762	82.46	4.328
2	677.19	142.19	33.345	82.646	4.323
AVG	**669.515**	**141.485**	**33.0535**	**82.553**	**4.3255**
SD	10.85409	0.997021	0.412243	0.131522	0.003536
%RSD	**1.62**	**0.705**	**1.25**	**0.16**	**0.08**

Replicate	ClO_2	ClO_2^-	Cl_2	Yield	Ratio
1	3024.7	147.58	41.075	95.348	4.044
2	2924.6	145.65	42.572	95.256	4.039
AVG	**2974.65**	**146.615**	**41.8235**	**95.302**	**4.0415**
SD	70.78139	1.364716	1.058539	0.065054	0.003536
%RSD	**2.38**	**0.93**	**2.53**	**0.07**	**0.087**

9. Bibliography

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

10. Appendix

10.1. Titrant calibration

10.1.1. Principle

The actual concentration of the sodium thiosulfate titrant can most easily entered directly from the C.O.A. through the method edit window. Alternatively, the thiosulfate titrant can be calibrated against a standard solution of Iodine 0.0282 N Iodine. Refer to the customer laboratory SOP for guidance.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad (S_2O_3^{2-} = \text{thiosulfate})$$

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 (Hach PN 2333353, 1L), the real value has to be manually entered as the concentration of the standard.

10.1.2. Procedure

Accurately pipette **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 1g KI powder and 1 mL pH 4 buffer when prompted.

10.1.3. 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.

$$C_{(S2O32-)} = \frac{V_{(I2)} * C_{(I2)}}{V_{(PS2O32-\,AO)}}$$

$C_{(S_2O_3^{2-})}$: 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 (I_2) in mL, currently 0.5 mL
$V_{(S2O32-)}$: 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 5.0 mL of standard solution of iodine 0.0282 eq/L.
- **Addition of:** 1 g KI and 1 mL buffer pH 4
- **Titrant**: Sodium thiosulfate 0.1000 eq/L

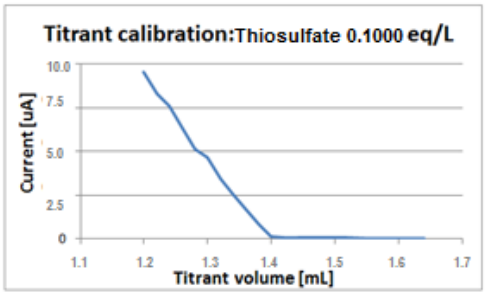
Settings:

- **Settings:** Refer to 10.1.4 Titrant calibration settings (default parameters)
- **Number of determinations**: 5 samples
- **Temperature of analysis**: room temperature

Results:

Average concentration	0.095	eq/L
SD	0.00035	eq/L
RSD	0.37	%

Titration curve: µA *vs*. volume of titrant:



10.1.4. Titrant calibration settings (default parameters)

	Setting	Unit
Titrant name	Sodium Thiosulfate	
Nominal concentration	0.1000	eq/L
Calibration frequency	0	days
Stirring speed (%)	1	%
Predose volume	0.75	mL
Delay	20	seconds
Stop on last EQP	Yes	
Min increment size	0.02	mL
Max increment size	0.05	mL
EQP min. ordinate	0.01	µA
EQP max. ordinate	0.02	µA
Titrant calibration result		
Min. titrant concentration	0.090	eq/L
Max. titrant concentration	0.110	eq/L
Standard		
Name	Iodine	
Amount	5.00	mL
Min amount	4.5	mL
Max amount	5.5	mL
Concentration	0.0282	eq/L

10.1.5. Modification of the parameters

The **titrant calibration** application has been optimized for an amount of standard higher than 0.90mL, a standard concentration higher than 0.0270 eq/L and a titrant concentration between 0.090 eq/L and 0.110 eq/L. 5mL of iodine is used for titrant calibration. If the value is different than 0.0282N, this needs to be entered through the method edit window. A predose of 0.75 mL of titrant speeds the titration up while allowing enough points in the titration for determination of the linear zones and the equivalence point

10.2. Decrease the titration duration—Portion 2 degassing

Prepare and degass the second sample portion during the first two titrations to decrease the analysis duration. Dilute the sample in DI water to approximately 200 mL. Add one mL of buffer. Put the gas washing bottle, start the flow of nitrogen and start the timing. **If a second degassed portion of sample is ready:**

1. Select OK when prompted to put sample in GWB
2. Select ADD 1 ML OF PH 7 BUFFER and then push **OK**.
3. Select SKIP to pass the 15-minute degassing time (or whatever portion of the 15 minutes is left when the degassing is complete). Follow the instruction instructions.

