Chlorine, Total

DOC316.53.01221

Amperometric Back Titration[1]

Method 10025

(6 to 1000 µg/L Chlorine as Cl_2)

Digital Titrator

Scope and Application: For drinking water and wastewater; USEPA accepted for reporting

[1] Procedure is equivalent to *Standard Method (18th ed.)* 4500-Cl C for wastewater.

Test preparation

Before starting the test

When a new probe is used or the probe has not been used recently, prepare it according to the Probe Stabilization instructions in the *Amperometric Titrator Instruction Manual*.
Use the proper stir bar (Catalog number 2095355). The wrong size can cause the loss of chlorine, unstable readings, and loss of method sensitivity, especially when measuring low level chlorine concentrations.
To preserve the strength of the iodine titrant solution, always remove the delivery tube from the Digital Titrator cartridge and replace the cap when not in use. Protect the iodine titrant solution from direct sunlight.
The sample may be fixed at the sample site for brief transportation delays— but not for sample storage. (This fixing technique is not acceptable for USEPA compliance monitoring.). See *Sample collection, preservation and storage* for more information.

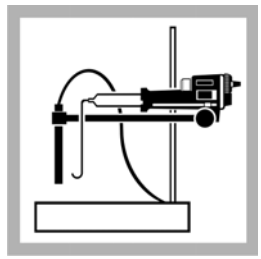
Collect the following items:

Description	Quantity
Standard Iodine Titrant Solution, Cartridge, 0.028 N	each
Digital Titrator	each
Cylinder, graduated, 250-mL	each
Amperometric Titrator Assembly	each
Beaker, low-form, 250-mL	each
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each
Acetate Buffer Solution, pH 4.0	100 mL MDB
Potassium Iodide Powder Pillows	100/pkg
TitraStir® Mixer/Stand Assembly, 115 or 230 VAC	each
Pipet, Volumetric, Class A, 1-mL	each
Pipet Filler	each
Sodium Thiosulfate Standard Solution, 0.00564 N	100 mL
Probe Assembly, Amperometric Titrator	each
Delivery Tubes, 90° with hook	5/pkg

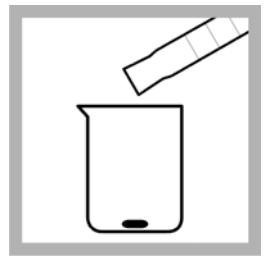
See *Consumables and replacement items* for reorder information.

Part 1—Adjusting the electrode response slope

1. Install the Standard Iodine Titrant Cartridge, 0.028 N. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

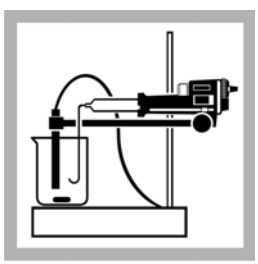


2. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.

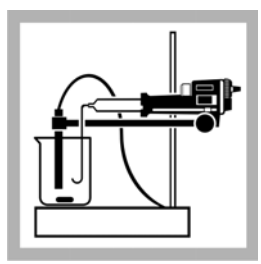


3. Use a graduated cylinder to measure 200 mL of deionized water into a clean 250-mL beaker. Place the 50-mm stirring bar into the beaker.

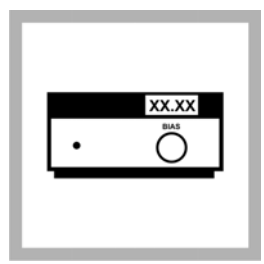
4. Add 1 mL of pH 4 Acetate Buffer and the contents of one Potassium Iodide Pillow.



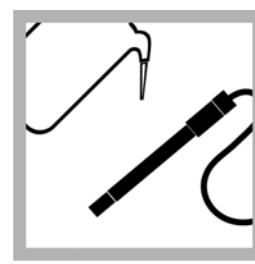
5. Place the beaker on the TitraStir stand and immerse the tips of both the probe and the delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



6. Use the Digital Titrator delivery knob to add 50 digits of Standard Iodine Titrant Solution.



7. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control knob until a stable reading between 0.50 and 0.60 is obtained. Lock the bias control.

