19300-08

Amperometric Titrator

Model 19300

al/dp 04/98 5ed

TRADEMARKS OF HACH COMPANY

AccuVac®
ACS-Plus™
AgriTrak™
AluVer®
AmVer™
APA 6000™
AquaTrend®
BariVer®
BiVer™
BoroTrace™
BODTrak™
BoroVer®
CalVer®
ChromaVer®
CuVer®
CyaniVer®
Digesdahl®
DithiVer®
FerroVer®
FerroMo™
FerroZine®
Formula 2533™
Formula 2589™
Gelex®
HachLink™
Hach.com™
Hach Logo®
Hach One®
Hach Oval®
HexaVer®
HgEx™
HydraVer®
IncuTrol®
LeadTrak®
m-ColiBlue 24®
ManVer®
MercuVer®
MolyVer®
Mug-O-Meter®
NTrak®
NitraVer®
NitriVer®
OriFlo™
PathoScreen™
PbEx™
PermaChem®
PhosVer®
Pocket Colorimeter™
Pocket Turbidimeter™
Pocket Pal™
PourRite™
ProNetic™
Pump Colorimeter™
Rapid Liquid™
RapidSilver™
Ratio™
RegeneVer™
RoVer®
Spec√™
StablCal™
StannaVer®
StillVer®
SulfaVer®
Surface Scatter®
TanniVer®
TenSette®
Test ’N Tube™
TitraStir®
TitraVer®
ToxTrak™
UniVer®
VIScreen™
Voluette®
WasteAway™
ZincoVer®

SAFETY PRECAUTIONS

Before attempting to unpack, set up, or operate this instrument, please read this entire manual. Pay particular attention to all warnings, cautions and notes. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure the protection provided by this equipment is not impaired, this equipment MUST NOT be installed or used in any manner other than that which is specified in this manual.

Use of Hazard Information

If multiple hazards exist, the signal word corresponding to the greatest hazard shall be used.

DANGER
Indicates a potentially or imminently hazardous situation which, if not avoided, could result in death or serious injury

CAUTION
Indicates a potentially hazardous situation that may result in minor or moderate injury

NOTE
Information that requires special emphasis

Precautionary Labels

Please pay particular attention to labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.

⚠ **This symbol, if noted on the instrument, references the instruction manual for operational and/or safety information.**

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SPECIFICATIONS

Amperometric Titrator

Electrode: Pt-Pt electrode

Electrode Potential: - 25 to -735 mV

Display: 2 1/2 Digit LED, 0.3 in. digits

Display Range: ±1.99 µA ±2%

Power Requirement: 115 Vac/230 Vac ±17%, 50/60 Hz, 12 VA

Operating Temperature: 0 to 50 °C (32 to 122 °F), non-condensing

Storage Temperature: -2 to 60 °C (28 to 140 °F)

Recorder Output Range: ±199.9 mV

Recorder Impedance: 10 Kohm or greater

Recorder Accuracy: Zero shift = ±0.2 mV; Span = ±2% of output

Size: 22.8 x 9.5 x 19.6 cm (9 x 3.75 x 7.75 in.)

Case: Epoxy painted steel

TitraStir Stir Plate

Stirring Speed: About 300 rpm at 60 Hz; 250 rpm at 50 Hz

Largest Stirring Magnet Size: 5 cm (2 in.)

Power Requirements:
Model 19400-00: 103 to 127 VAC, 50-60 Hz, 20 VA max
Model 19400-10: 207 to 253 VAC, 50-60 Hz, 20 VA max

Operating Temperature: 0 to 50 °C (32 to 122 °F)

Storage Temperature: -2 to 60 °C (28 to 140 °F)

Dimensions:
Case: 22.8 x 15.2 x 9.6 cm (9 x 6 x 3 in.)Rod Height: 26.6 cm (10.5 in.)

Analytical Specifications

Procedure	Analysis Range (as Cl_2)	EDL* (as Cl_2)	Estimated Precision**	Free/Total Chlorine	Method #
Forward Titrations:					
Digital Titrator	0-1000 µg/L	15 µg/L	1%	Free and Total	10024, 10026
	0-10 mg/L	0.05 mg/L	1%	Free and Total	8335, 8314
Buret	0-5 mg/L	0.05 mg/L	1-2%	Free and Total	8334, 8168
Back Titration:					
Digital Titrator	6-1000 µg/L	6 µg/L	15%	Total	10025

* Estimated Detection Limit (typical)

** Estimated Precision = % relative standard deviation with good operator technique

OPERATION

DANGER

Handling chemical samples, standards, and reagents can be dangerous. Review the necessary Material Safety Data Sheets and become familiar with all safety procedures before handling any chemicals.

PELIGRO

La manipulación de muestras químicas, patrones y reactivos puede ser peligrosa. Antes de manipular cualquier productor químico, conviene leer las Fichas Técnicas de Seguridad y familiarizarse con los procedimientos de sugeridad.

PERIGO

A manipulação de amostras, padrões e reagentes químicos pode ser perigosa. Reveja as necessárias Fichas Técnicas de Segurança do Material e familiarizese com os procedimentos de segurança antes de manipular quaisquer substãncias químicas.

DANGER

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les fiches de données de sécurité des produits nécessaires et se familiariser avec toutes les procédures de sécurité avant de manipuler tout produit chimique.

GEFAHR

Da das Arbeiten mit chemikalischen Proben, Standards, Reagenzien und Abfällen mit Gefahren verbunden ist, empfiehlt die Hach Company dem Benutzer dieser Produkte dringend, sich vor der Arbeit mit sicheren Verfahrensweisen und dem richtigen Gebrauch der Chemikalien oder Biogefahrgut vertraut zu machen und alle entsprechenden Materialsicherheitsdatenblätter aufmerksam zu lesen.

SECTION 1 GENERAL INFORMATION

1.1 Chlorine Measurement by Amperometric Titration

1.1.1 Forward Titration

Amperometry is an electrochemical technique where a small electrical voltage is applied across two electrodes through a solution. The chemical reaction during the titration causes a change in current. Amperometric titration measures the current change as titrant is added. Typical instrumentation for amperometric titration include:

- Probe or cell which contains dual platinum electrodes (biamperometric) or two dissimilar electrodes (i.e., silver/platinum)
- Microampere meter
- Titrant dispensation device.

In the amperometric determination of free chlorine, chlorine (existing as either hypochlorous acid or hypochlorite ion) is titrated with a standard reducing agent, such as phenylarsine oxide (PAO), at a neutral pH. A small potential is applied across the electrodes before the titration starts. Current cannot 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. During the titration, chlorine is reduced at the cathode to chloride (Cl^-) from the reaction with PAO. PAO is oxidized from the +3 to the +5 oxidation state at the anode:

$PhAsO + Cl_2 + 2H_2O \rightarrow PhAsO(OH)_2 + 2Cl^- + 2H^+$

(Ph = phenyl)

As long as oxidant (free chlorine) is present in the sample, a current will flow through the cell. When all of the oxidant is reacted, the rate of current change is zero, signifying the titration endpoint. After the endpoint is reached, the solution cannot conduct current even though excess PAO is added. The amount of PAO used at the titration endpoint is proportional to the sample chlorine concentration.

In the case of chloramine determination, the pH is lowered to 4 and potassium iodide is added to convert the chloramine species to an equivalent amount of triiodide ion:

$NH_2Cl + 3I^- + H_20 + H^+ \rightarrow NH_4OH + Cl^- + I_3^-$

(monochloramine)

$NHCl_2 + 3I^- + H_20 + 2H^+ \rightarrow NH_4OH + 2Cl^- + I_3^-$

(dichloramine)

The triiodide is titrated with PAO with the current change measured amperometrically:

$PhAsO + I_3^- + 2H_2O \rightarrow 3I^- + PhAsO(OH)_2 + 2H^+$

(Ph = phenyl)

1.1.2 Back Titration

The direct amperometric titration of chlorine or chloramines with a standard reducing agent is known as a “forward” titration. For waters which contain potential chemical interferences, a “back-titration” for total chlorine is recommended. In the back titration procedure, a known excess amount of thiosulfate (or PAO) is added to the sample at pH 4 with an excess of iodide. The thiosulfate (or PAO) reacts with the free chlorine and chloramines present. The amount of unreacted thiosulfate (or PAO) is titrated with a standard iodine solution. The total chlorine is then calculated based on the thiosulfate left in the sample. The back amperometric endpoint is signaled when free iodine (triiodide ion) is present, which is indicated by a current flow between the electrodes. The chemical reactions are:

$Cl_2 + 2S_2O_3^{2-} \rightarrow 2Cl^- + S_4O_6^{2-}$

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

The back titration method is popular in wastewater laboratories because:

- The sample chlorine can be "fixed" at the sampling site with the addition of excess reductant.
- Since the endpoint is reversed, there is less interference from iodine-demand substances in the sample.

Performing amperometric titration requires more skill and care than the colorimetric methods for chlorine analysis. *Standard Methods** states the amperometric method “is the standard of comparison for the determination of free or combined chlorine”. However, the amperometric method is no longer accepted by International Standards Organization (ISO) for the determination of chlorine species. Considerable conflicting information exists about interferences with the amperometric methods for chlorine in treated wastewaters and effluents *(see Section 5* and *Current Technology of Chlorine Analysis for Water and Wastewater* [literature number 7019]).

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* *Standard Methods for the Examination of Water and Wastewater*, 18th edition, Section 4500-Cl A.3.a.

Figure 1 Digital Amperometric Titrator System

1.2 Hach Amperometric Systems

Hach offers both forward and backward amperometric methods for determining free and total chlorine in water. Hach's Amperometric Titrator, Model 19300, *Figure 1*, is based on a biamperometric system using a dual platinum electrode (DPE) probe. Hach's titrator meter displays the actual current in microamperes measured by the DPE. The amount of applied potential is adjustable using a “bias” control.

The titrant is metered into the sample using Hach's Digital Titrator (DT), a precise dispensing device with a digital counter for monitoring titrant delivery. Dispensing accuracy is rated at 1% for titrations over 100 digits and within 1 digit for titrations of 100 digits or less.

Hach offers three systems for the amperometric determination of chlorine species in water:

- Forward Titration for Free and Total Chlorine using the Digital Titrator
- Forward Titration for Free and Total Chlorine using a Glass Buret
- Back Titration for Total Chlorine using the Digital Titrator

The forward Digital Titrator procedures use PAO titrant packaged in disposable plastic cartridges. Each cartridge contains approximately 13 mL of titration solution, sufficient for 60 to 120 average titrations, depending on the chlorine concentration in the samples. The high range procedure (0-10 mg/L Cl_2), uses 0.0451N PAO in which 1 digit of the Digital Titrator equates to 0.01 mg/L Cl_2. The low range procedure (0-1000 µg/L Cl_2) uses 0.00564N PAO which equates to 1.25 µg/L Cl_2 per digit.

A 5-mL glass buret system is also available which also uses 0.00564N PAO. This system dispenses the titrant in accordance with Standard Methods 4500-Cl-D.2*. The buret method has a range of 0-5 mg/L Cl_2 with a detection level of about 0.05 mg/L Cl_2.

Hach's back titration system uses 0.0282N standard iodine titrant, which is packaged into a special chemical resistant Digital Titrator cartridge. The test range for this procedure is 6-1000 µg/L total chlorine.

To select the correct amperometric procedure for your application, use the Procedure Selection Flow Chart, *Figure 2,* which shows only methods accepted by the U.S. Environmental Protection Agency (USEPA). With micro-dispensation of the titrant and graphical determination of the end-point, lower detection levels are possible with Hach's Amperometric Titration system compared to any other commercial amperometric system. Estimated detection limits (EDL) using the Digital Titrator for Hach's forward titration procedures are about 15 µg/L (as Cl_2) and approximately 6 µg/L Cl_2 for the back-titration procedure. For general information about chlorine testing, see *Current Technology of Chlorine Analysis for Water and Wastewater* (literature number 7019).

Typical titration plots for Hach's forward and back amperometric procedures using the Digital Titrator are shown in *Figure 3* and *Figure 4* on page *8*. As the endpoint is approached, deliver titrant in small amounts, usually 5 to 10 digits, and record the microamp reading after each addition. Record at least 3 points before and 3 points after the endpoint. The endpoint is determined by the intersection of the two best lines through the points. The number of digits (titrant volume) is multiplied by a factor to obtain the sample chlorine concentration.

Hach's amperometric titration methods meet the testing guidelines for measuring chlorine in accordance with the U.S. National Drinking Water Regulations and the National Pollutant Discharge Elimination System (NPDES) compliance monitoring programs.

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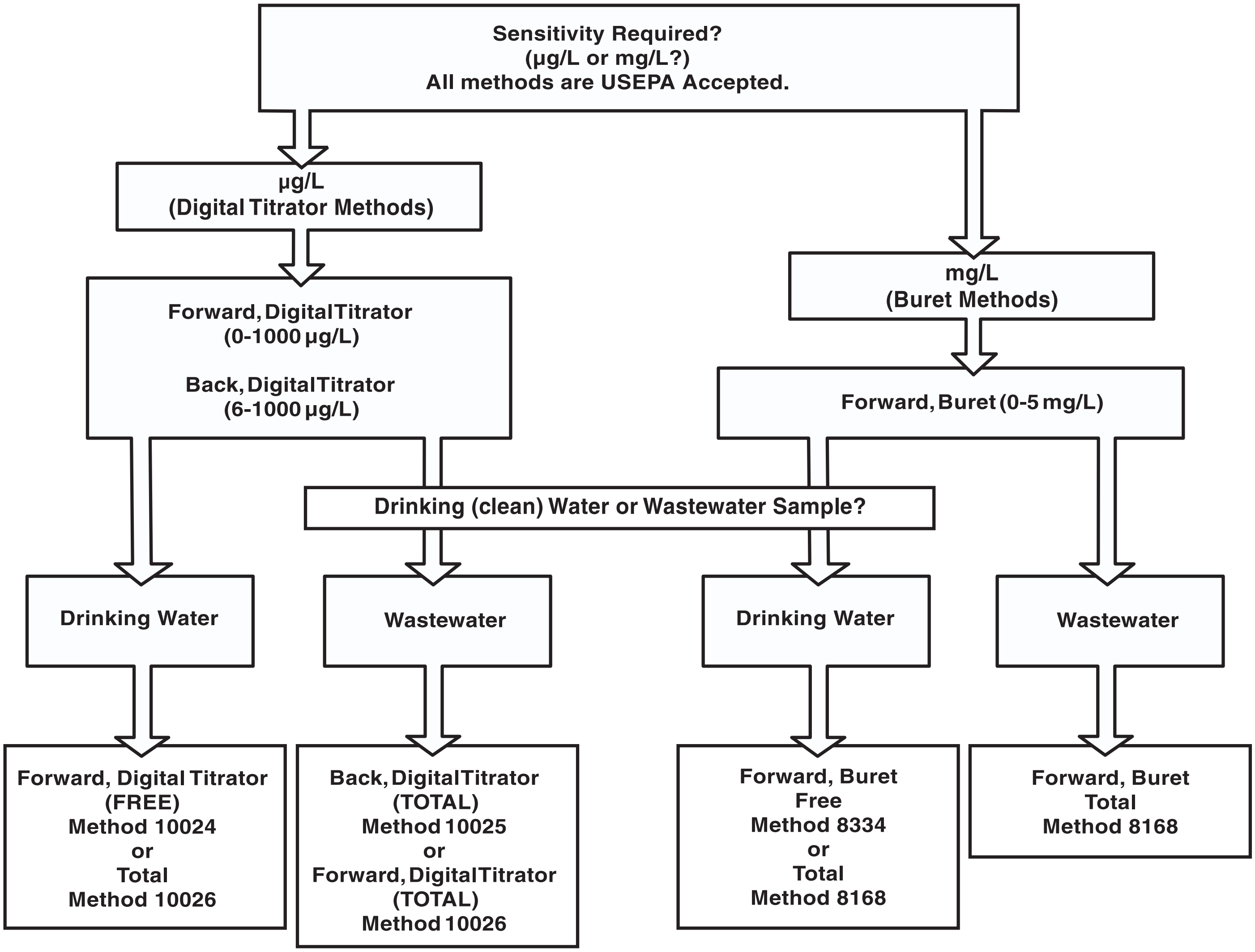
* *Standard Methods for the Examination of Water and Wastewater*, 18th edition, Section 4500-Cl D.2, page 4-42.

