Chlorine, Free

DOC316.53.01220

Amperometric Forward Titration using 0.00564 N PAO[1]

Method 10024

(0 to 1000 µg/L Chlorine as Cl_2)

Digital Titrator

Scope and Application: For drinking water; USEPA Accepted for reporting

[1] Procedure is equivalent to Standard Method (18th ed.) 4500 Cl D for drinking water.

Test preparation

Before starting the test:

Make sure that the proper stir bar is used. The wrong size can cause the loss of chlorine, unstable readings and loss of method sensitivity, especially when measuring low level chlorine concentrations.
When a new probe is placed in service or when the probe has not been used recently, prepare it according to the Probe Stabilization instructions in the *Amperometric Titrator Instruction Manual*.

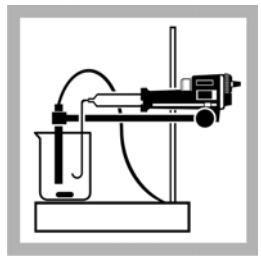
Collect the following items:

Description	Quantity
Amperometric Titrator assembly	each
Digital Titrator	each
Beaker, low-form, 250-mL	each
Stir bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each
Cylinder, graduated, 250-mL	each
TitraStir® mixer/stand assembly, 115 VAC	each
Probe Assembly, Amperometric Titrator	each
Delivery Tubes, 90° with hook	5/pkg
Phenylarsine Oxide Solution, 0.00564 N Digital Titrator Cartridge	each
Phosphate Buffer Solution, pH 7	1 bottle

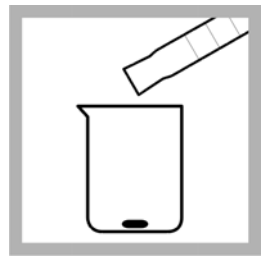
See *Consumables and replacement items* for reorder information.

Amperometric forward titration using 0.00564 N PAO

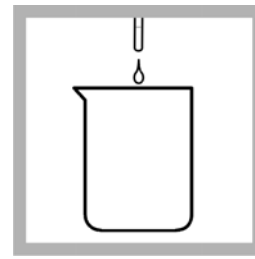
1. Install the 0.00564 N Phenylarsine Oxide (PAO) cartridge. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.



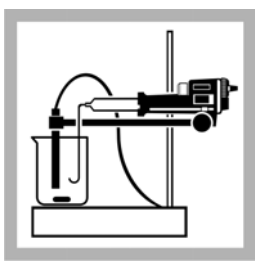
2. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.



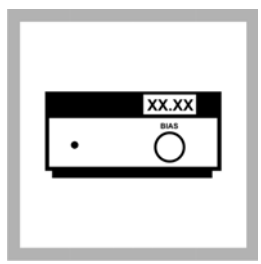
3. Without excessive agitation, measure 200 mL of sample with a clean graduated cylinder. Transfer the sample to a clean, 250-mL beaker containing the 50-mm stirring bar supplied with the system.



4. If the pH is less than 6 or greater than 7.5, add 1.0 mL of pH 7 Phosphate Buffer Solution to make the prepared sample.

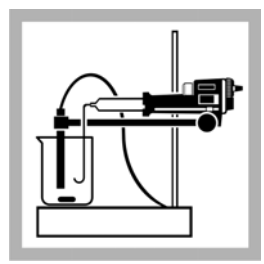


5. Place the beaker on the TitraStir® stand and immerse the tips of both the probe and the delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



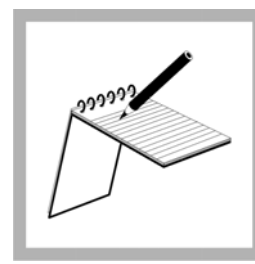
6. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control and adjust the BIAS control knob until a reading between 0.50 and 0.06 is obtained. Lock the bias control.

The BIAS adjustment controls the slope of the titration curve. The actual instrument reading is not important; the relative readings as the titration proceeds are important. A precise adjustment is not required.



