Total Chlorine Back Titration

DOC316.52.93102

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

Amperometric Back Titration 0.005–5.00 mg/L as Cl_2

1. Introduction

This application note follows method number 4500-Cl C 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 waste water samples.

By using a back titration, the chlorine concentration is fixed at the collection of the sample, allowing the sample to be stored for later analysis.

Three applications for total chlorine determination are available:

- **High range**: Bk Cl_2 0.5-5 mg/L for a sample concentration between 0.5 and 5 mg/L
- **Medium range**: Bk Cl_2 0.05-0.5 mg/L for a sample concentration between 0.05 and 0.5 mg/L
- **Low range**: Bk Cl_2 0.005-0.05 mg/L for a sample concentration between 0.005 and 0.05 mg/L

2. Principle

In the amperometric back titration, a measured volume of reductant (phenylarsine oxide) is added directly to a measured volume of the sample at collection time.

At analysis time, the sample is adjusted to pH 4 with acetate buffer, and an excess of potassium iodide is added. The unreacted reductant is then titrated with a standard Iodine solution.

The chlorine concentration is derived from the difference in the amount of reductant originally added to the sample and the amount remaining before titration.

The chemical reactions are (where Ph = phenyl):

First reaction (with reductant): $PhAsO\ (PAO) + Cl_2 + 2H_2O \rightarrow PhAsO(OH)_2 + 2Cl^- + 2H^+$

Second reaction (with titrant): $I_3 + PhAsO\ (PAO) + 2H_2O \rightarrow 3I^- + PhAsO(OH)_2 + 2H^+$

3. Electrode and reagents

Electrodes: Pt-electrode with temperature sensor, Intellical MTC695

Description	Qty. required per test
Required reagents	
Iodine standard solution, titrant 0.0282 N	Varies
Phenylarsine oxide (PAO), reductant 0.00564 N	Varies
Acetate buffer solution, pH 4, w/dropper	1 mL
Potassium iodide, SwifTest™ refill	0.1 g
Phenylarsine Oxide (PAO) Digital Titrator Cartridge, 0.00564 N	Varies
Sodium Thiosulfate Digital Titrator Cartridge, Stabilized, 0.0250 N	Varies
Required apparatus	
Beaker, glass, 250 mL	1
Cylinder, graduated, 250 mL	1
Magnetic stir bar, Teflon® coated	1
Pipet, volumetric, class A, 10 mL	1
SwifTest™ dispenser	1
Digital Titrator	1
Delivery Tubes, straight w/"J" hook	Varies
Optional reagents	
Chlorine standard solution, Voluette® ampoules	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
- Reductant: Phenylarsine oxide (PAO) 0.00564 N
- Titrant: Iodine (I_2) 0.0282 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 0.005 to 5 mg/L as Cl_2.

In the higher range, with an amount of reductant (PAO 0.00564 N) of 10 mL, it is possible to measure samples up to 7 mg/L. It is also possible to use a smaller amount of sample and to dilute it to 200 mL (refer to **4.4 Modification of the parameters).**

1 mL of reductant (0.00564 N PAO) corresponds to 1 mg/L of chlorine.

0.2 ml of titrant (iodine 0.0282 N) corresponds to 1 mg/L of Cl_2 or 1 mL of reductant (PAO).

4.3. Titration settings (default parameters)

4.3.1. Application

	Low range setting (0.005 to 0.05 mg/L)	Medium range setting (0.05 to 0.5 mg/L)	High range setting (0.5 to 5 mg/L)
Application name	Bk Cl2 0.005-0.05 mg/L	Bk Cl2 0.05-0.5 mg/L	Bk Cl2 0.5-5 mg/L
Advisable syringe	5mL (Hamilton)	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	I2	
Real concentration	0.0282	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	Pump 2	
Time	0.3	seconds
Stirring speed	0	%

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

4.3.6. Back titration and detection settings

	Low range setting (0.005 to 0.05 mg/L)	Medium range setting (0.05 to 0.5 mg/L)	High range setting (0.5 to 5 mg/L)	Unit
Stirring speed	1	1	1	%
Measured parameter	µA	µA	µA	
Predose volume	0.17	0.05	0.5	mL
Delay	30	5	5	seconds
Max. vol. stop point	0.3	0.3	3	mL
Ordinate stop point	0.3	1	10	µA
Stop on last EQP	Yes	Yes	Yes	
Increment size	0.001	0.005	0.05	mL
EQP min. ordinate	-0.05	-0.1	-0.5	µA
EQP max. ordinate	0.05	0.1	0.5	µA