Figure 2 Procedure Selection Flow Chart*



1.2.1 Amperometric Titrator

The Amperometric Titrator is an analytical laboratory instrument for the electrical determination of titration end points. A 2 ½-digit LED indicator displays the current in microamperes measured by the dual platinum electrode in the sample. The front panel BIAS control adjusts the potential between the two platinum electrodes. A 0-100 mV recorder output lets the operator see the titration and identify the endpoint on a recorder chart rather than manually plotting the endpoint on graph paper. Using a recorder is not recommended for the low range or buret procedures.

The instrument operates on either 115- or 230-volt power by selecting the appropriate switch position with the rear panel switch. Appropriate fuses for both settings are supplied.

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* Hach has determined that “Hach Equivalent” methods meet or exceed specification criteria of the equivalent USEPA-approved methods.

1.2.2 TitraStir Stir Plate

This unit consists of a constant-speed magnetic stirrer with a support rod and holder assembly designed specifically for the Hach Digital Titrator. In addition to the Digital Titrator, the holder assembly can suspend up to three electrodes. Both 115- and 230-volt units are available.

Figure 3 Forward Amperometric Titration

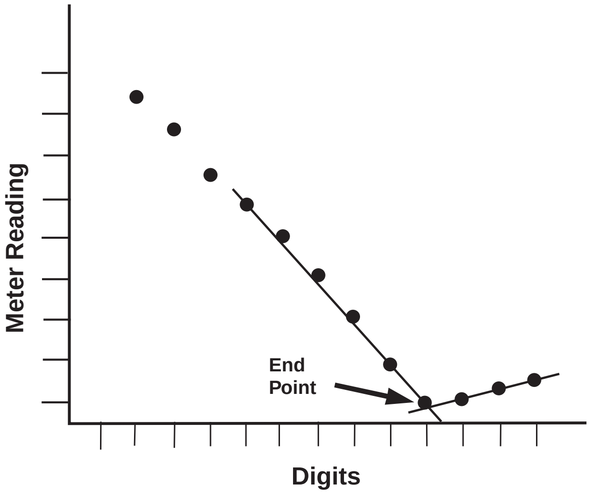
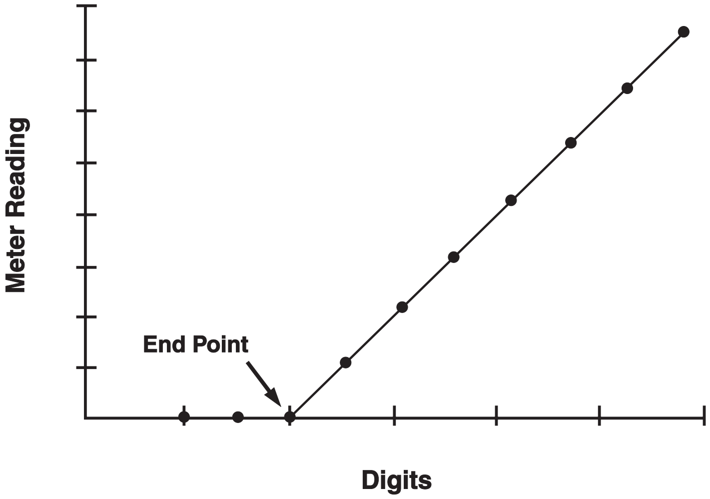


Figure 4 Back Amperometric Titration



SECTION 2 PREPARATION FOR USE

2.1 Unpacking

Remove the instrument and accessories from the shipping cartons and inspect each item for any damage that may have occurred during shipment. Verify from the appropriate system listing below that your order is complete (catalog numbers are in parentheses).

2.1.1 Amperometric Digital Titrator Systems

2.1.1.1 Forward Digital Titrator System for Free and Total Chlorine, Cat. No. 19300-00 (115 Vac) or Cat. No. 19300-02 (230 Vac)

- Amperometric Titrator (19299-00)—includes power cord, 1/8-amp fuse, 1/16-amp fuse, recorder cable plug, probe assembly.
- TitraStir Stir Plate (19400-00 or 19400-10)—includes power cord, electrode holder, support rod with washer, instruction sheet.
- Digital Titrator (16900-01)—with delivery tubes, methods manual.
- Delivery Tubes (5), 90° with hook (41578-00)
- Stirring Bar, 50-mm (20953-55).
- Graduated Cylinder, 250 mL (508-46)
- Beaker, 250-mL (500-46)
- Potassium Iodide Powder Pillows, 100 (1077-99)
- Acetate Buffer Solution, pH 4, 100 mL (14909-32)
- Phosphate Buffer Solution, pH 7, 100 mL (21553-32)
- Phenylarsine Oxide (PAO) Titration Cartridge, 0.0451 N (21420-01)
- Phenylarsine Oxide (PAO) Titration Cartridge, 0.00564 N (1999-01)
- Instruction Manual (19300-08)

2.1.1.2 Back Digital Titrator System for Total Chlorine, Cat. No. 19300-20 (115 Vac) or Cat. No. 19300-22 (230 Vac)

- Amperometric Titrator (19299-00)—includes power cord, 1/8-amp fuse, 1/16-amp fuse, recorder cable plug, probe assembly.
- TitraStir Stir Plate (19400-00 or 19400-10)—includes power cord, electrode holder, support rod with washer, instruction sheet
- Digital Titrator (16900-01)—with delivery tubes, methods manual
- Delivery Tubes (5), 90° with hook (41578-00)
- Stirring Bar, 50-mm (20953-55)
- Graduated Cylinder, 250-mL (508-46)

- Beaker, 250-mL (500-46)
- Pipet, Class A, 1.0-mL (14515-35)
- Potassium Iodide Powder Pillows, 100 (1077-99)
- Acetate Buffer Solution, pH 4, 100 mL (14909-32)
- Standard Iodine Titrant Solution, 0.028 N (23333-01)
- Sodium Thiosulfate, 0.00564 N (24088-42)
- Instruction Manual (19300-08)

2.1.1.3 Glassware System for Free and Total Chlorine, Cat. No. 19300-10 (115 Vac) or Cat. No. 19300-12 (230 Vac)

- Amperometric Titrator (19299-99)—includes power cord, 1/8-amp fuse, 1/16-amp fuse, recorder cable plug, probe assembly.
- TitraStir Stir Plate (19400-00 or 19400-10)—includes power cord, electrode holder, support rod with washer, instruction sheet.
- Automatic Buret, Class A, 5-mL (20550-37)
- Buret Holder, double (328-00)
- Stirring Bar, 50-mm (20953-55)
- Graduated Cylinder, 250-mL (508-46)
- Beaker, 250-mL (500-46)
- Support Stand (563-00)
- Potassium Iodide Powder Pillows, 100 (1077-99)
- Acetate Buffer Solution, pH 4, 100 mL (14909-32)
- Phosphate Buffer Solution, pH 7, 100 mL (21553-32)
- Phenylarsine Oxide (PAO) Standard Solution, 0.00564 N (1999-42)
- Instruction Manual (19300-08)

2.2 Assembly

2.2.1 Digital Amperometric Titrator System

Figure 1 on page *5* illustrates the digital amperometric titration system. A recorder may be used to automatically plot the titrations, rather than graphing the results manually. Using a recorder is not recommended for the low range or buret procedures.

1. Check the voltage selector switch on the rear panel of the instrument. Verify it is in the correct position for the line voltage to be used. The switch is set for 115 volt operation at the factory and must be reset for 230 volt operation. If the switch is reset for 230 volts, replace the 1/8-amp fuse with the 1/16-amp fuse.

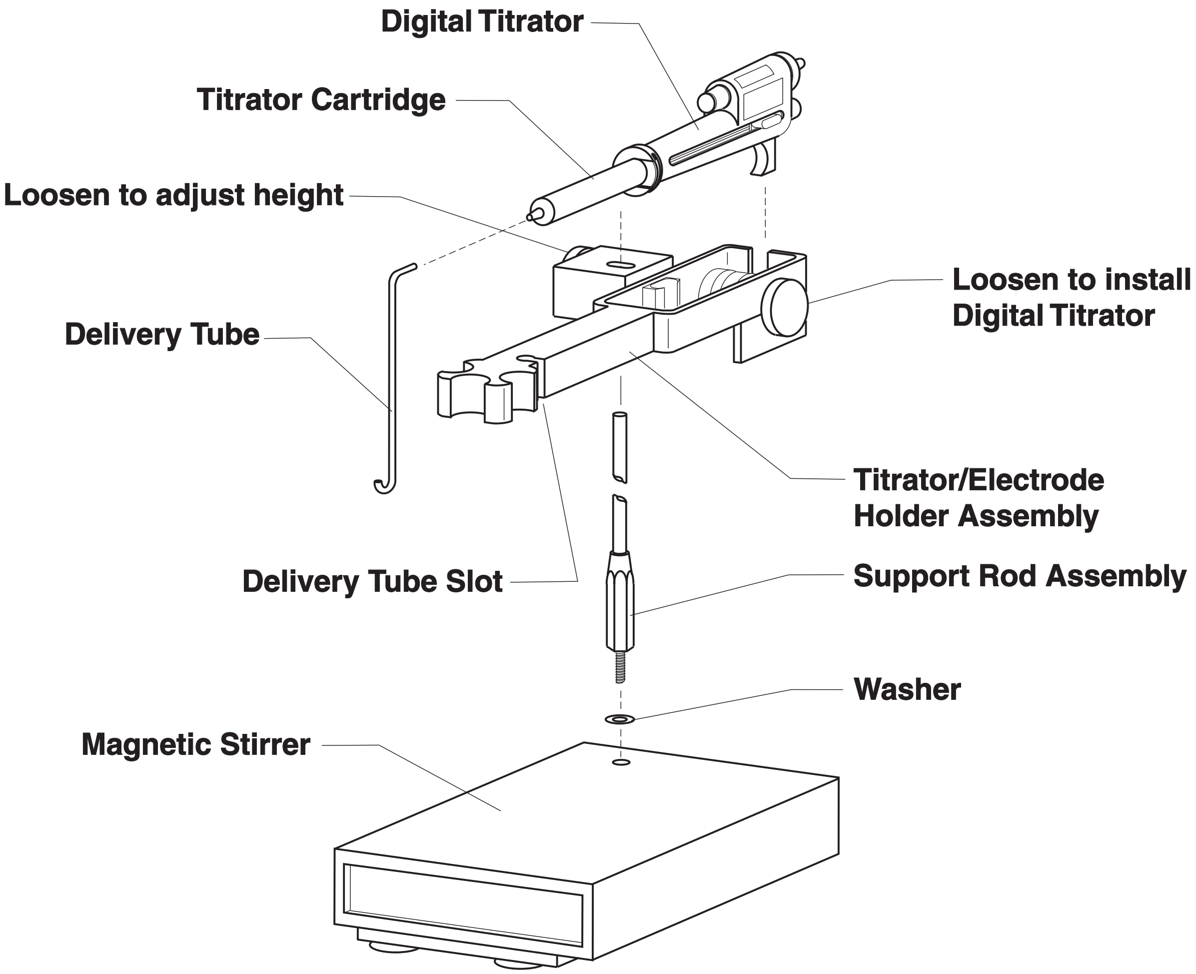
Caution
Power must be off when resetting the voltage selector switch. Improper setting of the power conversion switch can cause serious damage to the instrument if the instrument is turned on.

2. Connect the power cord and electrode assembly to the rear panel receptacles. If using a recorder, connect its cable to the recorder plug supplied.

3. Assemble the TitraStir Stir Plate as shown in *Figure 5*. Use the fiber washer supplied with the unit and tighten the rod with a 1/2-inch wrench.

4. Connect the power cord.

Figure 5 TitraStir Stir Plate



5. Attach the appropriate titration cartridge to the Digital Titrator. Slide the cartridge into the titrator receptacle and lock in position with a quarter turn. Remove the plastic cap from the cartridge tip and insert one of the 90° delivery tubes. Do not insert past the cartridge extension.

Note: *The delivery tubes supplied with the Digital Amperometric Titrator System and pictured in Figure 5 are specially designed for this application and differ from the standard delivery tubes in the Digital Titrator carton.*

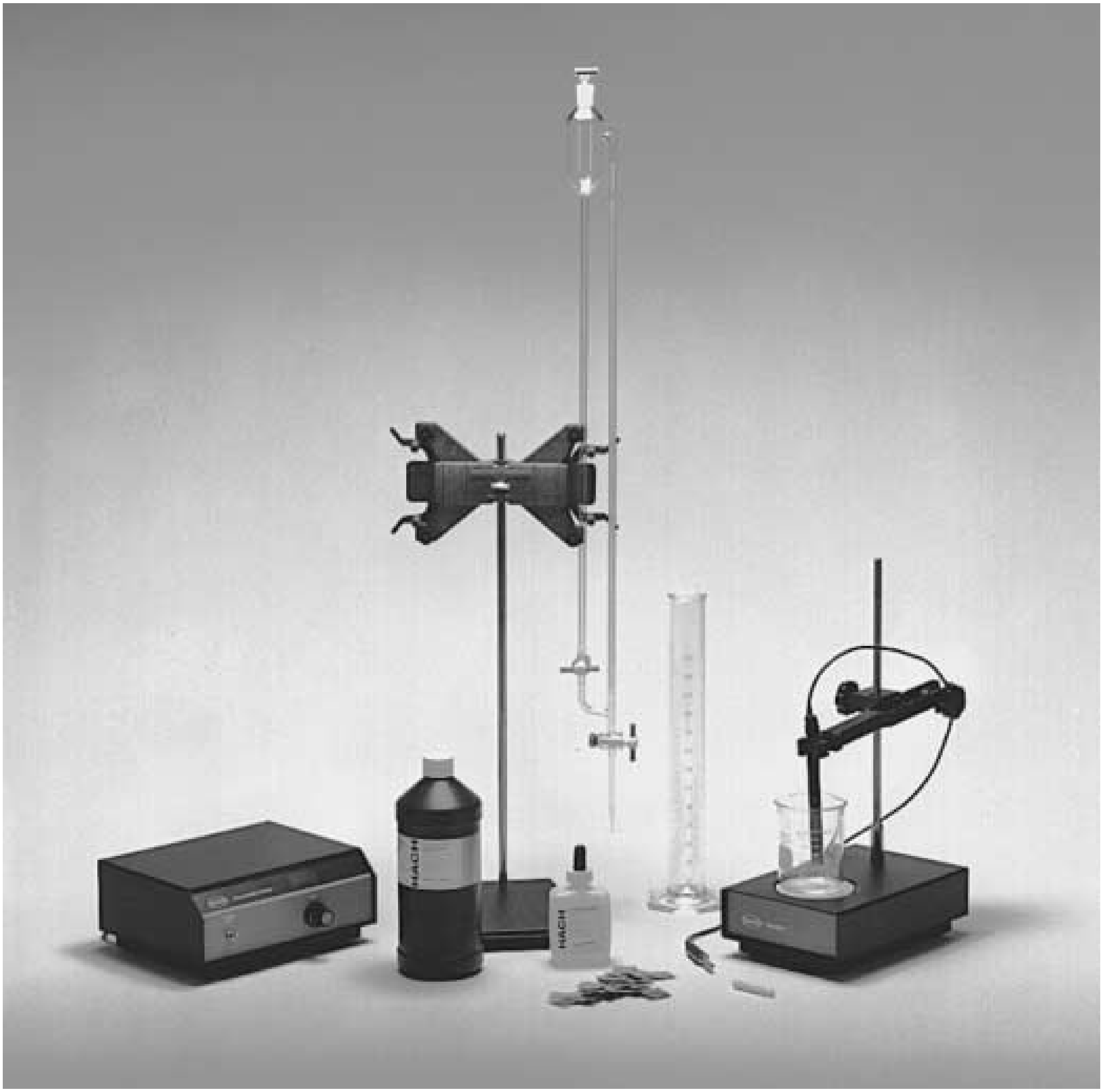
6. Install the Digital Titrator in the titrator/electrode holder assembly and tighten securely. The delivery tube shown has its own slot in the holder assembly.
7. Slip the holder assembly over the titration stand support rod and tighten at the appropriate height.