   ***Note**: If STOP is selected at any point, the entire process is fully stopped. It is not possible to resume a stopped titration.*

4. If after 15 minutes degassing the sample has a yellow coloration, increase the degassing time until the sample coloration is gone.

10.3. Changing 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:

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

10.4. 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 and down arrows.*
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.

10.5. Simple application customization

10.5.1. Duplicating an Application

When making changes to an application, it is best to make a copy of the provided version (duplicate it) before making changes. Below is the process for duplicating an application:

1. From the Home screen select SETTINGS and then APPLICATIONS
2. Select DUPLICATE from the list of actions
3. Use the side to side arrow keys to select the application(s) to duplicate
4. Select DUPLICATE and then OK after the SUCCESSFULLY LOADED message shows
   a. Example: Duplicating the application Chlorine Dioxide Yield will create a copy of this application in the application list titled Chlorine Dioxide Yield (2)
5. Select EDIT from the list of actions on the Application settings screen
6. Highlight the duplicated application and select EDIT
7. Edit the name of the duplicated application using the up and down and right or left arrow keys
   a. A USB keyboard can be connected to the AT1000 to make typing easier
8. When the naming is complete, select OK then go back to the edit screen

10.5.2. Changing the Sample Volume

The applications discussed in this document were designed to use a 2 mL sample, but they can be easily customized in the Edit Application Window on the AT1000 if a different sample volume is required:

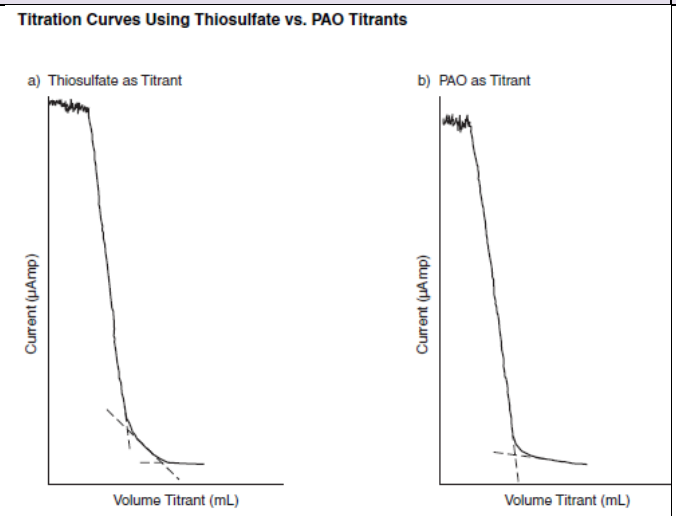
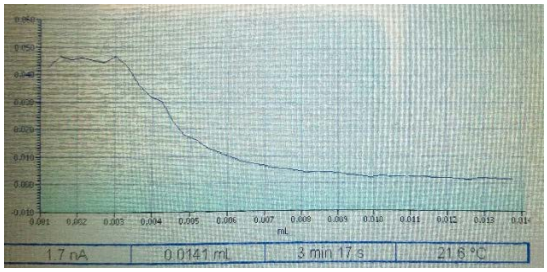
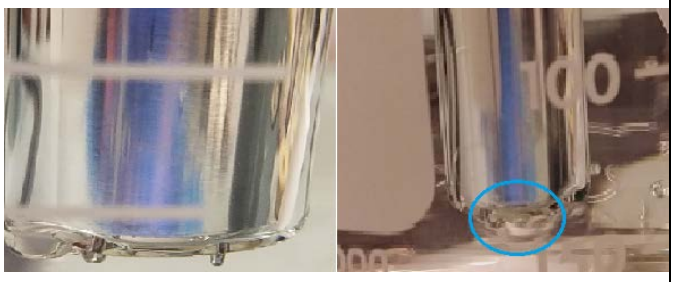
1. From the Home screen select SETTINGS>APPLICATIONS
2. Select EDIT from the list of actions
3. Highlight the application to modify the sample volume and push **EDIT**
4. Use the down arrow to scroll down to AMOUNT under the *SAMPLE* heading
5. Push **EDIT**
6. Enter the sample volume and push **OK**