4.3.7. Excess reductant settings used for the calculation

	Low range setting (0.005 to 0.05 mg/L)	Medium range setting (0.05 to 0.5 mg/L)	High range setting (0.5 to 5 mg/L)	Unit
Back titration mode	manual	manual	manual	
Excess volume	1.00	1.00	10.00	mL
Excess titrant Name	PAO	PAO	PAO	
Real conc. of excess titrant	0.00564	0.00564	0.00564	eq/L

4.3.8. Results settings

	Low range setting (0.005 to 0.05 mg/L)	Medium range setting (0.05 to 0.5 mg/L)	High range setting (0.5 to 5 mg/L)
Result 1 name	Total chlorine	Total chlorine	Total chlorine
R1 min	0.000mg/L	0.05 mg/L	0.5 mg/L
R1 max	0.05 mg/L	0.5 mg/L	5 mg/L
R1 QC min	0.005 mg/L	0.05 mg/L	0.5 mg/L
R1 QC max	0.05 mg/L	0.5 mg/L	5 mg/L
R1 molar weight	70.906	70.906	70.906

4.4. Modification of the parameters

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

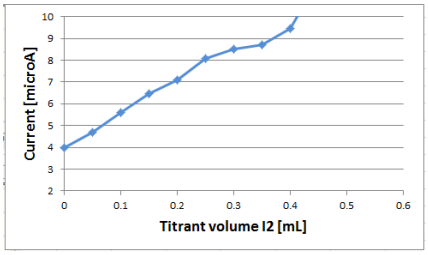
Standard Methods recommends a default sample volume of 200 mL, also the parameters have been optimized in three sets to cover sample concentrations from 0.005 to 5 mg/L as Cl_2 (refer to **1 Introduction**). The final results are calculated based on the sample volume. If the sample amount is different, you need to **enter the real sample volume** in the application edit window.

If a high volume of titrant is delivered before the equivalence point, the titration time can be reduced by **increasing the predose volume**. A minimum of 3 increment additions before the current increases are needed for the equivalence point detection.

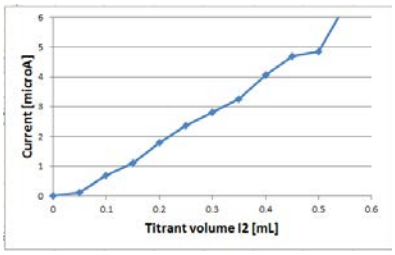
For the higher range, reductant volume is fixed at 10 mL by default but it can be adjusted as a function of the sample concentration. An excess of 5 mL of PAO is sufficient for analyzing samples up to 4.5 mg/L. The PAO amount can be reduced by keeping a minimum of 0.5 mL of PAO in excess for the equivalence point detection. The predose also needs to be adjusted.

The tables and graphics below show the effect of reducing the PAO amount on the titration curve shapes and on the detection:

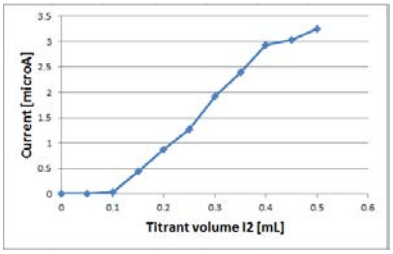
	Chlorine concentration	Reductant volume	Predose volume	Theoretical titrant volume	Number of additions before equivalence point	Detection
Sample 1	6 mg/L	5 mL	0 mL	Not enough excess reductant	0	Not possible
Sample 2	4.7 mg/L	5 mL	0 mL	0.06 mL	1	Not possible
Sample 3	4.5 mg/L	5 mL	0 mL	0.100 mL	2	OK



Sample 1:
Back titration with reductant volume much too low (same behavior as if predose is too high). The current increases from the beginning of the titration. Equivalence point exceeded.