2.2.2 Glassware Amperometric Titrator System

Figure 6 illustrates the system using the automatic buret as the dispensing apparatus. This system is in accordance with the 18th edition of Standard Methods 4500-Cl-D where a buret is used for measuring free or total chlorine in the range of 0-5 mg/L Cl_2.

1. Assemble the Amperometric Titrator and TitraStir Stir Plate described in Steps 1-4 in *Section 2.2.1*.
2. Install the titrator/electrode holder on the titration stand support rod. Install the Amperometric probe in the holder.
3. Assemble the buret support stand by inserting the support rod into the base. Slip the double buret holder over the support rod and secure at a suitable height using the flat-headed screw.
4. Assemble the automatic buret by inserting the stopcocks as shown in the instructions shipped inside the buret container. Install the stopper and place the buret in the buret holder.

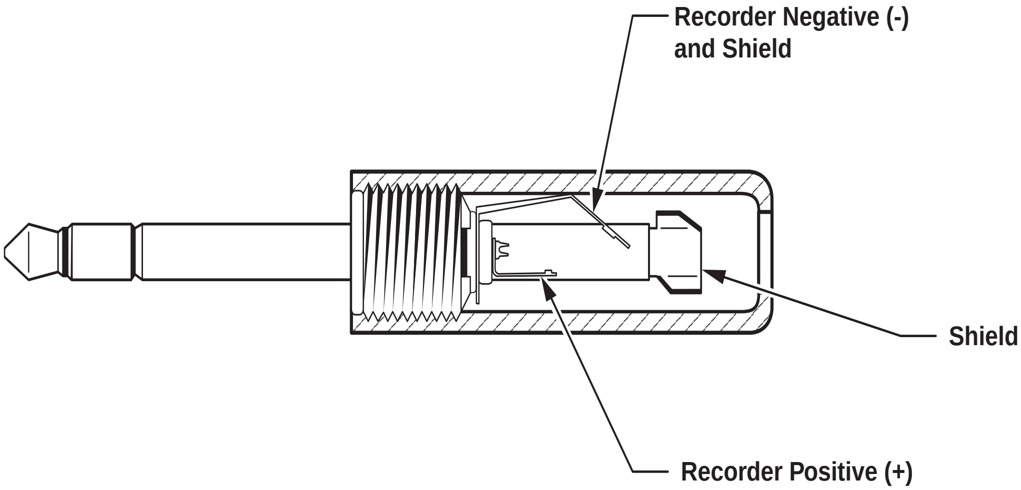
Figure 6 Buret Titration System



2.2.3 Recorder Connection

Solder a twisted-pair shielded cable (not supplied) to the recorder plug supplied with the instrument. See *Figure 7* to identify the recorder plug terminals. The RECORDER jack is on the back panel of the Amperometric Titrator.

Figure 7 Recorder Plug Connections



2.3 Probe Stabilization

When a new probe is used, prepare it as follows to ensure good sensitivity.

1. Connect the probe to the Amperometric Titrator probe jack (marked PROBE) on the rear panel. Turn the POWER switch on.
2. Fill the 250-mL beaker with 200 mL of chlorinated tap water. If chlorinated tap water is not available, add a few drops of commercial bleach to200 mL of deionized water.
3. Place the beaker on the Titration Stand and add a stirring bar to it. Turn the stirring motor on.
4. Lower the electrode holder until the probe tip is immersed in the chlorinated water. Soak for at least 10 minutes. Initial microampere readings may be fairly high.
5. After conditioning, rinse the probe repeatedly with deionized water.
6. Performing several test titrations may further stabilize the probe before titrating “for the record”.

3.1 Operating Controls

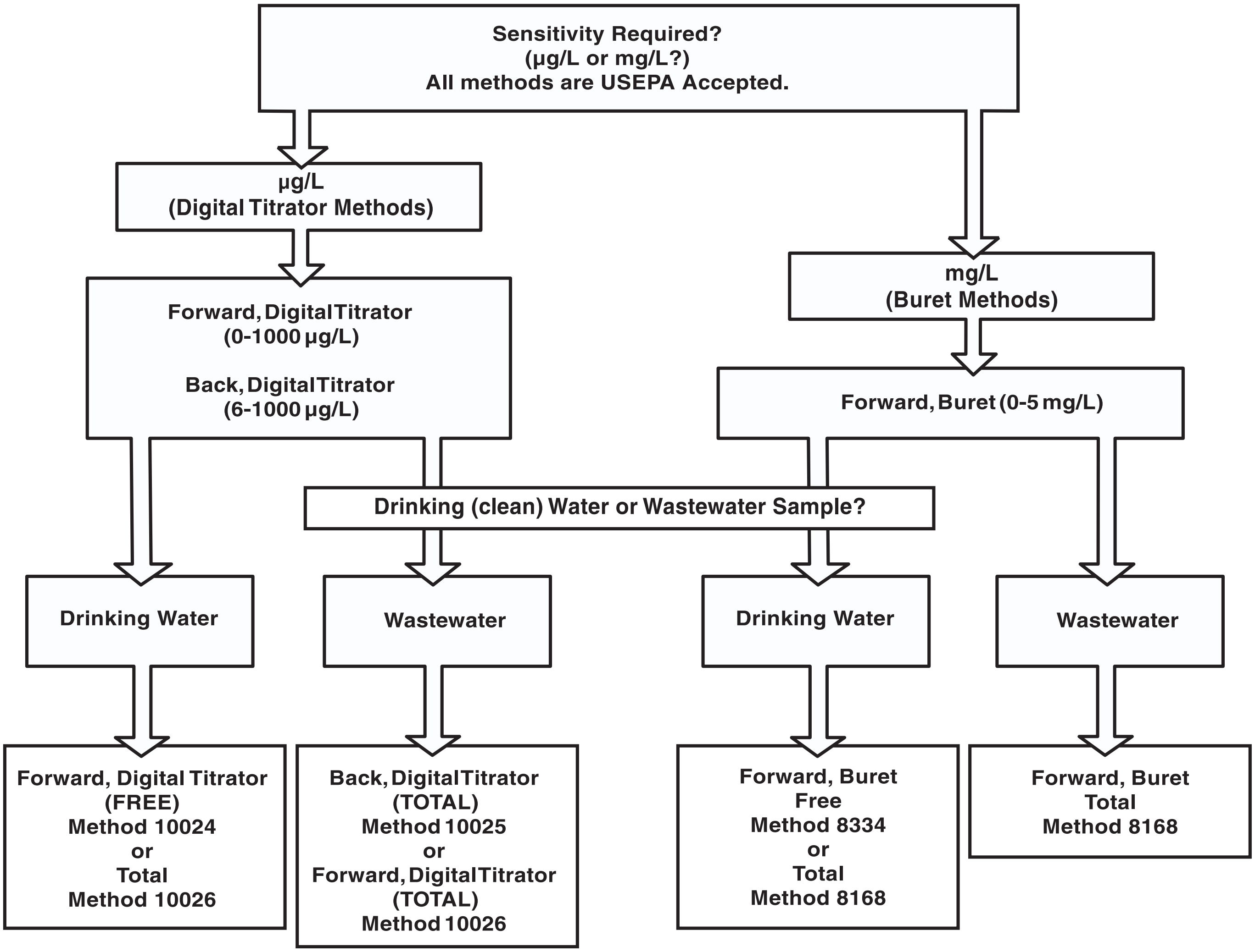
Operating controls for the Amperometric Titrator are on the front panel and consist of a POWER switch, the BIAS control knob, and the locking ring around the BIAS control knob. Use the bias control to adjust the voltage across the electrode and thus set the slope of the electrode response. When turned clockwise, the locking ring around the BIAS control knob prevents the BIAS knob from being moved. The LED display shows the microamperes of current detected by the probe in the test sample. See the specific procedures in *SECTION 8* on page *31* for step-by-step operation of these controls.

Digital Titrator controls include the delivery knob, reset knob and plunger release button. Refer to the General Description Section in the *Digital Titrator Manual* for information on their use.

When a new probe is being placed in service or if your used probe has been out of service for a long period of time or just cleaned, perform probe stabilization as described in *2.3* on page *14*.

Use the Procedure Selection Flow Chart, *Figure 8*, to choose the appropriate procedures for your application. *Figure 8* does not show the 0-10 mg/L free and total chlorine procedures (Methods 8335 and 8314), which are not acceptable for USEPA reporting.

Figure 8 Procedure Selection Flow Chart



SECTION 4 SAMPLE COLLECTION PROCEDURES

4.1 Sample Collection

A common source of error in testing water samples for chlorine is not obtaining a representative sample. Free chlorine is a strong oxidizing agent and very unstable in natural waters. It readily reacts with various inorganic compounds and more slowly oxidizes organic compounds. Various factors, including reactant concentrations, pH, temperature, salinity, and sunlight influence the decomposition of free chlorine in water. Monochloramine, on the other hand, is much more persistent in the environment. Typically, the decay rate of monochloramine is tenfold slower than the decay of free chlorine in natural waters*.

Ideally, samples should be analyzed for chlorine on site. Since the amperometric method is usually performed in the laboratory, the delay between sample collection and analysis should be minimized. If sampling from a tap, allow water to flow at least 5 minutes to ensure a representative sample.

Avoid plastic sample containers, since these may have a high chlorine demand (reacts with and reduces chlorine in samples). Pretreat sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach solution to 1 liter of water) for at least one hour. After soaking, rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, pre-treatment is required only occasionally.

Do not use the same sample containers for free and total chlorine analysis. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. Use separate and dedicated sample containers for free and total chlorine determinations.

Avoid excess agitation and exposure to sunlight when sampling. Allow several volumes of the container to overflow and cap the sample container so that there is no headspace above the sample.

If the **back-titration** method is used for total chlorine determinations, preserve the sample on site. Add 1.00 mL 0.00564 N Standard Thiosulfate (or PAO) and 1.0 mL pH 4 Acetate Buffer to a clean, dry glass container with at least 250 mL capacity (such as a BOD bottle). At the sampling site, measure 200 mL of sample and carefully transfer it to the sample container. Swirl to mix. Do not overflow the sample container with preservative in it. Head space will remain above the sample.

The delay between sample fixing and analysis should be minimized (usually less than 1 hour) to prevent bacterial decomposition of excess thiosulfate (or PAO) in the sample. It is important that the entire contents of the sample container be transferred to the beaker used in the titration.

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* *Water Chlorination: Environmental Impact and Health Effects,* Vol. 4, Book 1: *Chemistry and Water Treatment,* page 33.

SECTION 5 SOURCES OF ERRORS AND INTERFERENCES

5.1 Overview

Standard Methods section 4500 Cl-Ab states that “the amperometric method is the method of choice because it is not subject to interference from color, turbidity, iron, manganese, or nitrite-nitrogen”. In reality, several of these factors may affect the determination of chlorine species when using amperometric methods. This is a brief review of common sources of error encountered with real-world samples.

In general, all of the common chlorine methods will detect other disinfectants such as chlorine dioxide (ClO_2), ozone (O_3), bromine (Br_2), hydrogen peroxide (H_2O_2) and disinfectant by-products such as chlorite and chlorate. In the free chlorine determinations, these oxidants will be reduced to varying degrees by thiosulfate or PAO in the titration method. Each of these oxidants will oxidize iodide to iodine, interfering in the total chlorine determination.

5.2 Deposition on the Electrode Surfaces

Sharp amperometric titration endpoints require clean and regularly conditioned electrodes. Since the electrodes contact the sample, certain species in the sample may plate out or coat the electrode's metallic surface. Metal ions such as copper (+2), silver (+1) and iron (+3) have been reported as either interferences in the forward amperometric method or will diminish the electrode response. In some waters, foaming or surface-active agents will coat the metallic electrodes, resulting in decreased sensitivity.

For Hach's dual platinum electrodes (DPE), regular cleaning and conditioning are necessary to remove any oxidation of the metal surfaces and to sensitize the electrodes to chlorine. Cleaning involves soaking the electrode in a 1:1 Nitric Acid Solution for two hours and then rinsing with distilled or deionized water. The cleaned probe is then stabilized by soaking the platinum electrodes in chlorinated tap water or a dilute solution of commercial bleach. Performing a couple of test titrations with chlorine or iodine standards prior to actual sample titration helps stabilize the probe. The frequency of use and quality of samples titrated will dictate the need for probe cleaning and conditioning.

5.3 Manganese Compounds

Manganese exists in oxidation states of +2 through +7. The higher oxidation states, typically +3 to +7, will interfere with all the common chlorine methods. Free chlorine reacts to oxidize soluble manganese compounds, for example:

$$Mn\ (+2) + HOCl + 3OH^- \rightarrow MnO_2 + Cl^- + H_2O$$

Apparently, chloramines will not oxidize manganous compounds. The oxidized forms of manganese (+4 to +7) will titrate with PAO in the forward titration procedure for free chlorine.

Iodide can be oxidized by Mn (+4 to +7) to I_2 which will interfere in the titrimetric methods for total chlorine. Oxidized forms of manganese will react with iodide at pH 4 producing iodine, which titrates with PAO, causing an interference. The interference of oxidized manganese in the back-titration methods appears to be a function of iodide concentration and the test pH*.

---

* *EPA Report 600/7-77-053*, U.S. Environmental Protection Agency, 1977.

5.4 Nitrite Interference

Nitrite can exist as a transitory compound in certain waters due to the biological oxidation of ammonia:

$$NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

There is conflicting information about the interference of nitrites in either the forward or backward amperometric methods for total chlorine. *Standard Methods*, section 4500-Cl D.1.b, states that nitrites do not interfere in the forward titration methods. Section 4500-Cl C.1.b, the Iodometric Method II, states that nitrite interference can be minimized by buffering to pH 4.0 before addition of iodide. It also states that interference from more than 0.2 mg/L nitrites can be controlled by the use of a phosphoric acid-sulfamic acid reagent. This reagent is used with iodate as titrant since a higher acidity is required to liberate free iodine.

Hach researchers confirmed that nitrites can oxidize KI to iodine at low pH values, similar to the reaction of KI with chlorine or chloramines. The reaction of KI with iodide is dependent on the titration pH and the order of reagent addition.

In the forward titration for total chlorine, nitrites seem to cause either a positive or negative interference depending on the order of reagent addition. If iodide is added to the sample before the pH 4 buffer, the error increases as a function of nitrite concentration. If buffer is added before the iodide, a large negative error occurs, which is independent of the nitrite level.

In the back titration using iodate (*Standard Methods* 4500-Cl C), a lower solution pH occurs due to the addition of phosphoric acid-sulfamic acid mixture. In this case, nitrites as low as 1 mg/L will react quickly with the added iodide, liberating free iodine.

The preferred procedure, which shows little interference from nitrites, is the back titration at pH 4 using standard iodine titrant. The iodometric procedure in which KI is added first, then buffered, is least affected with increasing amounts of nitrites. The back titration procedure buffered at pH 4 is recommended for the amperometric titration of total chlorine in treated wastewaters, and agricultural and industrial discharges.

5.5 Choice of Reductant

In the *forward* amperometric titration method, use only phenylarsine oxide (PAO) as the titrant when measuring total chlorine. PAO gives a sharper end point than standard thiosulfate at pH 4.0. This is shown comparatively in *Figure 9*. The titration plots show the titration of a 80 µg/L monochloramine standard using a continuous titrant feed of a) standard thiosulfate and b) standard PAO. The rate at which triiodide is generated with thiosulfate evidently changes as the end-point is approached. This can lead to uncertainty when determining the end point graphically (see *Figure 9 a*). The use of PAO gives a relatively sharper end-point (see *Figure 9 b*).

In the case of the amperometric *back* titration method, adding excess PAO or thiosulfate is acceptable. The titration end-points for both reductants are equivalent when standard iodine is the titrant.