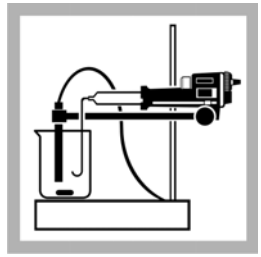


8. Remove the probe arm from the beaker and rinse the platinum wires with deionized water. Discard the sample.

The adjustment of the electrode response slope is complete.

Part 2—Standardization of the Iodine Titrant

1. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.



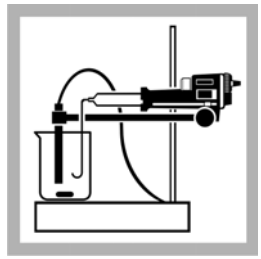
2. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.

3. Use a graduated cylinder to measure 200 mL of deionized water into a clean 250-mL beaker. Place the 50-mm stirring bar into the beaker.

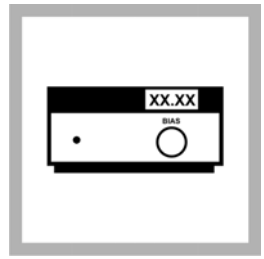
4. Use a Class A pipet to transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the beaker. Swirl to mix.

Alternatively, use 0.00564 N Phenylarsine Oxide (PAO) (Catalog No. 199942) instead of sodium thiosulfate.

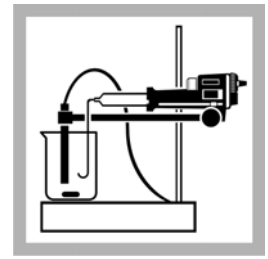
5. Add 1 mL of pH 4 Acetate Buffer Solution and the contents of one Potassium Iodide Powder Pillow.



6. Place the beaker on the TitraStir stand and immerse the tips of both the probe and the delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.

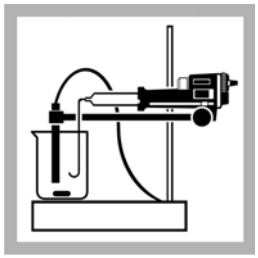


7. Note the LED reading on the Amperometric Titrator. It should read 0.00 ±0.05. **DO NOT** adjust the bias control.



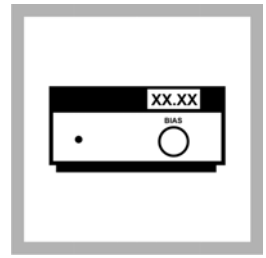
8. Using the Digital Titrator delivery knob, dispense 100 digits of Standard Iodine Titrant Solution and note the reading.

Part 2—Standardization of the Iodine Titrant (continued)

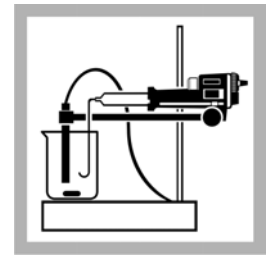


9. Continue dispensing titrant in five to ten digit increments while noting the reading.

10. Record at least three points (the null current values) before the end point is reached.

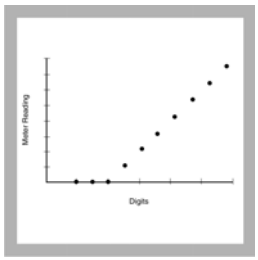


11. After the end point of the titration (nominal 160 digits), record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter.

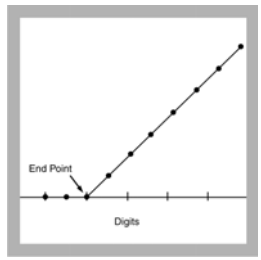


12. Add five to ten digits of titrant and wait a few seconds for a stable reading. Record it.

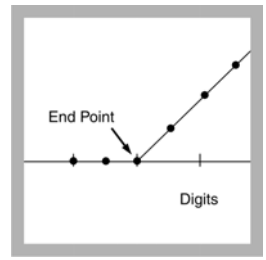
Stop adding titrant when the LED readings exceed 0.60. LED readings above 0.60 will be excessively noisy.