Sample 2:
Back titration with 0.3 mL excess reductant volume is just too low. The current increases after one increment addition. Detection is not still possible.

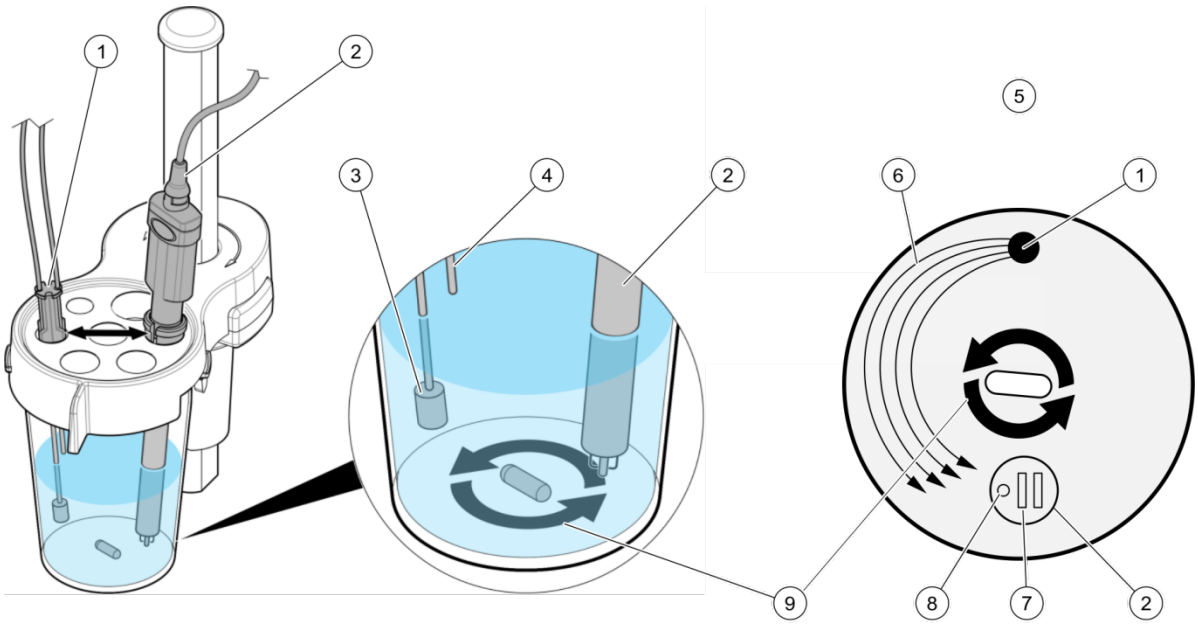


Sample 3:
Back titration with 0.5 mL excess reductant volume. Equivalence point detection is possible.

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 and enter the real concentration values in the application parameters (refer to **4.3.3 Titrant settings used for the calculation** and **4.3.7 Excess reductant settings used for the calculation**).
- 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

- 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**.
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. Add the required amount of reductant (PAO) as a function of the sample chlorine concentration. To ensure a **good accuracy of the analysis**, for total chlorine samples with concentrations below 0.5 mg/L, dispense 800 digits of 0.00564 N PAO with a Digital Titrator.
5. Dip the electrodes and the titrant tip into the sample.
6. Adjust the tip from the peristaltic pump to **above the sample surface** and press **Start**.
7. 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. For very low applications, the amount of KI should not exceed 0.1 g (use of the SwifTest™ is **not** recommended).
8. 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
9. There is a delay of between 5 and 30 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.
10. During the delay, if needed, adjust the stirrer speed to ensure an efficient stirring and prevent the formation of bubbles.
11. The titration curve will appear on the display. The TitraLab AT1000 Series performs the analysis based on the automatic selection of linear segments.
12. 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. Result calculation

The Hach TitraLab AT1000 calculates the result R directly in mg/L of chlorine (Cl_2).