5.6 Errors Common to Total Chlorine Determinations

Most of the common total chlorine methods are based on the oxidation of iodide to triiodide ion. Several potential sources of errors related to the iodide/triiodide reaction exist:

- oxidation of the iodide reagent
- volatilization of produced iodine
- iodine or iodate contamination in the iodide reagent
- consumption of triiodide by sample components

Potassium iodide reagent is subject to oxidation by the reaction:

$$4I^- + O_2 + 4H^+ \rightarrow 2I_2 + H_20$$

The reaction is accelerated by low pH, light, and trace metal ions. Iodide reagent *solutions* are quite susceptible to oxidation from exposure to light and oxygen. Work by the Electric Power Research Institute (EPRI)* indicates that oxidants equivalent to 1 mg/L chlorine can be generated in one day in a 0.1 M (molar) KI stock solution.

Potassium iodide purity is critical in trace total chlorine determinations. The iodide should be free of iodine or iodate which can react directly with chlorine or chloramines in the sample. Even solid potassium iodide can be oxidized with enough exposure to oxygen and ultraviolet light. Hach's Potassium Iodide reagent is sealed in a PermaChem pouch, minimizing oxidation and light exposure. Hach controls its KI reagent for iodine and trace oxidant contamination before packaging.

Volatilization of free iodine from the reaction of oxidant with iodide is decreased somewhat because excess iodide is present in the sample. Excess iodide causes formation of the less volatile triiodide species. EPRI* reported the error due to iodine volatilization is probably a small percent. Quick analysis will also minimize iodine loss by volatilization.

Adsorption of the produced iodine on suspended particles can be a serious problem in the case of muddy or highly organic-rich waters. A good example is the blue complex formed between I_2 and starch, which is the visual indicator for the starch iodine test. In addition to adsorption, iodine can react with organic matter, forming carbon-iodine bonds. This is one reason for the traditional preference of the back titration methods for total chlorine in sewage treatment plant effluents.

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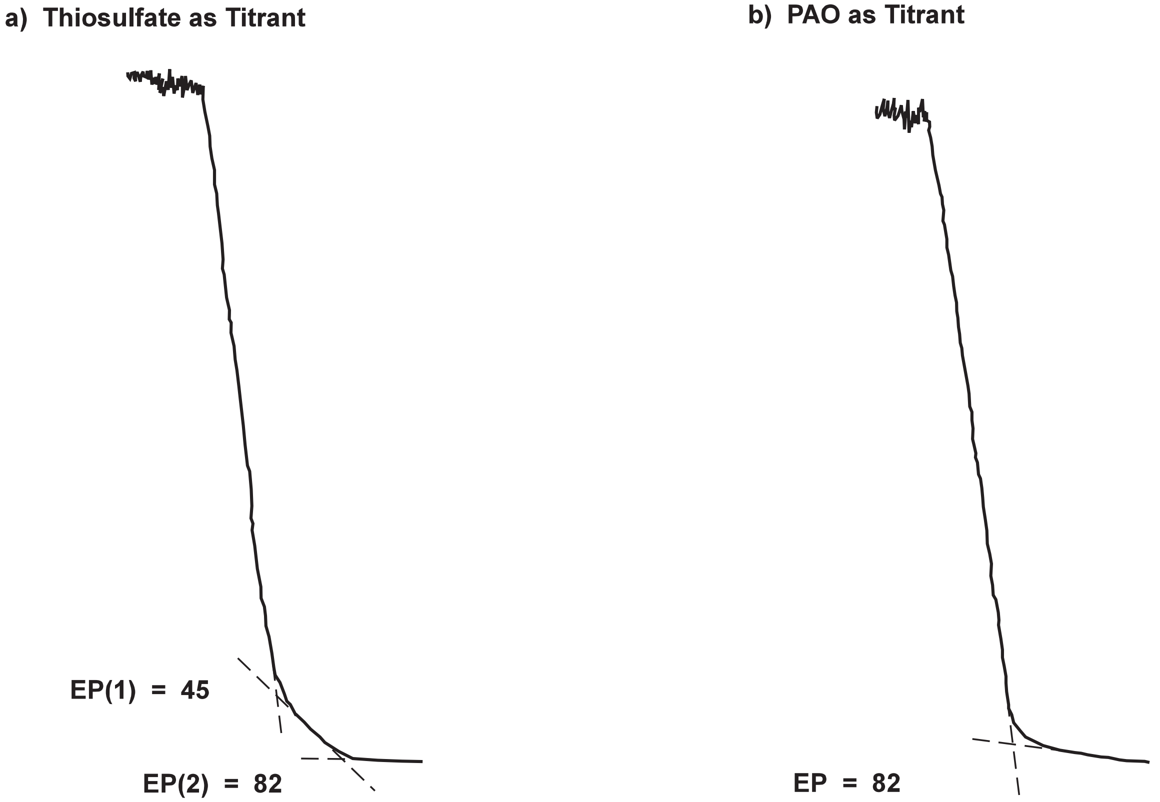
* EPRI Report EA-929, Project 879-1, October 1978.

Figure 9 Titration Curves Using Thiosulfate vs. PAO Titrants



5.7 Shift of Endpoints Due to Sample Iodine Demand

In samples which contain certain organic compounds, these compounds may exert an "iodine demand" which can shift the titration end point, even if the back titration procedure is used. An example of this effect is shown in *Figure 10*. If the sample contains suspended particles, generated iodine can readily adsorb into the particles, resulting in a shift of the current readings. In addition to adsorption, iodine can react with dissolved organic matter in the sample.

For samples that have a high iodine demand, it may be difficult to accurately estimate the end point. Continuing the titration for several readings after the end point helps estimate the value for the two intersecting lines. Also, a rapid titration will minimize iodine demand. Sample dilution with chlorine demand-free water will also minimize iodine demand, although this may cause chlorine loss and decreases sensitivity.

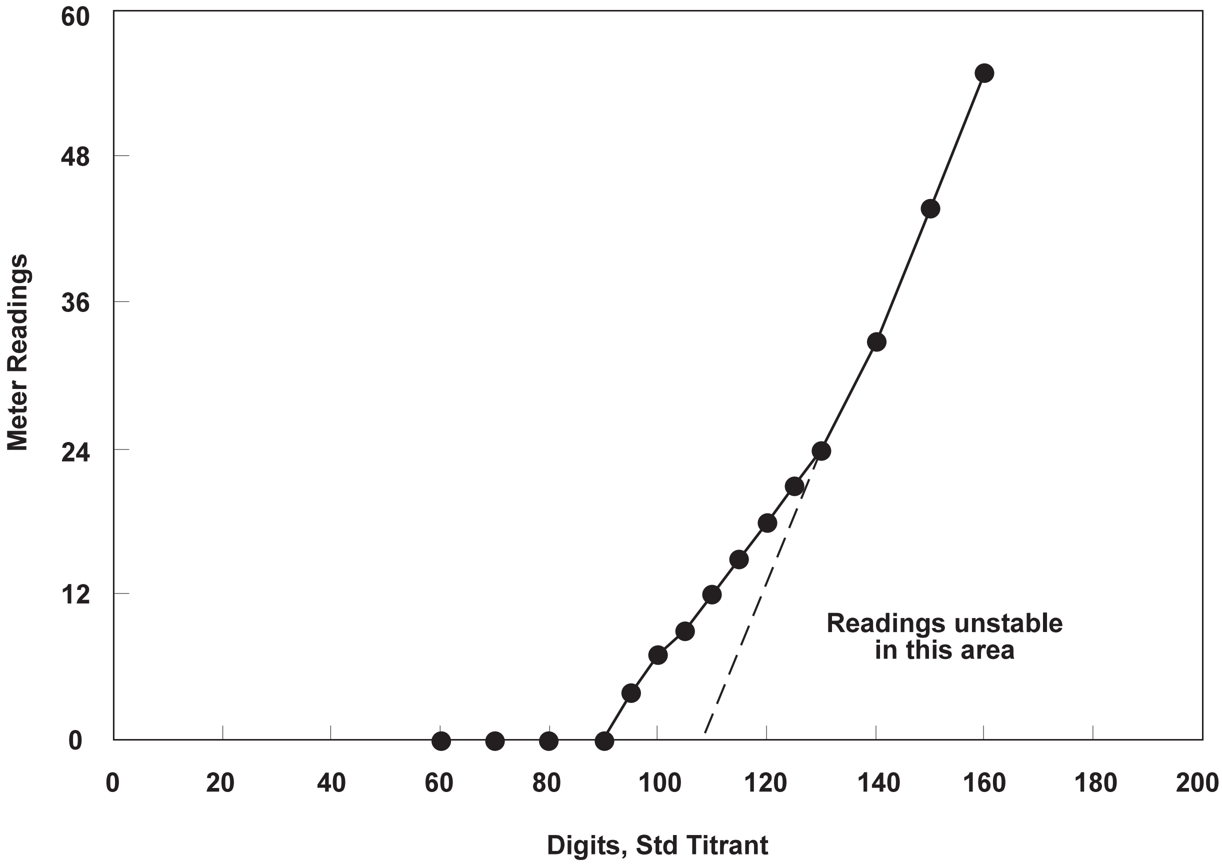
5.8 Order of Reagent Addition

Measuring chlorine in saline, estuary or seawater is exceedingly difficult with any of the available methods. The literature concerning the amperometric determination of total chlorine in salt water is somewhat confusing. Several studies indicate the order of reagent addition (KI and buffer) may underestimate the total chlorine concentration when determined amperometrically.

The chemistry of chlorine in sea water is exceedingly complex. Saline waters usually contain an appreciable chlorine demand, partly due to oxidation of carbon and nitrogen-containing compounds. Bromide, usually present in seawater, will oxidize to bromine when chlorine is added. Also, the concentration of chlorine-containing and secondary oxidants produced by chlorination depends on the characteristics of the water being chlorinated. Salinity, organic load, water temperature and incident sunlight can influence the level of chlorine-containing compounds and oxidants.

There is general agreement that in the amperometric determination for "total chlorine" in saline waters, iodide reagent should be added before, or simultaneously with, the pH 4 buffer. If the saline sample is buffered prior to addition of the iodide, the total oxidant concentration may be underestimated.

Figure 10 Iodine Demand (back titration curve)



SECTION 6 MAINTENANCE

6.1 Cleaning

6.1.1 Amperometric Titrator Probe

Acid clean and stabilized the DPE probe on a regular schedule. The frequency of use and the type of samples will dictate the need for probe cleaning and conditioning. Clean the probe as follows:

1. Immerse the probe tip in 1:1 Nitric Acid Solution. Allow to soak for 2 hours.
2. Rinse the probe repeatedly with deionized water.
3. Stabilize the probe as described in *Section 2.3* on page *14*.

6.1.2 Glassware

Treat all glassware used in chlorine analysis to remove any chlorine demand. After normal washing with laboratory detergent, soak the glassware in water containing at least 10 mg/L residual chlorine for at least 3 hours before use. Rinse thoroughly with deionized water.

6.2 Probe Stabilization

Stabilize the probe according to *Section 2.3* on page *14* when:

- A new probe is placed in service.
- The probe has been out of service for a long time.
- The probe has just been cleaned.

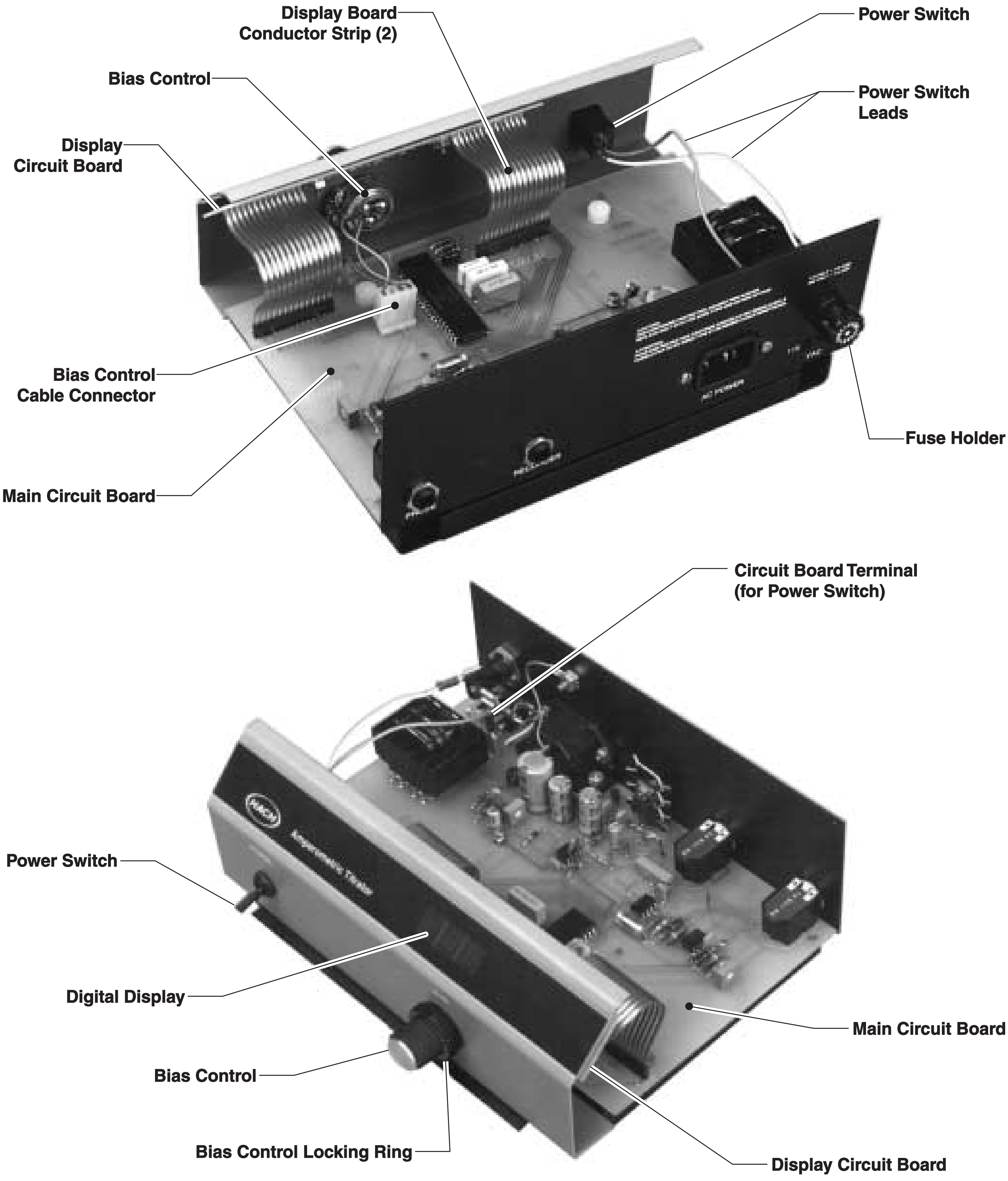
6.3 Component Replacement

The following paragraphs describe the removal and replacement of components that can be changed in the field (and do not require factory calibration). Refer to the Replacement Parts list for the proper replacements.

CAUTION
The instrument contains static-sensitive devices. Ground the work surface, the operator, and any electrical tools properly when performing any of the following replacement procedures.

WARNING
Disconnect the power cord before removing the instrument cover. Electrical shock can cause serious injury.

Figure 11 Component Locations



6.3.1 Display Circuit Board Replacement

Replace the display circuit board* as follows (see *Figure 11*).

1. Set the POWER switch to off and disconnect the power cord. Disconnect the probe and recorder cables.
2. Place the instrument upside down on a grounded surface and remove the two screws that secure the slide-out electrode support bracket (not used when the TitraStir Stir Plate is used.) Remove the bracket.
3. Remove the four screws on the under side that secure the instrument cover. These screws are nearest to the side edges of the bottom cover.
4. Return the instrument to the upright position. Slide the cover toward the back of the instrument until the cover comes off.
5. Disconnect the two display board conductor strips from the receptacles on the main circuit board (located on the floor of the instrument). See *Figure 11*. The display board is located directly behind the display window.
6. Remove the two nuts that secure the display board to the instrument front panel. Remove the board.
7. Install the new replacement circuit board assembly in reverse order of removal.