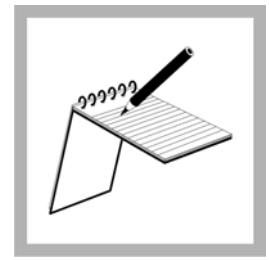
13. Use a linear graph paper to plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis.



14. Draw the two best intersecting lines through the plotted points as shown above.



15. Determine the number of digits at the intersection of the lines. That is the standard end point.



16. Record the standard end point digits value. Find the multiplier from the *Digit multipliers* table. This multiplier will be used to calculate the sample chlorine concentration.

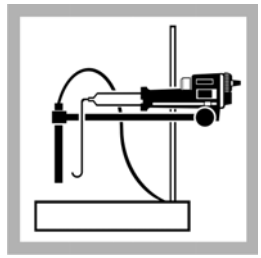
Discard the sample.

Table 127 Digit multipliers

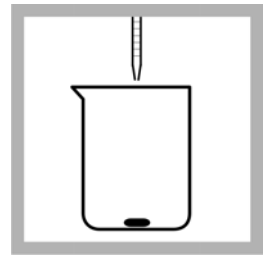
Digits (standard end point)	Multiplier
160	6.25
165	6.06
170	5.88
175	5.71
180	5.56
185	5.40
190	5.26
195	5.13
200	5.00

Part 3—Titration of sample for total residual Chlorine

1. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.



2. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.



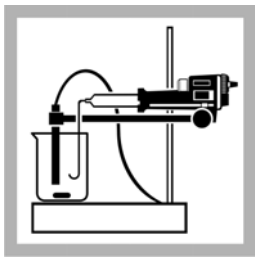
3. Place a clean, 50-mm stir bar into a clean 250-mL beaker. Use a Class A pipet to transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the beaker.

Alternatively, use 0.00564 N Phenylarsine Oxide (PAO) (Catalog No. 199942) instead of sodium thiosulfate.

4. Add 1 mL of pH 4 Acetate Buffer Solution to the beaker. Then add 200 mL of the sample to the beaker.

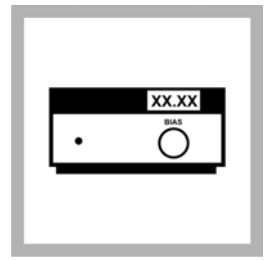
Minimize agitation when adding the sample.

Swirl to mix.

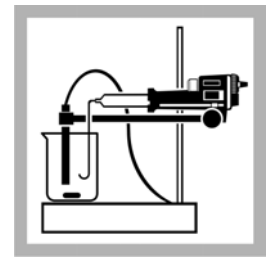


5. Place the beaker on the TitraStir stand and immerse the tips of both the probe and the delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.

6. Add the contents of one Potassium Iodide Reagent Power Pillow to the beaker and allow the powder to dissolve.



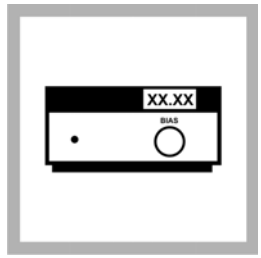
7. Note the LED reading on the Amperometric Titrator. It should read 0.00 ±0.05. **DO NOT** adjust the bias control.



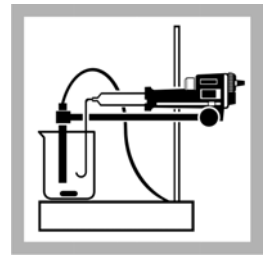
8. Using the Digital Titrator delivery knob, dispense Standard Iodine Titrant Solution in five to ten digit increments while noting the reading.

Part 3—Titration of sample for total residual Chlorine (continued)

9. Record at least three points (the null current values) before the end point is reached.

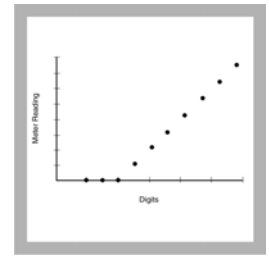


10. After the end point of the titration is reached, record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter.

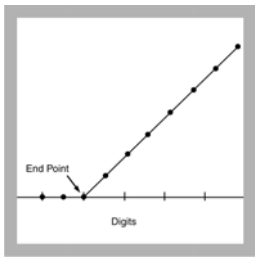


11. Add five to ten digits of titrant and wait a few seconds for a stable reading. Record it.

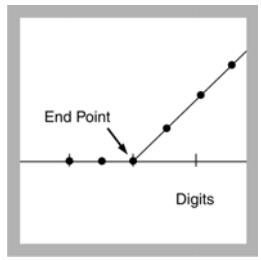
Stop adding titrant when the LED readings exceed 0.60. LED readings above 0.60 will be excessively noisy.



12. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis.



13. Draw the two best intersecting lines through the plotted points as shown above.



14. Determine the number of digits at the intersection of the lines. That is the sample end point.

15. Calculate the µg/L total chlorine:

[Digits (Standard End Point) – Digits (Sample End Point)] x Multiplier = µg/L Cl_2

Use the multiplier from *Part 2—Standardization of the Iodine Titrant*, step 16.

Interpolation between values in the table is not necessary.

Example:
Standard EP = 160 digits
Sample EP = 150 digits
Multiplier = 6.25, so:

µg/L total chlorine [160 – 150] x 6.25 = 62.5, or 63 (round up)

Table 128 Interfering substances

Interfering substance	Interference
Silver ions	Silver ions poison the electrode
Copper ions	Interfere by plating on the electrode.
Turbid water	Interferences are sometimes found in highly turbid water and those containing surface active agents
Oxidized manganese	Oxidized manganese and other oxidizing reagents give positive interferences.
Samples containing high organic content.	Some uncertainty in the end point may be observed with samples containing high organic content.
Iron and nitrite	Iron and nitrite interference are minimized by buffering to pH 4 before adding potassium iodide.
Buffered samples or sample pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the buffer reagent. If necessary, add additional buffer and check pH of sample prior to titration.
Dechlorinating agents	In samples that contain excess dechlorinating agents, such as sulfur dioxide, sulfite or bisulfite, the titration end point (number of digits) will be greater than the number of digits obtained during the standardization. It is not necessary to continue the titrant addition if the number of digits used in the sample titration exceeds that calculated for the standardization end point. This indicates that no free or combined chlorine is present in the sample.

Sample collection, preservation and storage

Chlorine is rapidly lost from water. Avoid exposure to sunlight or other strong light. Avoid excessive agitation. Analyze samples immediately or fix the sample by pre-addition of standard thiosulfate and buffer. To fix the sample:

1. Pipet 1.00 mL of 0.00564 N Sodium Thiosulfate and add 1.0 mL of Acetate Buffer into a clean, dry glass sampling bottle (e.g. BOD bottle).
2. At the sample site, measure 200 mL of sample with a graduated cylinder and transfer to the sampling bottle. Swirl to mix.
3. Before analysis, quantitatively transfer the entire contents of the sampling bottle to the 250-mL beaker. Minimize delay between sampling and analysis (1 hour maximum) to prevent decomposition of thiosulfate in the sample. (This fixing technique is not acceptable for USEPA compliance monitoring and should be used for brief transportation delays—not for sample storage.)
4. Start the analysis in *Part 3—Titration of sample for total residual Chlorine* at step 5.

Accuracy check

Use the bias control prior to performing the analysis to adjust the electrode sensitivity. Set the bias adjustment by adding a known amount of standard iodine titrant to deionized water and adjusting the bias control to a given value on the display. The electrode sensitivity will vary depending on the probe conditioning. Adjustment should be made at least daily or before each series of samples.

The iodine titrant concentration is approximately 0.0282 N, which relates to 160 digits needed to titrate 1.00 mL of 0.00564 N Thiosulfate. If the calculated end point is greater than 160 digits, this indicates that the Standard Iodine Titrant is weaker than when packaged. Discard the Standard Iodine Titrant cartridge if the calculated standard end point in *Part 2—Standardization of the Iodine Titrant* is greater than 200 digits.

To preserve the strength of the iodine titrant solution, always remove the delivery tube from the Digital Titrator cartridge and replace the cap when not in use. Protect the iodine titrant solution from direct sunlight.