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

$$R = \frac{1}{2} * MW * 1000 * \frac{V_{(PAO)} * C_{(PAO)} - C_{(I_2)} * V_{(I_2)}}{V_{smp}}$$

- $C_{(PAO)}$ = Concentration of reductant phenylarsine oxide (PAO), in eq/L: 0.00564 eq/L
- $V_{(PAO)}$ = Volume of reductant phenylarsine oxide (PAO) added, in mL
- $C_{(I2)}$ = Concentration of titrant iodine (I_2), in eq/L: 0.0282eq/L
- $V_{(I2)}$ = Volume of titrant iodine (I_2) added, in mL
- $V_{(smp)}$ = Volume of the sample in mL: 200 mL
- MW = Molar weight chlorine: 70.906 g/mol

After calculation with the previous values:

$$R = V_{(PAO)} - 5 * V_{(I_2)}$$

6.3. Comment on result calculation

As it is a back titration, the result obtained by calculation involving a difference between two values can be displayed with a negative value.

With the lower range application, due to the limit of the detection of the method, a chlorine concentration result between -0.005 mg/l and 0.005 mg/L can be considered as below the detection limit.

A more negative result means that the titrant and/or the reductant have to be accurately calibrated, or at least the values from the calibration certificates have to be entered in the application parameter (refer to **4.3.3 Titrant settings used for the calculation** and **4.3.7 Excess reductant settings used for the calculation**). The calibration of the PAO is described and available in the Total Chlorine Application.

7. Example of chlorine determination

The results described below are indicative and obtained for a given water type in optimized conditions, and 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 0.15 mL of standard solution of chlorine equivalent standard (Cl_2) at 64.19 mg/L and 0.1 g KI and 1 mL buffer pH 4
- **Titrant**: I_2 0.0282 eq/L
- **Reductant**: PAO 0.00564 eq/L, addition of 1 mL

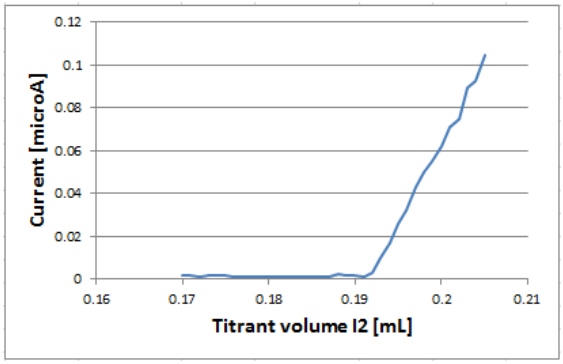
Settings:

- **Settings:** Refer to default values in **4.3 Titration settings (default parameters)**
- **Number of determinations**: 8 samples
- **Temperature of analysis**: Room temperature

Results:

Average concentration	0.049	mg/L Cl_2
SD	0.0022	mg/L Cl_2
RSD	5	%

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



8. Bibliography

- *Standard Methods for the Examination of Water and Wastewater,* Standard 4500-Cl2 C

9. Appendix: Titrant calibration

9.1. Principle

The Iodine solution can be calibrated: its exact concentration can be determined from an amperometric titration using a 0.025 N Sodium Thiosulfate standard solution.

$$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

If the Sodium Thiosulfate concentration given in the "Certificate of Analysis" is different from the default concentration: 0.025 N, the real value has to be manually entered as the concentration of the standard (in titrant calibration settings 9.4).

9.2. Procedure

1. Pipette accurately 2 mL of thiosulfate solution 0.025 N. Dispense 1600 digits with a Digital Titrator and dilute the thiosulfate standard to 200 mL with deionized water.
2. Add 1 mL of buffer pH 4 solution and 0.1 g of KI.
3. Calibrate the titrant using the titrant calibration module instead of the sample analysis.

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 Hach Titralab AT1xxx calculates the titrant concentration directly in eq/L.

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

- $C_{(I2)}$ = Concentration of titrant: Iodine (I_2) in eq/L,
- $C_{(Std)}$ = Concentration of standard: Sodium Thiosulfate in eq/L, currently 0.025 eq/L
- $V_{(Std)}$ = Volume of standard Sodium Thiosulfate in mL: currently 2.00 mL
- $V_{(I2)}$ = Volume of the titrant: Iodine (I_2) in mL added to reach the equivalent point

Experimental conditions:

- **Burette volume**: 5 mL
- **Sample:** 200 mL of deionized water with 2 mL of standard solution of sodium thiosulfate 0.025 eq/L.
- **Addition of:** 0.1 g KI and 1 mL buffer pH 4
- **Titrant**: I_2 0.0282 eq/L