6.3.2 Bias Control Replacement

The bias control is part of an assembly that includes the wires and connector. Replace it as follows:

1. Set POWER switch to off and disconnect the power cord. Disconnect the probe and recorder cables.
2. Place the instrument upside down on a grounded surface. Remove the two screws that secure the slide-out electrode support bracket (not used when TitraStir Stir Plate is used). Remove the bracket.
3. Remove the four screws on the under side that secure the instrument cover. These screws are nearest to the side edges of the bottom cover.
4. Return the instrument to the upright position. Slide the cover toward the back of the instrument until the cover comes off.
5. Disconnect the bias control cable connector from the main circuit board. See *Figure 11*.
6. Remove the knob from the bias control by loosening the two set screws. Rotate the locking ring around the BIAS control counterclockwise and remove the nut securing the control with a 1/2-inch wrench or nut driver. Remove the control assembly.
7. Install the replacement control assembly in reverse order of removal.

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* For a schematic, request Drawing Number 19318-00.

6.3.3 Power Switch Replacement

The power switch includes wires and quick-disconnect terminations. Replace the switch as follows:

1. Set the POWER switch to off. Disconnect the power cord. Disconnect the probe and recorder cables.
2. Place the instrument upside down on a grounded surface. Remove the two screws that secure the slide-out electrode support bracket (not used when TitraStir Stir Plate is used). Remove the bracket.
3. Remove the four screws on the under side that secure the instrument cover. These screws are those nearest the side edges of the bottom cover.
4. Return the instrument to the upright position. Slide the cover toward the back of the instrument until the cover comes off.
5. Disconnect the two power switch leads from the fuse holder and circuit board terminals. See *Figure 11*.
6. Remove the round nut that secures the switch to the front of the instrument. Remove the switch.
7. Install the replacement switch in reverse order of removal.

6.3.4 Fuse Replacement

Replace the fuse as follows:

1. Set the POWER switch to off. Disconnect the power cord.

WARNING
Be sure to disconnect the power cord before removing or installing a fuse.

2. The fuse holder is on the rear panel of the instrument (see *Figure 11*). To remove the fuse, press in on the holder cap and turn counterclockwise until the cap comes off.
3. Remove the old fuse from the holder cap.
4. Install the replacement fuse. Use a 1/8-ampere, 3 AG, slow blow fuse for 115-volt operation. Use a 1/16-ampere, 3 AG, slow blow fuse for 230-volt operation.
5. Reconnect the power cord.

SECTION 7 TROUBLESHOOTING

The following troubleshooting guide will help determine if a malfunction is the result of a faulty probe or a problem with the instrument itself. If the problem is with the instrument, contact your nearest factory service center for instructions. Recalibration requires special test equipment, and it may be necessary to return the instrument for repair.

Table 1 Troubleshooting Guide

Symptom	Probable Cause	Corrective Action
1. Display does not light.	No operating power	Check power switch position, fuse and power cord connection. Verify the outlet the instrument is plugged into has power.
2. Display is dim and erratic.	Problem with power supply	Check voltage conversion switch S2 on back panel for proper setting (see *2.2.1* on page *10*).
3. Instrument readout is erratic.	Problem with platinum probe	Check for good electrode connection to the instrument. Disconnect probe from the instrument. If a stable reading can be obtained, the probe is probably causing the problem; clean and stabilize the probe (see *Section 2.3* on page *14*).

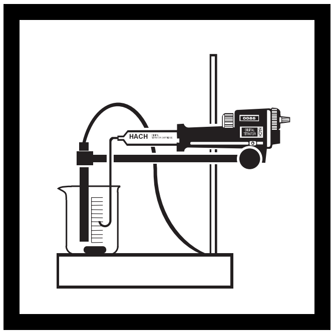
SECTION 8 CHLORINE AMPEROMETRIC TITRATION PROCEDURES

Method 10024

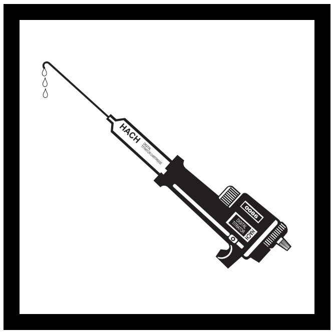
CHLORINE, FREE (0-1000 μg/L Chlorine as Cl_2)

For drinking water

Forward Titration Method—Using a Digital Titrator and 0.00564 N PAO
USEPA Accepted for reporting*



1. Assemble the Amperometric Digital Titrator System according to the instructions in *Section 2.2.1* on page *10*.



2. 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.

Note: *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 Section 2.3 on page 14.*

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.

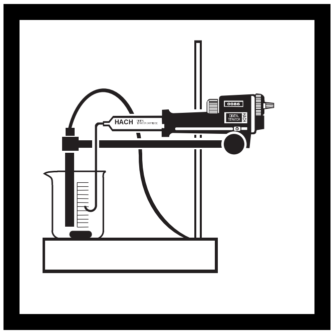
Note: *An improper stirring bar size can result in volatilization of chlorine, unstable readings, and loss of sensitivity.*

4. Add 1 mL of pH 7 Phosphate Buffer Solution.

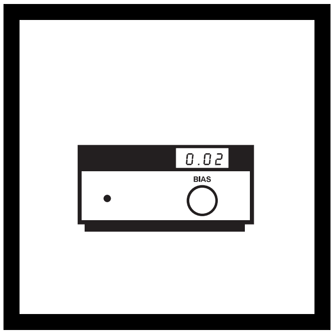
Note: *If the sample pH is between 6.5 and 7.5 it is not necessary to add the buffer.*

---

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

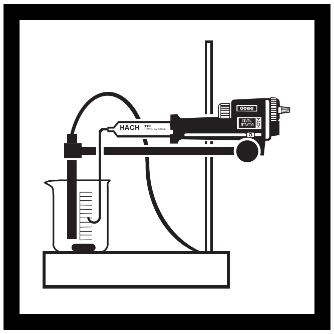


5. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



6. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control and adjust the BIAS control knob until a reading between 0.50-0.60 is obtained. Lock the BIAS control.

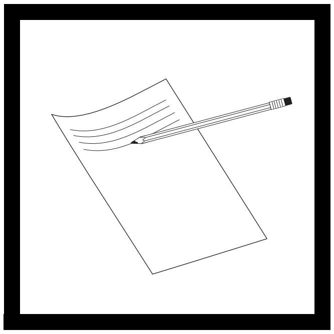
Note: *The bias adjustment controls the slope of the titration curve. The actual instrument reading is not important; but rather the change in the readings as the titration proceeds. The adjustment need not be precise.*



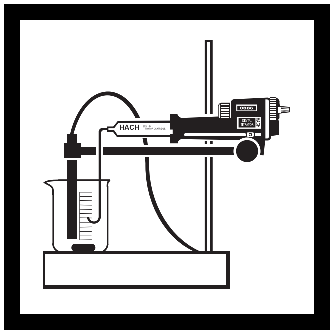
7. Using the Digital Titrator delivery knob, dispense the PAO titrant Solution in 5 to 10 digit increments while noting the downward reading.

Note: *If the chlorine content of the sample is high, add titrant at a faster rate; only the end point of the titration and the volume of titrant used at the end point are of concern. For example, if the chlorine content is about 500 µg/L, up to 300 digits of 0.00564 N PAO could be added at once. As the end point is approached, dispense in small increments.*

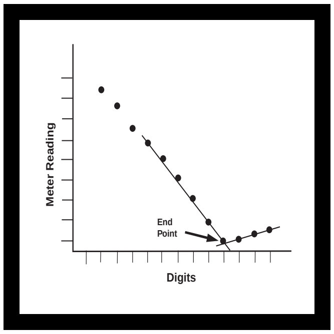
Note: *If excess reductant such as sulfite, bisulfite or sulfur dioxide is present in the sample, the LED readings will not decrease and may even increase. This indicates that o free chlorine is present in the sample.*



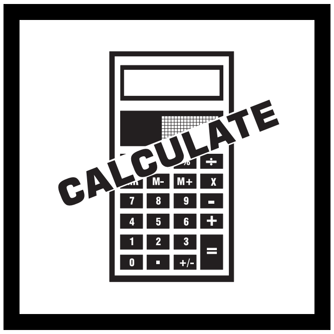
8. As the end point of the titration is approached, record the LED readings along with the corresponding digits displayed on the Digital Titrator counter. Near the titration end point, add 2 to 5 digits of titrant; wait a few seconds for a stable reading and record.



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



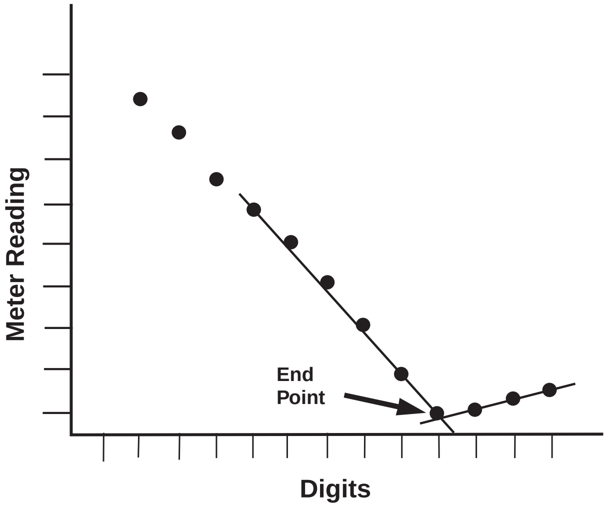
10. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis. Draw the two best intersecting lines through the points; see *Figure 12*. Determine the number of digits at the intersection of the lines; this is the end point.



11. Calculate the µg/L free chlorine:

Digits at End Point x 1.25 = µg/L free chlorine as Cl_2

Figure 12 Sample Plot



Accuracy Check

Standard Additions Method*

1. Snap the top off a Chlorine Standard Solution Ampule. Note the certificate value of the standard in mg/L.
2. Split a fresh sample into two 200-mL portions.
3. Using a TenSette Pipet, add from 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:

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

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

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

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

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

6. Calculate the percent spiked recovery:

$$\text{\% Spike Recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}} \times 100$$

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

Precision

In a single laboratory, using a standard solution of 338 µg/L chlorine, a single operator obtained 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.

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* The standard additions technique is not applicable for samples containing excess reducing agents such as sulfur dioxide, sulfite, or bisulfite.

Sampling And Storage

Chlorine is rapidly lost from water. Avoid exposure to sunlight or other strong light. Avoid excessive agitation. Analyze samples immediately.

Interferences

- Silver ions poison the electrode.
- Copper ions interfere.
- Interferences are sometimes found in highly turbid water and those containing surface active agents.
- Oxidized manganese and other oxidizing reagents give positive interferences.
- Some uncertainty in the end point may be observed with samples containing high organic content.
- Samples containing excess reducing agents, such as sulfur dioxide, sulfite, and bisulfite, do not contain free chlorine and can not be titrated under the conditions of the test.
- 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.

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 at the cathode to chloride 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 reacted.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Phenylarsine Oxide Solution, 0.00564 N Digital Titrator Cartridge	each	1999-01
Phosphate Buffer Solution, pH 7	100 mL MDB	21553-32

REQUIRED APPARATUS

Amperometric Titrator Assembly	each	19299-00
Digital Titrator	each	16900-01
Beaker, low-form, 250 mL	each	500-46
Cylinder, graduated, 250 mL	each	508-46
Delivery Tubes, 90° with hook	5/pkg	41578-00
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	20953-55
TitraStir Stir Plate, 115 Vac	each	19400-00
TitraStir Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite Ampule, 50-75 mg/L Cl_2, 2 mL	20/pkg	14268-20
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Handbook: Standard Methods for the Examination of Water and Wastewater, 19th edition	each	22708-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Ampule Breaker Kit for Voluette Ampules	each	21968-00

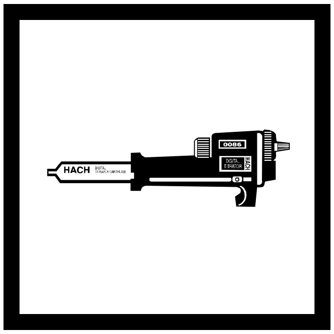
For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8335

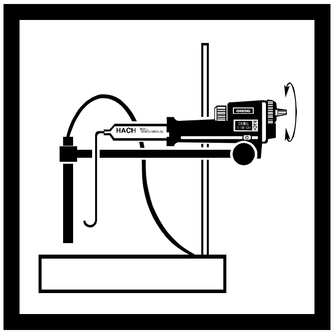
CHLORINE, FREE (0-10 mg/L)

For water and wastewater

Forward Titration Method—Using a Digital Titrator and 0.0451 N PAO

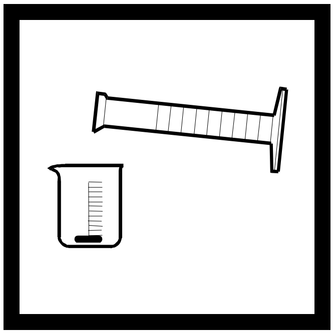


1. Install the 0.0451 N Phenylarsine Oxide Titration Cartridge (PAO) on the Digital Titrator.



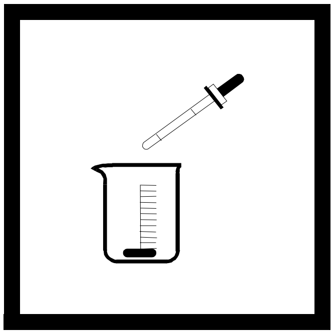
2. Assemble the Amperometric Digital Titrator System according to the instructions in *SECTION 2* on page *9*. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

***Note:** When using a new probe or a probe that has not been used recently, prepare the probe according to the Probe Stabilization instructions in Section 2.3 on page 14.*



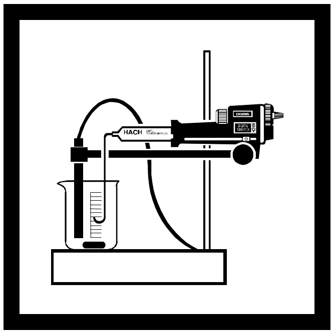
3. Without excessive agitation, measure 200 mL of sample with a clean graduated cylinder. Transfer the sample to a clean 250-mL beaker containing the 50-mm stirring bar supplied with the system.

***Note:** An improper-sized stirring bar can cause volatilization of chlorine, unstable readings and decreased sensitivity. This is especially true when measuring low chlorine levels.*

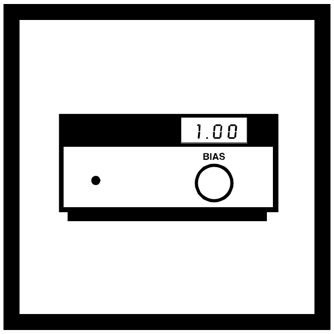


4. Add 1 mL of pH 7 Phosphate Buffer Solution.

***Note:** If the pH of the sample is between 6.0 and 7.5, it is not necessary to add the buffer.*

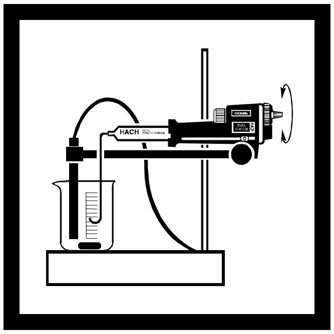


5. Place the beaker on the TitraStir Stir Plate. Turn on the stirring motor. Immerse the tips of the probe and delivery tube into the sample. Make sure the platinum wires are submerged.



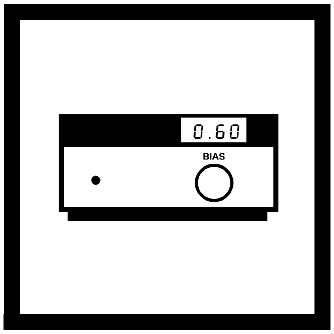
6. Note the LED reading on the Amperometric Titrator. Using the BIAS control, adjust the LED reading to about 1.00.