7. Using the Digital Titrator delivery knob, dispense the PAO Titrant Solution in 5 to 10 digit increments while noting the downward reading.

If the chlorine content of the sample is high, add titrant at a faster rate.



8. As the end point of the titration is approached, record the LED readings along with the corresponding digits displayed on the Digital Titrator counter. Near the titration end point, add 2 to 5 digits of titrant; wait a few seconds for a stable reading and record.

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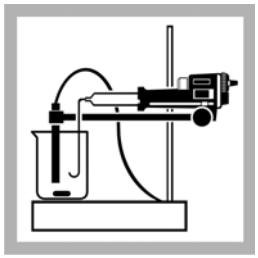
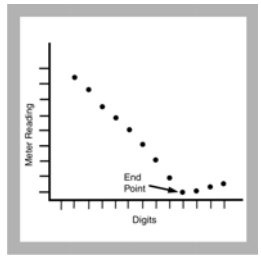
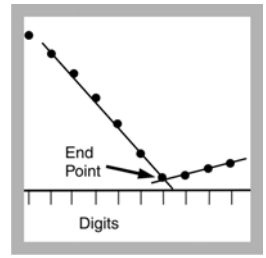


9. Continue the titration, recording at least three points on the downward sloping curve and at least three points after the end point is reached. The latter points will cause little change in the LED readings.



10. Use 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.



11. Draw the two best intersecting lines through the points plotted as shown above. Determine the number of digits at the intersection of the two lines. This is the end point.

12. Determine the mg/L free chlorine concentration:

Digits at end point x 1.25 = µg/L free chlorine as Cl_2

Interferences

Table 125 Interfering substances

Interfering substance	Interference
Silver ions	Silver ions poison the electrode.
Copper ions	Interfere by plating on the electrode
High turbid water	Turbid water containing surface active agents
Oxidized manganese and other oxidizing reagents	Positive interference
Samples containing organic content	Some uncertainty in the endpoint may be observed on samples with high organic content.
Samples containing reducing agents	Excess reducing agents, such as sulfur dioxide, sulfite and bisulfite, will cause either static, or increasing LED readings because no free chlorine is present; these samples cannot be titrated under the conditions of the test.
Buffered samples or extreme 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.

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.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Chlorine Standard Solution Ampule
- TenSette® Pipet and tips
- Fresh sample

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. Use a TenSette® Pipet to 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, a single operator used a standard solution of 338 µg/L chlorine to obtain a standard deviation of ±5.2 µg/L chlorine.

Detection Limit
With good operator technique, the estimated detectable concentration is approximately 15 µg/L chlorine using 0.00564 N PAO.

Summary of method

In the amperometric forward titration procedure for free chlorine, a small electrical current is applied across two identical platinum electrodes. No current can flow between the electrodes unless a substance that can be oxidized at the anode and a substance that can be reduced at the cathode are both present. In the case of the free chlorine titration with phenylarsine oxide (PAO), chlorine is reduced to chloride at the cathode due to the addition of PAO, and PAO is oxidized from the +3 oxidation state to the +5 oxidation state at the anode. Prior to the end point of the titration, both free chlorine and chloride are present in solution; allowing current to flow, even with a very small applied potential. At the end point, no free chlorine remains and the solution cannot conduct even if excess PAO titrant is added. The end point is defined when no change in current occurs, signaling all free chlorine has been reacted.

Consumables and replacement items

Required reagents

Description	Unit	Catalog number
Phenylarsine Oxide Solution, 0.00564 N Digital Titrator Cartridge	each	199901
Phosphate Buffer Solution, pH 7	100 mL MDB	2155332

Required apparatus

Description	Unit	Catalog number
Amperometric Titrator Assembly	each	1929900
Digital Titrator	each	1690001
Beaker, low-form, 250-mL	each	50046H
Cylinder, graduated, 250-mL	each	50846
Delivery Tubes, 90° with hook	5/pkg	4157800
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

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