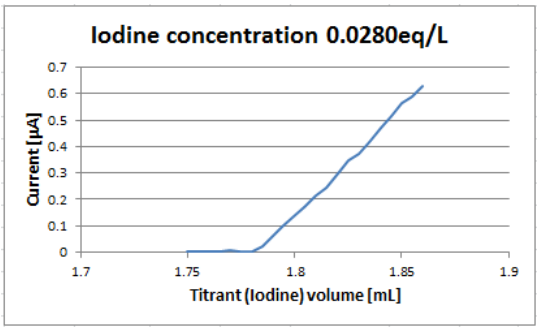
Settings:

- **Settings:** Refer to default values in **9.4 Titrant calibration settings (default parameters)**
- **Number of determinations**: 9 samples
- **Temperature of analysis**: Room temperature

Results:

Average concentration	0.02801	eq/L
SD	0.00002	eq/L
RSD	0.07	%

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



9.4. Titrant calibration settings (default parameters)

	Setting	Unit
Titrant name	I2	
Nominal concentration	0.0282	eq/L
Calibration frequency	0	days
Stirring speed (%)	1	%
Predose volume	1.6	mL
Delay	10	seconds
Stop on last EQP	Yes	
Max. vol. stop point	2	mL
Ordinate stop point	1	µA
Increment size	0.005	mL
EQP min. ordinate	-0.1	µA
EQP max. ordinate	0.1	µA
Titer result		
Min. titrant concentration	0.0270	eq/L
Max. titrant concentration	0.0290	eq/L
Standard		
Name	Thiosulfate	
Amount	2.000	mL
Min amount	1.900	mL
Max amount	2.100	mL

9.5. Modification of the parameters

The predose volume and the maximum volume can be adjusted as a function of the concentration of the iodine concentration.

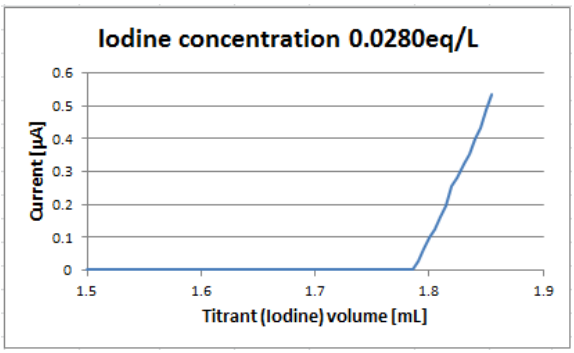
The default value of the predose is 1.60 mL, to enable a titration of iodine for a concentration of up to 0.0305 eq/L. The maximum volume is 2.00 mL, to enable a titration of iodine for a concentration of up to 0.0255 eq/L.

For a lower iodine concentration, the equivalent volume will be greater. The maximum volume has to be increased and the titration time will be reduced by increasing the predose.

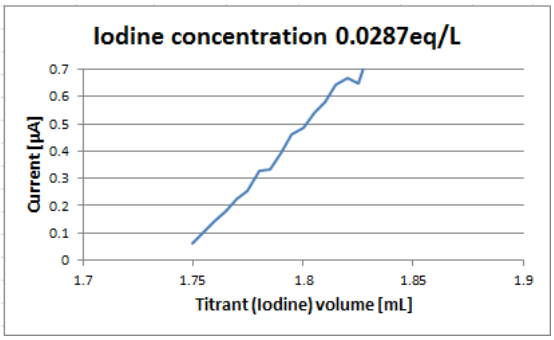
At least 3 points before and after the equivalence are necessary to ensure a good calculation of the titer.

The table below indicates the optimum predose volume as a function of the iodine solution concentration.

Iodine concentration	Theoretical equivalent volume	Predose volume	Number of addition point before equivalent point detection
0.0270 eq/L	1.852 mL	1.75 mL	20
0.0282 eq/L	1.773 mL	1.70 mL	15
0.0290 eq/L	1.724 mL	1.65 mL	15



Titration with predose volume too low. Accurate result but higher titration duration.



Titration with predose volume too high. No equivalent point will be found. The current at the beginning of the titration is not equal to 0 mA and it increases from the beginning of the addition.

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