Note: *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. A precise adjustment is not required.*

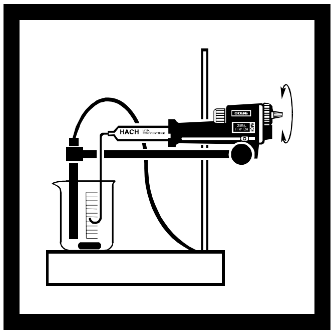


7. Using the Digital Titrator delivery knob, dispense the titrant in small increments (5 to 10 digits). The readings on the Amperometric Titrator will decrease.

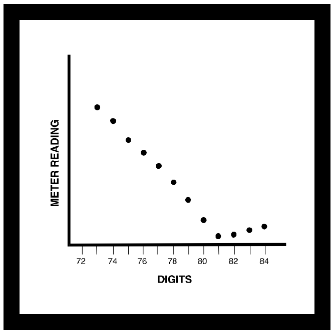
Note: *If the chlorine level is high, add large volumes of titrant at first- only the endpoint of the titration and the volume of titrant at the end point are important. For example, if the chlorine level is 5 mg/L, up to 400 digits of 0.0451 N titrant could be added at once.*



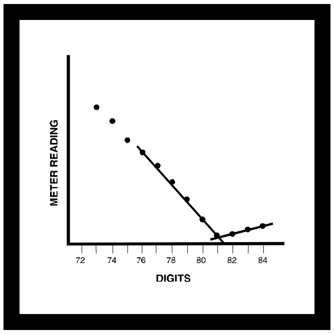
8. As the end point approaches, record the LED reading and the corresponding digits on the Digital Titrator. Add a small amount of titrant; wait a few seconds for a stable reading and record the reading.



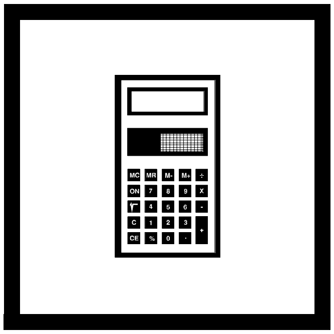
9. Continue the titration. Record at least three points on the downward sloping curve and at least three points after the end point has been reached. The last three points will show very little change in the meter readings.



10. Plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis. See *Figure 13*.



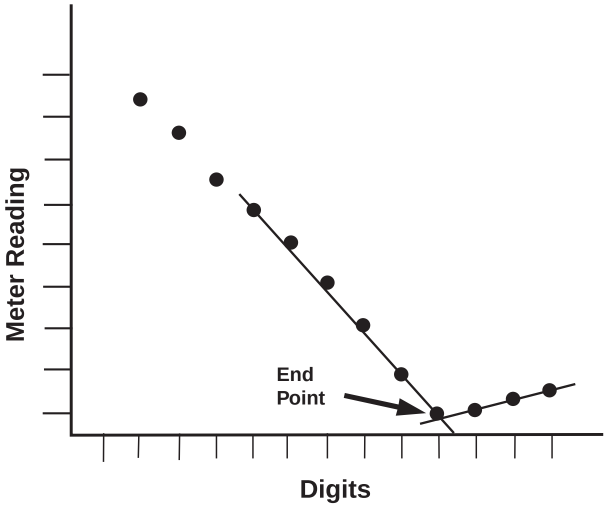
11. Draw the two best-fit intersecting lines through the points. Determine the number of digits at the intersection of the lines; this is the end point.



12. Calculate the mg/L of free chlorine as follows:

Digits at End Point x 0.01
= mg/L free chlorine as Cl_2

Figure 13 Forward Amperometric Titration Graph

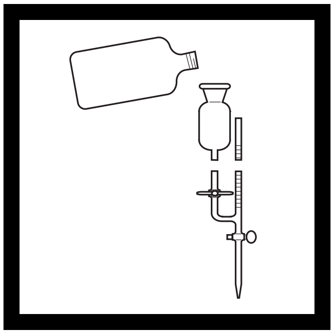


Method 8334

CHLORINE, FREE

For water and wastewater

Forward Titration Method—Using a Buret and 0.00564 N PAO* Hach Equivalent Method**

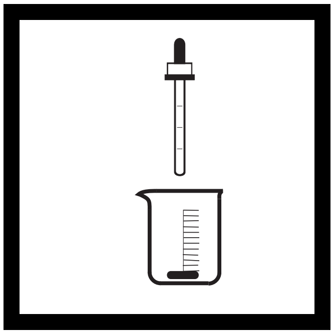


1. Fill the 5-mL automatic buret to the zero mark with 0.00564 N Phenylarsine Oxide (PAO) Solution.

2. Use a graduated cylinder to measure 200 mL of sample. Transfer to a 250-mL beaker.

3. Place a 50-mm stir bar into a 250-mL beaker. Use a graduated cylinder to transfer 200 mL of sample to the beaker.

Note: *An improper size of stirring bar can result in volatilization of chlorine, unstable readings and loss of sensitivity. This is especially evident when measuring low level chlorine concentrations.*



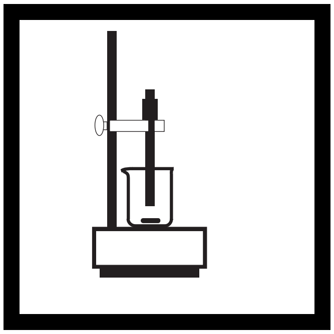
4. Add 1.0 mL of pH 7 Phosphate Buffer Solution to make the prepared sample.

Note: *If the pH of the sample is between 6.0 and 7.5, it is not necessary to add the buffer.*

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater*, 18th edition, 4500-C1 D; 40 CFR Part 141 Section 141.74.

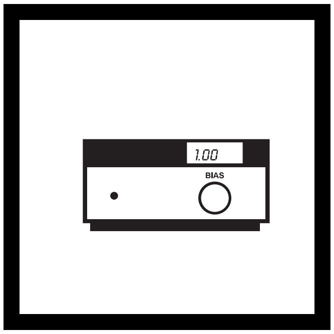
** Hach has determined that “Hach equivalent” methods meet or exceed specification criteria of the equivalent USEPA-approved methods.



5. Place the beaker of prepared sample on the TitraStir Stir Plate and turn on the stirring motor. Immerse the tip of the probe in the prepared sample. The platinum wires must be submerged.

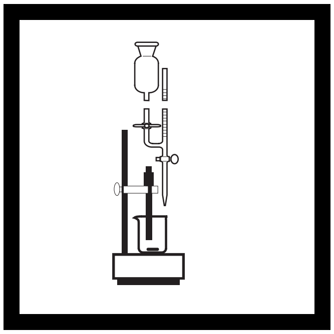
Note: *If a stir plate other than the TitraStir Stir Plate is used, set the speed for moderate mixing do not adjust the speed after this point.*

Note: *If the probe is new or has not been used recently, condition the probe as described in the instrument manual.*

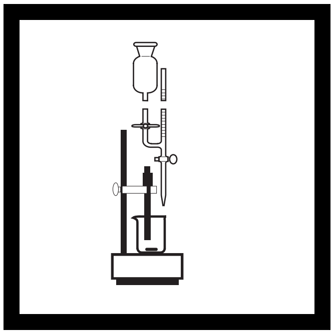


6. Note the LED reading on the Amperometric Titrator. Using the BIAS control, adjust the LED reading to about 1.00.

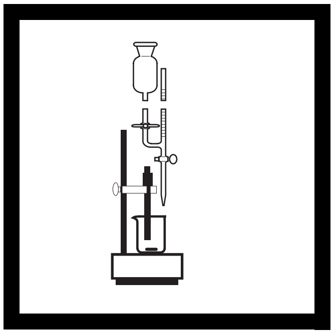
Note: *The BIAS adjustment controls the slope of the titration curve. The actual instrument reading is not important; the relative readings as the titration proceeds are. A precise adjustment is not required.*



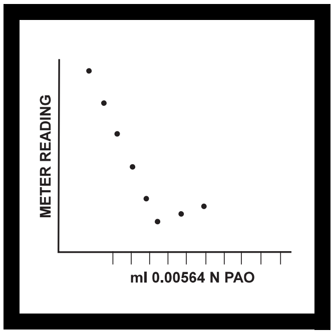
7. Dispense the titrant into the beaker in small increments while observing the downward readings on the Amperometric Titrator.



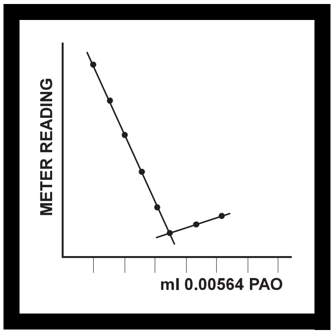
8. Continue dispensing slowly. As the end point of the titration is approached, record the LED reading along with the corresponding total volume of titrant added to the nearest 0.01 mL. Add a small amount of titrant; wait a few seconds and record an average value.



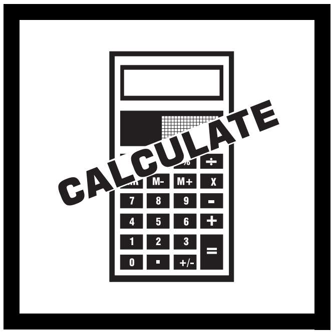
9. Continue the titration by recording at least three points on the downward sloping curve and at least three points after the end point has been reached. The latter points will indicate little change in the meter readings.



10. Construct a graph of the titration by plotting the readings obtained from the Amperometric Titrator display on the vertical axis and the corresponding volume of titrant used on the horizontal axis.



11. Draw the two best intersecting lines through points plotted as shown above. Determine the volume of titrant used to the nearest 0.01 mL at the intersection of the two lines. This is the mL titrant at End Point.

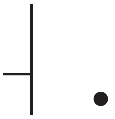


12. Determine the free chlorine concentration:

mL Titrant at End Point

= mg/L Free Chlorine Cl_2

Figure 14 Forward Buret Titration Graph



Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

Do not use the same sample containers for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to separate dedicated sample containers for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. Perform the chlorine analysis immediately.

Interferences

Refer to *SECTION 5* on page *19* for a discussion of sources of errors and interferences using the amperometric methods.

Summary of Method

The amperometric titration method has greater sensitivity and accuracy when compared to colorimetric methods. Chlorine is determined by titrating at pH 7 with PAO to the amperometric end point. Refer to *SECTION 1* on page *3* for more information.

REQUIRED REAGENTS

	Cat. No.
Chlorine Reagent Set (about 100 tests)	24587-00

Includes: (1) 1999-53, (1) 21553-32

Description	**Quantity Required Per Test**	**Unit**	**Cat. No.**
Phenylarsine Oxide Solution, 0.00564 N	varies	1 L	1999-53
Phenylarsine Oxide Solution, 0.0451 N (for Digital Titrator)	varies	1 L	22599-01
Phosphate Buffer Solution, pH 7	1 mL	118 mL MDB	21553-32

REQUIRED APPARATUS

Select one for buret titration based on available voltage:

Amperometric Buret Titrator System (115 Vac) Includes: 14909-37, 1999-16, 1077-99, 19299-00, 20550-37, 328-00, 508-46, 19300-08, 20953-55, 563-00, 19400-00, 500-46	each	19300-10
Amperometric Buret Titrator System (230 Vac)	each	19300-12

Includes: 14909-37, 1999-16, 1077-99, 19299-00, 20550-37, 328-00, 508-46, 19300-08, 20953-55, 563-00, 19400-10, 500-46

For Digital Titrator method:

Beaker, 250 mL	1	each	500-46
Amperometric Titrator Assembly	1	each	19299-00
Beaker, low-form, 250 mL	1	each	500-46
Cylinder, graduated, 250 mL	1	each	508-46
Digital Titrator	1	each	16900-01
Delivery Tubes, 90° with hook	1	5/pkg	41578-00
Pipet, volumetric, Class A, 1 mL	1	each	14515-35
Probe Assembly, Amperometric Titrator	1	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm,	1	each	20953-55
TitraStir Stir Plate, 115 Vac	1	each	19400-00
TitraStir Stir Plate, 230 Vac	1	each	19400-10

OPTIONAL APPARATUS

Buret, automatic, 5 mL	each	20550-37
Buret Clamp	each	328-00
Graduated Cylinder, 250 mL	each	508-46
Instruction Manual, Amperometric Titrator	each	19300-08
Strip Chart Recorder	each	24080-00
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, 50 mm	each	20953-55
Support Stand	each	563-00

For Technical Assistance, Price and Ordering

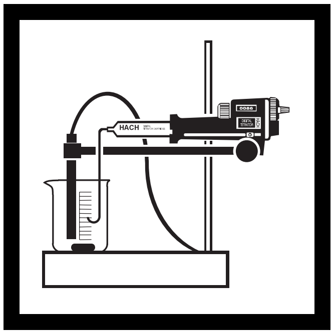
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

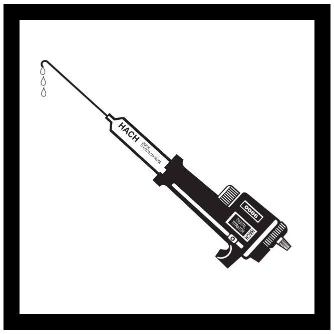
Method 10026

CHLORINE, TOTAL (0-1000 µg/L Chlorine as Cl_2) For drinking water or wastewater

Forward Titration Method—Using a Digital Titrator and 0.00564 N PAO*
USEPA Accepted for water and wastewater



1. Assemble the Amperometric Digital Titrator System according to the instructions in *SECTION 2* on page *9*.



2. 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.

***Note:** When a new probe is used or when the probe has not been used recently, prepare it according to the Probe Stabilization instructions in Section 2.3 on page 14.*

3. Without excessive agitation, measure 200 mL 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.

***Note:** An improper size of stirring bar can result in volatilization of chlorine, instability of readings and loss of sensitivity.*

4. Add the contents of one Potassium Iodide Powder Pillow and swirl to dissolve.

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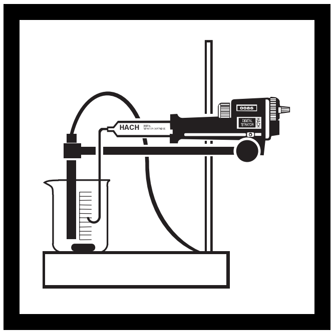
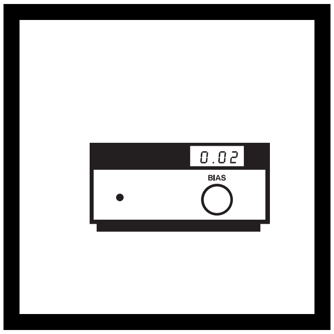
* Procedure is equivalent to USEPA method 330.1 and 330.3 and Standard Method (18th ed.) 4500-Cl D.

5. Add 1 mL of pH 4 Acetate Buffer Solution.

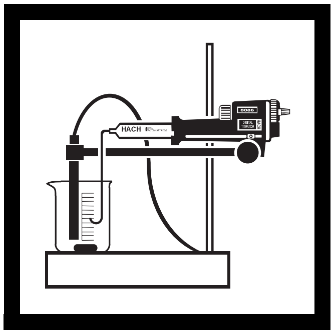


6. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



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

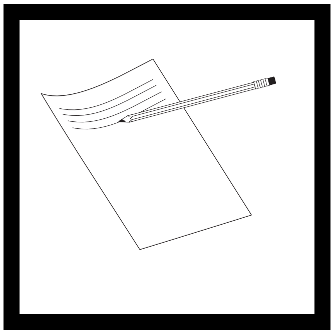
Note: *The bias adjustment controls the slope of the titration curve. The actual instrument reading is not important; but rather the change in the readings as the titration proceeds. The adjustment need not be precise.*



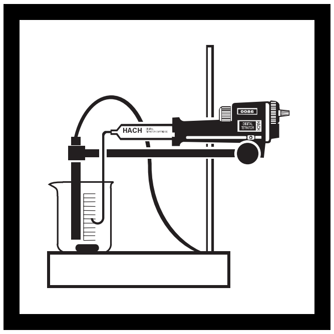
8. Using the Digital Titrator delivery knob, dispense the PAO titrant Solution in 5 to 10 digit increments while noting the downward reading.