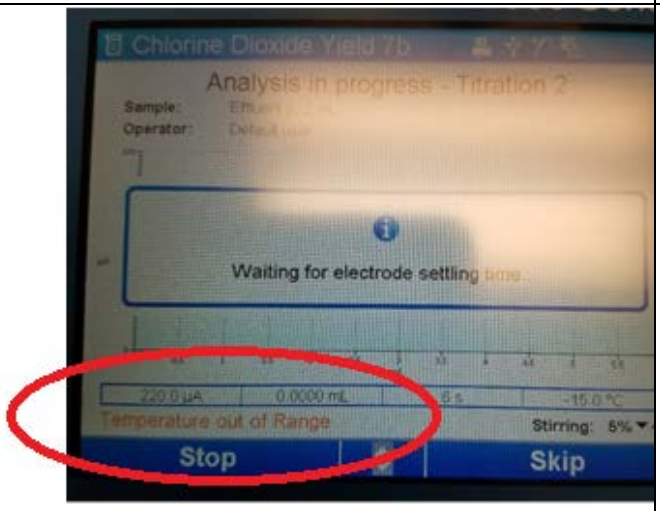
10.5.3. Changing the Predose Speed

Predose is used to improve sample throughput (speed of titration) and can be adjusted as follows if the samples take too long (higher concentration) or if the ordinate is exceeded by too much (concentration too low). Make sure that changes are done to the correct titration:

1. From the Home screen select SETTINGS>APPLICATIONS
2. Select EDIT from the list of actions
3. Highlight the application to modify and push **EDIT**
4. Use the down arrow to scroll down to the PREDOSE SPEED under the METHOD heading
5. Push **Edit**, adjust the value and push **OK**

11. Troubleshooting

Symptom	Probable cause	Solution
The endpoint is not correctly identified. The EQP is not sharp. The curve is noisy.		Thiosulfate titrant inherently produces less sharp curves. A clean electrode will allow the best identification of the EQP. Assess volume difference between apparent and detected EQP. The difference is most often less than 1-2%. Clean the electrode.
Curve is '' lumpy'' or ''spiky'' or '' flat ''	It is possible for air bubbles to be trapped in the system and pass through the burette. This can result in flat spots, spikes and an apparent concentration that is higher than expected because the titrant volume is accounted for incorrectly. Syringe refilling can cause odd drop or flat spot when titrant volume exceeds 5 mL. Verify that the anti-diffusion dispensing tip is submerged in the sample. (When it is not, titrant drips into the beaker instead of being added in controlled increments.	Examine the syringe and tubing for bubbles. Make sure that all tubing connections are tight with no leaks. Purge the syringe routinely at the beginning of the day.
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.		Very little analyte (common for Titration 3) Check for bubble caught on electrode Verify electrode is properly oriented 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.

Symptom	Probable cause	Solution
Flat signal Noisy signal Electrode is dirty.		No analyte (blank) No buffer added No KI added Clean the electrode.
Temperature out of range warning; reading at 220 uA Titration 2 stops but the solution still contains iodine.		Let the titration to continue. If the titration stops and the sample still contains iodine (the sample is colored), the analyte concentrations are too high. More sample dilution is necessary.

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			
2.5N Hydrochloric acid	4 mL	100 mL	141832
Phosphate buffer, pH 7	2 mL	1 L	2155353
Potassium iodide, ACS	2 g	100 g	16726H
Potassium iodide, ACS	2 g	454 g	16701H
Sodium thiosulfate, 0.1N	varies	1 L	32353
Nitric acid, 1 :1 (for electrode cleaning)	20 mL	500 mL	254049
Required equipment			
1-g scoop	1	Each	2657201
Beaker, 250 mL glass, 1 EA	1	each	50046H
Magnetic stir bar, 1 EA	1	each	5008500
Measuring spoon, 1G, plastic, EA	1	each	51000
Pipet, volumetric, Class A, 5 mL	1	each	1451537
Gas washing bottle, EA	1	each	2662200
Support, ring stand, EA	1	each	56300
Support ring, for gas washing bottle, EA	1	each	2656300
Optional reagents			
Dilution water, organic free	varies	500 mL	2641549
0.0282N I_2, (for calibration of the PAO titrant)	5 mL	1 L	2333353
Acetate buffer solution, pH 4 bottle (automatic addition)	approimately 1 mL	1 L	1490953
Acetate buffer solution, pH 4, with dropper (manual addition)	1 mL	100 mL	1490932
Optional equipment			
Cylinder, graduated, 250 mL	1	each	50846
Timer, 5 channel	1	each	2630400
Mini-printer, thermal, USB	1	each	LQV161.53.10000
Paper for thermal printer	varies	5/pkg	5836000
Pipet, volumetric, Class A, 4 mL	1	each	1451504
Pipet, volumetric, Class A, 3 mL	1	each	1451503
Pipet, volumetric, Class A, 2 mL	1	each	1451536
Pipet, volumetric, Class A, 1 mL	1	each	1451535

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