Standard additions method (sample spike)

Note: *Standard additions is not applicable for samples containing excess reducing agents such as sulfur dioxide, sulfite, or bisulfite.*

Required for accuracy check:

- Chlorine Standard Solution Ampule
- TenSette Pipet and tips

1. Snap the top off a Chlorine Standard Solution Ampule. Note the certificate concentration of the standard in mg/L.
2. Split a fresh sample into two 200-mL portions.
3. Using a TenSette Pipet (Catalog number 1970001), add 0.1 to 0.5 mL of the standard to one portion and swirl to mix. This is the spiked sample.
4. Analyze both the sample and spiked sample and record the chlorine concentration of each.
5. Calculate the theoretical concentration of the spiked sample:

$$\text{Theoretical concentration} = \frac{(C_u \times V_u) + (C_s \times V_s)}{V_u + V_s}$$

Where:

C_u = measured concentration of sample, in mg/L (µg/L divided by 1000)

V_u = volume of sample

C_s = concentration of chlorine standard (mg/L, certificate value)

V_s = volume of standard added

6. Calculate the percent spiked recovery:

$$\text{\% Spike recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}}$$

Example:

Sample result (C_u) = 120 µg/L or 0.120 mg/L

Spiked sample result = 185 µg/L or 0.185 mg/L

Volume Sample (V_u) = 200 mL

Volume Standard (V_s) = 0.2 mL

Chlorine Standard (C_s) = 68.1 mg/L

$$\text{Theoretical concentration} = \frac{(0.120 \times 200) + (68.1 \times 0.2)}{200 + 0.2} = 0.188 \text{ mg/L}$$

$$\text{\% Spike recovery} = \frac{0.185 \text{ mg/L}}{0.188 \text{ mg/L}} \times 100 = 98\%$$

Ideally, the percent recovery should be 100%. Generally, results from 80–120% recovery are considered acceptable.

Method performance

Precision
In a single laboratory, using a standard solution of 120 µg/L chlorine, a single operator obtained a standard deviation of ±19 µg/L chlorine.

Detection limit
The estimated detectable concentration is equivalent to one digit of 0.0282 N Standard Iodine Titrant Solution, or approximately 6 µg/L chlorine.

Summary of method

The back titration procedure minimizes errors caused by liberating the full concentration of iodine in the sample and is the preferred method for amperometric measurement for total chlorine in wastewaters. In this procedure, the end point signal is reversed because the remaining thiosulfate (or phenylarsine oxide) added to the sample is titrated with standard iodine. The end point of the back titration is reached just when free iodine exists in the sample resulting in a measurable polarization current. The end point is estimated by continued addition of titrant, recording of the current at each titrant addition, and graphing the data points. Where the best line between the data points intersects the null current, the number of digits (from the Digital Titrator) at the end point can be determined and the chlorine concentration calculated.

Consumables and replacement items

Required reagents

Description	Unit	Catalog number
Acetate buffer solution, pH 4.0	100 mL MDB	1490932
Potassium Iodide powder pillows	100/pkg	107799
Standard Iodine titrant solution, cartridge, 0.028 N	each	2333301
Sodium Thiosulfate standard solution, 0.00564 N	100 mL	2408842

Required apparatus

Description	Unit	Catalog number
Amperometric titrator assembly	each	1929900
Beaker, low-form, 250-mL	each	50046H
Cylinder, graduated, 250-mL	each	50846
Delivery tubes, 90° with hook	5/pkg	4157800
Digital titrator	each	1690001
Pipet, volumetric, Class A, 1-mL	each	1451535
Probe assembly, Amperometric titrator	each	1939000
Stir bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	2095355
TitraStir® mixer/stand assembly, 115 VAC OR TitraStir® mixer/stand assembly, 230 VAC	each	1940000 1940010

Recommended standards

Description	Unit	Catalog number
Chlorine standard solution Ampule, 50–75 mg/L	20/pkg	1426820
Water, demineralized, each	4 L	27256

Optional reagents and apparatus

Description	Unit	Catalog number
Pipet, TenSette, 0.1–1.0 mL	each	1970001
Pipet Tips, for 1970001	50/pkg	2185696

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