Note: *If the chlorine content of the sample is high, add titrant at a faster rate; only the end point of the titration and the volume of titrant used at the end point are of concern. For example, if the chlorine content is approximately 500 µg/L, up to 300 digits of 0.00564 N PAO could be added at once. As the end point is approached, dispense in small increments.*

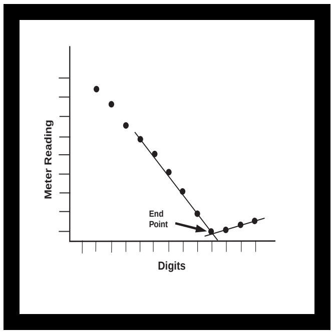
Note: *If excess reductant, such as sulfite, bisulfite or sulfur dioxide is present in the sample, the LED readings will not decrease and may even increase. This indicates that no free chlorine or chloramines are present in the sample.*



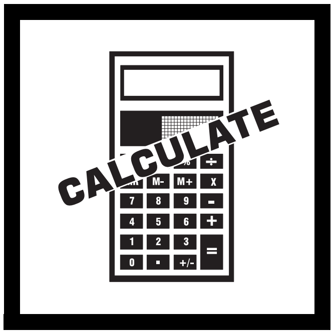
9. As the end point of the titration is approached, record the LED readings along with the corresponding digits displayed on the Digital Titrator counter. Near the titration end point, add 2 to 5 digits of titrant; wait a few seconds for a stable reading and record.



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



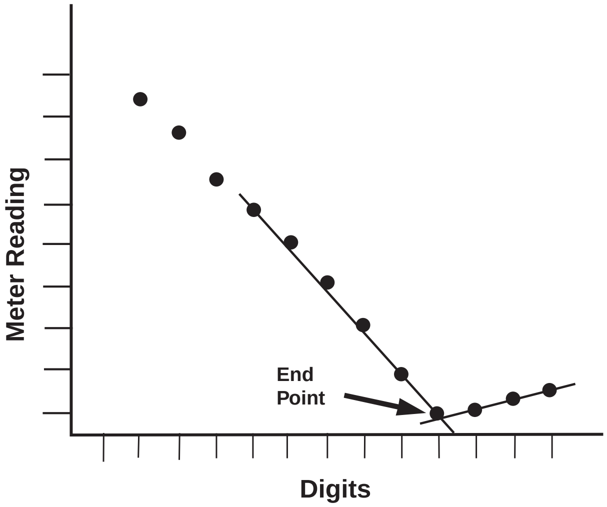
11. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the on the horizontal axis. Draw the two best intersecting lines through the points (see *Figure 15*). Determine the number of digits at the intersection of the lines; this is the end point.



12. Calculate the µg/L total chlorine:

Digits at End Point X 1.25 = µg/L total chlorine as Cl_2

Figure 15 Sample Plot



Accuracy Check

Standard Additions Method*

1. Snap the top off a Chlorine Standard Solution PourRite Ampule. Note the certificate value of the standard in mg/L.

2. Split a fresh sample into two 200-mL portions.

3. Using a TenSette Pipet, add from 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 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

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

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

6. Calculate the percent spiked recovery:

$$\%\ \text{Spike Recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}} \times 100$$

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

Precision

In a single laboratory, using a standard solution of 347 µg/L chlorine, a single operator obtained a standard deviation of ±3.2 µg/L chlorine.

Detection Limit

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

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* The standard additions technique is not applicable for samples containing excess reducing agents such as sulfur dioxide, sulfite, or bisulfite.

Sampling and Storage

Chlorine is rapidly lost from water. Avoid exposure to sunlight or other strong light. Avoid excessive agitation. Analyze samples immediately.

Interferences

- Silver ions poison the electrode.
- Copper ions interfere.
- Interferences are sometimes found in highly turbid water and those containing surface active agents. Oxidized manganese and other oxidizing reagents give positive interferences.
- Some uncertainty in the end point may be observed with samples containing high organic content.
- Samples containing excess reducing agents, such as sulfur dioxide, sulfite, and bisulfite, do not contain free chlorine or chloramines and can not be titrated under the conditions of the test.
- 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.

Summary of Method

In the amperometric forward titration procedure for total 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 total chlorine, an equivalent amount of iodine forms from the reaction of excess iodide with chlorine and combined chlorine at pH 4. During the titration with phenylarsine oxide (PAO), the free iodine is reduced to iodide at the cathode 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 iodine and iodide are present in solution; therefore current can flow, even with a very small applied potential. At the end point, no free iodine 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 total chlorine has been reacted.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Phenylarsine Oxide Solution, 0.00564 N Digital Titrator cartridge	each	1999-01
Acetate Buffer Solution, pH 4	100 mL MBD	14909-32
Potassium Iodide Powder Pillows	100/pkg	1077-99

REQUIRED APPARATUS

Amperometric Titrator Assembly	each	19299-00
Digital Titrator	each	16900-01
Beaker, low-form, 250 mL	each	500-46
Cylinder, graduated, 250 mL	each	508-46
Delivery Tubes, 90° with hook	5/pkg	41578-00
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	20953-55
TitraStir Stir Plate, 115 Vac	each	19400-00
TitraStir Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite Ampule, 50-75 mg/L Cl_2, 2 mL	20/pkg	14268-20
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
PourRite Ampule Breaker	each	24846-00
Handbook: Standard Methods for the Examination of Water and Wastewater, 19th edition	each	22708-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

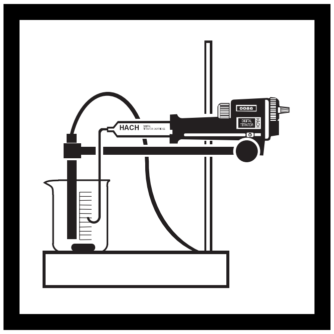
Method 10025

CHLORINE, TOTAL (6-1000 µg/L Chlorine)

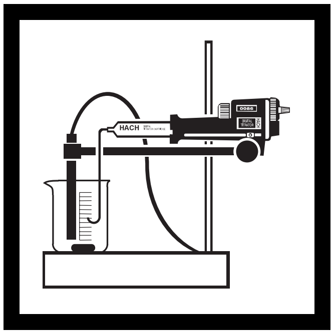
For wastewater

Back Titration Method—Using a Digital Titrator and 0.028 N Iodine USEPA Accepted for reporting*

Phase 1: Adjusting the Electrode Response Slope



1. Assemble the Amperometric Digital Titrator System according to the instructions in *SECTION 2* on page *9*.



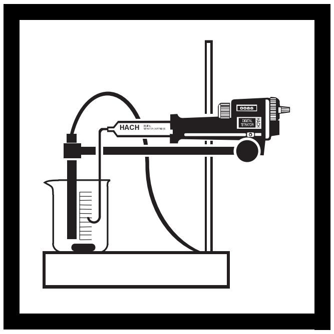
2. Install the Standard Iodine Titrant Cartridge, 0.028 N. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

***Note:** When a new probe is used or the probe has not been used recently, prepare it according to the Probe Stabilization instructions in 2.3 on page 14.*

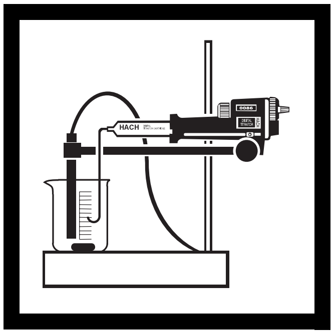
3. Using a graduated cylinder, measure 200 mL of deionized water into a clean 250-mL beaker. Place the 50-mm stirring bar supplied with the system into the beaker.

***Note:** An improper size stirring bar can result in volatilization of iodine, instability of readings and loss of sensitivity.*

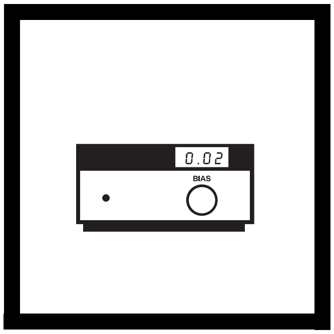
4. Add 1 mL of pH 4 Acetate Buffer and the contents of one Potassium Iodide Pillow.



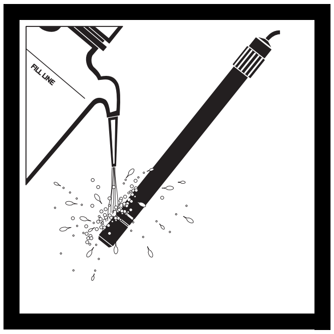
5. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



6. Using the Digital Titrator delivery knob, add 50 digits of Standard Iodine Titrant Solution.



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



8. Remove the probe arm from the beaker and rinse the platinum wires with deionized water. Adjustment of the electrode response slope is complete.

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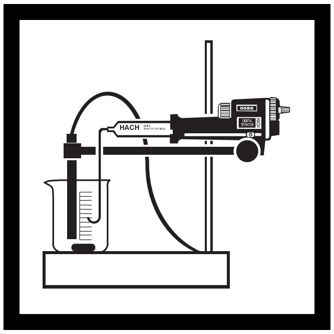
* Procedure is equivalent to USEPA method 330.2 and *Standard Method (18th ed.)* 4500-Cl C for wastewater.

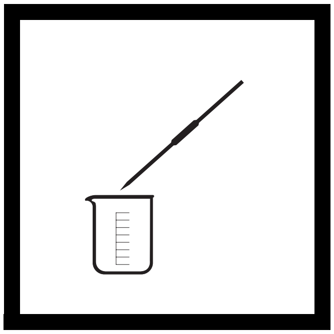
Phase 2: Standardization of the Iodine Titrant



1. Set-up the Amperometric Digital Titrator System as in *Phase 1: Adjusting the Electrode Response Slope* if it has not already been done. Reset the Digital Titrator counter to zero and wipe the tip.

2. Using a graduated cylinder, measure 200 mL of deionized water into a clean 250-mL beaker. Place the 50-mm stirring bar supplied with the system into the beaker.

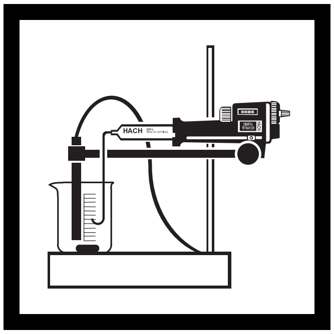
Note: *An improper size of stirring bar can result in volatilization of iodine, instability of readings and loss of sensitivity.*



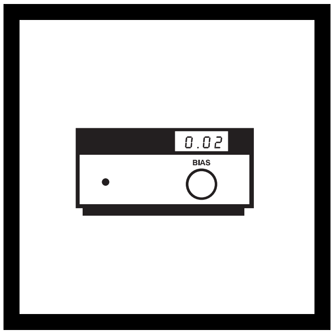
3. Using a Class A pipet, transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the beaker. Swirl to mix.

Note: *You may use 0.00564 N Phenylarsine Oxide (PAO), Cat. No. 1999, instead of thiosulfate.*

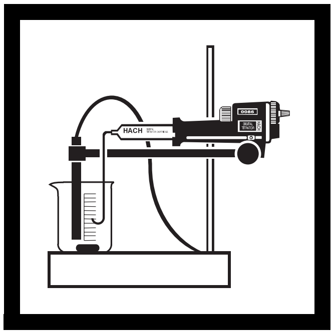
4. Add 1 mL of pH 4 Acetate Buffer Solution and the contents of one Potassium Iodide Powder Pillow.



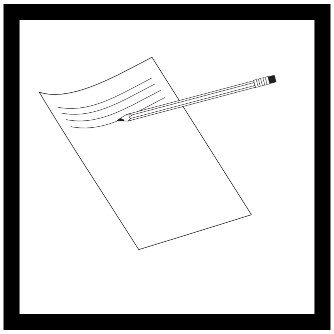
5. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



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

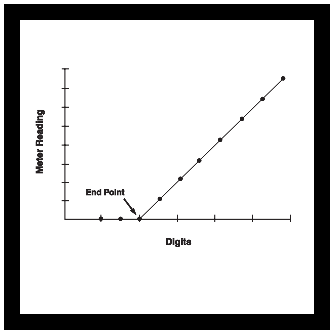


7. Using the Digital Titrator delivery knob, dispense 100 digits of Standard Iodine Titrant Solution and note the LED reading.

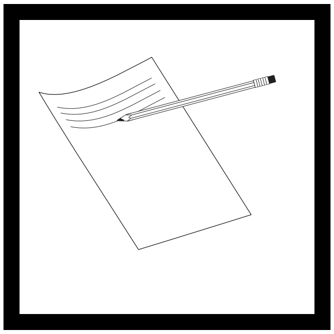


8. Continue dispensing titrant in 5 to 10 digit increments while noting the reading. Record at least three points (the null current values), before the end point is reached. After the end point of the titration (nominal 160 digits), record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter. Add 5 to 10 digits of titrant; wait a few seconds for a stable reading and record it. Stop adding titrant when the LED readings exceed 0.60.

Note: *LED readings above 0.60 will be excessively noisy.*



9. 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. Draw the two best intersecting lines through the points plotted. See *Figure 16*. Determine the number of digits at the intersection of the lines. This is the *standard* end point.



10. Record the standard end point digits value. This value will be used in calculation of the sample chlorine concentration.

Note: *The iodine titrant concentration is approximately 0.0282 N; it should take 160 digits to titrate 1.00 mL of 0.00564 N Thiosulfate. If the calculated end point is greater than 160 digits, this indicates the Standard Iodine Titrant is weaker than when packaged. Discard the Standard Iodine Titrant cartridge if the calculated standardization end point is greater than 200 digits.*

See Table 1.

11. Locate the appropriate multiplier based on the standard end point in *Table 1* . The multiplier is used in *Phase 3: Titration of Sample for Total Residual Chlorine*. Interpolation between values in the table is not necessary.

Calculate the µg/L total chlorine:

Digits (standard end point) - Digits (sample end point) x Multiplier = µg/L Cl_2

Use the appropriate multiplier based on the number of digits required for the standard end point:

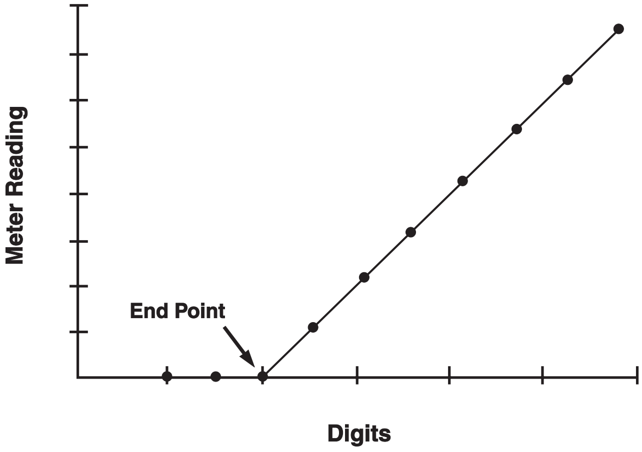
Example:

Standard EP = 160 digits
Sample EP = 150 digits
µg/L total chlorine =
[160 - 150] x 6.25 = 10 x 6.25 = 63 (round up)

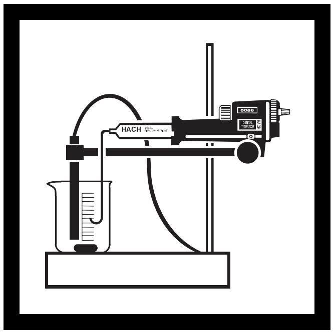
Table 1

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

Figure 16 Back Amperometric Titration Graph



Phase 3: Titration of Sample for Total Residual Chlorine



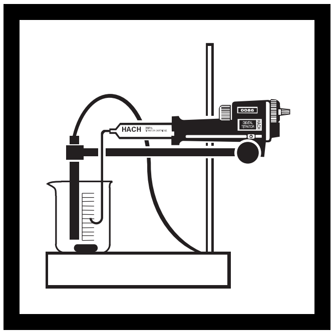
1. Set-up the Amperometric Digital Titrator System as in *Phase 1: Adjusting the Electrode Response Slope* if it has not already been done. Reset the Digital Titrator counter to zero and wipe the tip.

2. Place a clean 50-mm stirring bar supplied with the system into a clean 250-mL beaker. Using a Class A pipet, transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the a beaker. Add 1 mL of pH 4 Acetate Buffer Solution to the beaker.

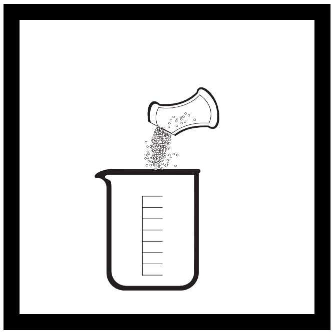
Note: *An improper size stirring bar can result in volatilization of chlorine, instability of readings and loss of sensitivity. Alternatively, use 0.00564 N Phenylarsine Oxide (PAO), Cat. No. 1999, instead of thiosulfate.*

3. With minimum agitation, measure 200 mL of sample with a clean graduated cylinder and transfer the sample to the beaker. Swirl to mix the reagents with sample.

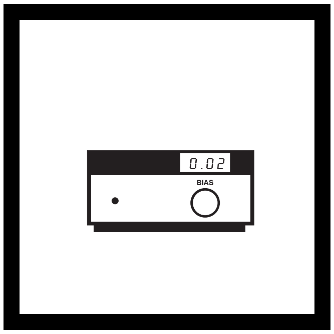
Note: *Steps 2-3 can be performed at the sampling site thereby "fixing" the sample for later analysis. Pipet 1.00 mL of 0.00564 N Sodium Thiosulfate and add 1.0 mL of Acetate Buffer into a clean, dry glass sampling bottle (e.g., BOD bottle). At the sample site, measure 200 mL of sample with a graduated cylinder and transfer to the sampling bottle. Swirl to mix. 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.)*



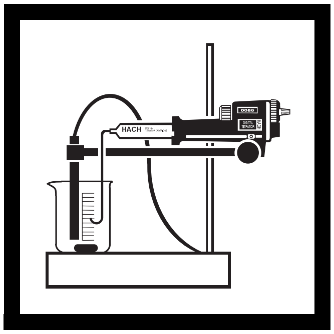
4. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



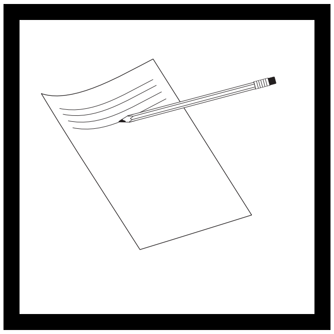
5. Add the contents of one pillow of Potassium Iodide Reagent to the beaker and allow the powder to dissolve.



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

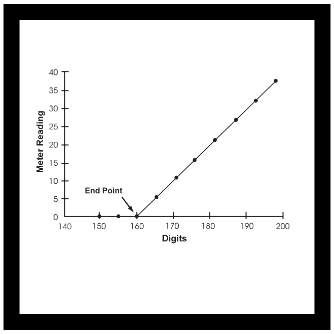


7. Using the Digital Titrator delivery knob, dispense the Standard Iodine Titrant Solution in 5 to 10 digit increments while noting the reading. Record at least three points (the null current values and Digital Titrator reading), before end point is reached.

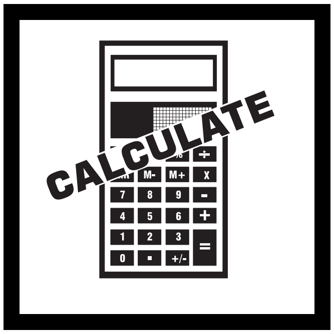


8. After the end point of the titration is reached, record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter. Add 5 to 10 digits of titrant; wait a few seconds for a stable reading and record. Stop the titrant addition when the LED readings exceed 0.60.

Note: *LED readings above 0.60 will be excessively noisy. With samples containing 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 combined or free chlorine is in the sample.*



9. 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. Draw the two best intersecting lines through the points plotted. See *Figure 16* on page *56*. Determine the number of digits at the intersection of the lines. This is the *sample* end point.



10. Calculate the µg/L total chlorine:

[Digits (Standard End Point) - Digits (Sample End Point)] x Multiplier = µg/L Cl_2
(Multiplier is from Phase 2.)

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

µg/L total chlorine =
[160 - 150] x 6.25 =
10 x 6.25 = 63 (round up)

***Note:** 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.*

Sampling 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 as indicated in *Titration of Sample*. The fixing procedure should be used for brief transportation delays **-** not for storage of samples.

Accuracy Check

Standard Additions Method*

Snap the top off a Chlorine Standard Solution PourRite Ampule. Note the certificate value of the standard in mg/L.

1. Split a fresh sample into two 200-mL portions.
2. Using a TenSette Pipet, add from 0.1 to 0.5 mL of the standard to one portion and swirl to mix. This is the *spiked sample*.

---

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

3. Analyze each sample as described above and record the chlorine concentrations.

4. 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 in mL
C_s = concentration of chlorine standard (mg/L, certificate value)
V_s = volume of standard added in mL

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

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

5. Calculate the percent spiked recovery:

$$\%\ \text{Spike recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}} \times 100$$

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

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.

Interferences

- Silver ions poison the electrode.
- Copper ions interfere.
- Interferences are sometimes found in highly turbid water and those containing surface active agents.
- Oxidized manganese and other oxidizing reagents give positive interferences.
- Some uncertainty in the end point may be observed with samples containing high organic content.
- Iron and nitrite interference are minimized by buffering to pH 4 before adding potassium iodide.
- In samples containing excess reducing agents, such as sulfur dioxide, sulfite, and bisulfite, the titration end point will be shifted, indicating the sample contains no free or combined chlorine.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the buffer reagent. If necessary, add additional buffer and check the pH of the sample prior to titration.

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 the back titration 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 with the null current, the number of digits (from the Digital Titrator) at the end point can be determined and the concentration of chlorine calculated.

It is necessary to adjust the electrode sensitivity by using the bias control prior to performing the analysis. The bias adjustment is set 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.

Although the iodine titrant solution is formulated and packaged to be quite stable it is recommended the iodine be routinely standardized against standard thiosulfate or phenylarsine oxide. The number of digits determined for the iodine standardization is recorded and used in the calculation of the sample's chlorine concentration.

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.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Acetate Buffer Solution, pH 4.0	100 mL MDB	14909-32
Potassium Iodide Powder Pillows	100/pkg	1077-99
Standard Iodine Titrant Solution Cartridge, 0.028 N	each	23333-01
Sodium Thiosulfate Standard Solution, 0.00564 N	100 mL	24088-42

REQUIRED APPARATUS

Amperometric Titrator Assembly	each	19299-00
Beaker, low-form, 250 mL	each	500-46
Cylinder, graduated, 250 mL	each	508-46
Digital Titrator	each	16900-01
Delivery Tubes, 90° with hook	5/pkg	41578-00
Pipet, volumetric, Class A, 1 mL	each	14515-35
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm,	each	20953-55
TitraStir Stir Plate, 115 Vac	each	19400-00
TitraStir Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite Ampule 50-75 mg/L Cl_2, 2 mL	20/pkg	14268-20
Phenylarsine Oxide Solution, 0.00564 N	100 mL	1999-42
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Bottle, BOD, 300 mL	each	621-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
PourRite Ampule Breaker	each	24846-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

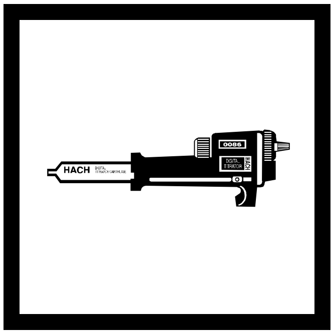
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8314

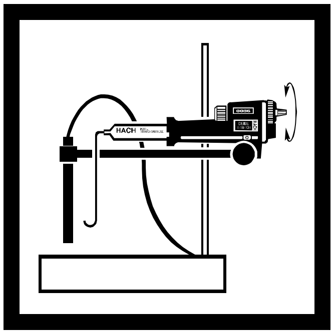
CHLORINE, TOTAL (0-10 mg/L)

For water and wastewater

Forward Titration Method—Using a Digital Titrator and 0.0451 N PAO

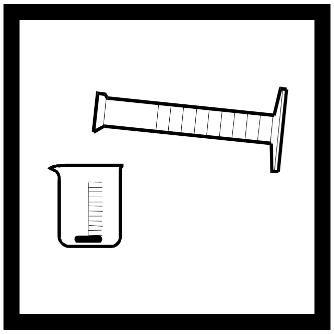


1. Install the 0.0451 N Phenylarsine Oxide Titration Cartridge (PAO) in the Digital Titrator.



2. Assemble the Amperometric Digital Titrator System according to the instructions in *SECTION 2* on page *9*. 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.

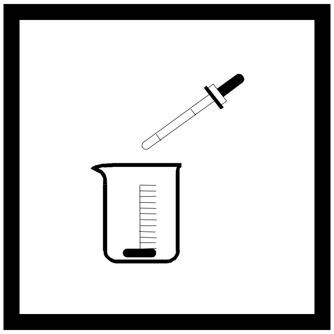
***Note:** When using a new probe or a probe that has not been used recently, prepare the probe according to the Probe Stabilization instructions in Section 2.3 on page 14.*



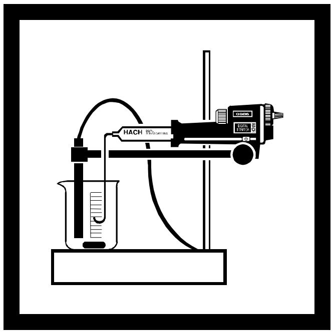
3. With minimal agitation, measure 200 mL of sample in a clean graduated cylinder. Transfer to a clean 250-mL beaker containing the 50-mm stirring bar supplied with the system.

***Note:** An improper-sized stirring bar can cause volatilization of chlorine, unstable readings and decreased sensitivity. This is especially true when measuring low chlorine levels.*

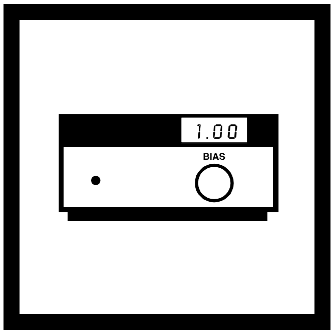
4. Add the contents of one Potassium Iodide Powder Pillow. Swirl to dissolve.



5. Add 1 mL of pH 4 Acetate Buffer Solution.



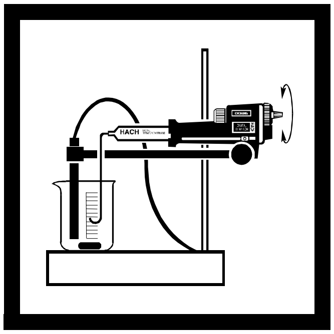
6. Place the beaker on the TitraStir Stir Plate. Turn on the stirring motor. Immerse the tips of the probe and delivery tube into the sample. Make sure the platinum wires are submerged.



7. Note the LED reading. Use the BIAS control to adjust the LED reading to about 1.00.

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

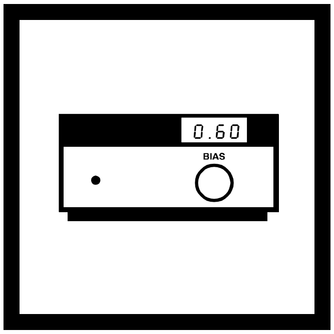
Note: *If using a chart recorder, adjust the BIA control or vary the recorder voltage for a full-scale recorder reading.*



8. Using the Digital Titrator delivery knob, dispense the titrant in small increments (5 to 10 digits). The readings on the Amperometric Titrator will decrease.

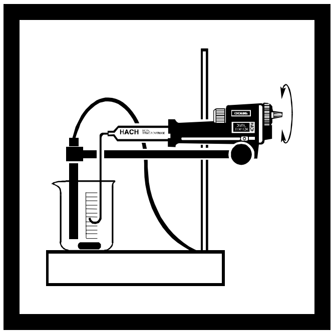
Note: *If the chlorine level is high, add large volumes of titrant at first- only the endpoint of the titration and the volume of titrant at the end point are important. For example, if the chlorine level is 5 mg/L, up to 400 digits of 0.0451 N titrant could be added at once.*

Note: *When using a chart recorder, dispense each increment of titrant at a uniform time interval (i.e., just as a fixed length of chart paper passes the chart pen.)*

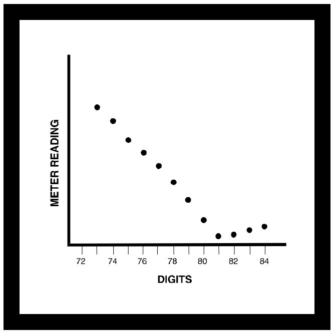


9. As the end point approaches, record the LED reading and the corresponding digits on the Digital Titrator. Add a small amount of titrant; wait a few seconds for a stable reading and record.

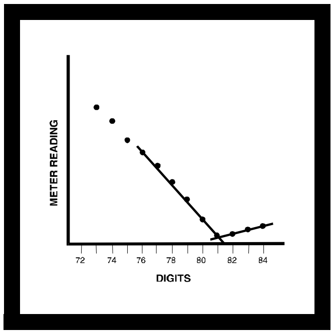
Note: *When using a chart recorder, record the digits on the chart paper. You do not need to record the LED readings.*



10. Continue the titration. Record at least three points on the downward sloping curve and at least three points after the end point has been reached. The last three points will show very little change in the meter readings.

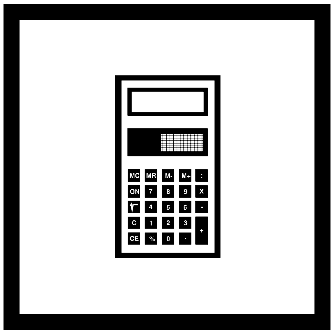


11. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis. See *Figure 13* on page *41*.



12. Draw the two best intersecting lines through the points. Determine the number of digits at the intersection of the lines; this is the end point.

Note: *If using a chart recorder, place a point at the edge of each step as shown in Figure 13 on page 41. Draw two best fitting lines through the points. Determine the number of digits of titrant at the intersection of the linear sections of the titration curve.*



13. Calculate the mg/L of total chlorine as follows:

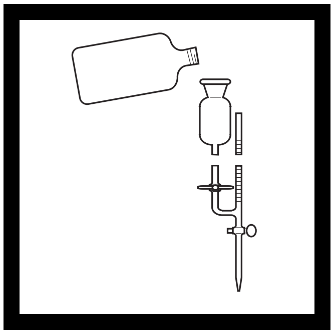
Digits at End Point x 0.01
= mg/L total chlorine as Cl_2

Method 8168

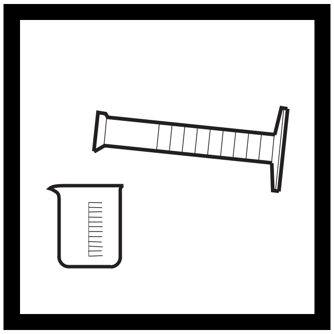
CHLORINE, TOTAL

For water and wastewater

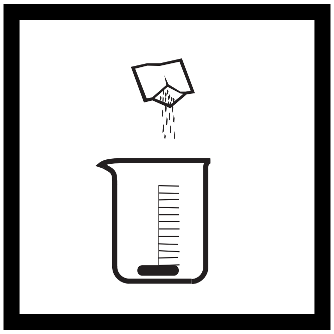
Forward Titration Method—Using a Buret and 0.00564 N PAO* ; USEPA Accepted for water and wastewater



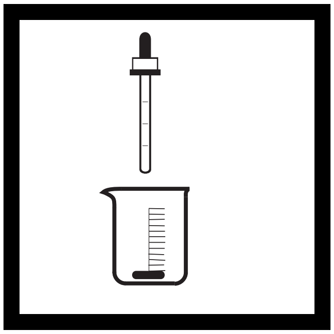
1. Fill the 5-mL automatic buret to the zero mark with 0.00564 N Phenylarsine Oxide (PAO) Solution.



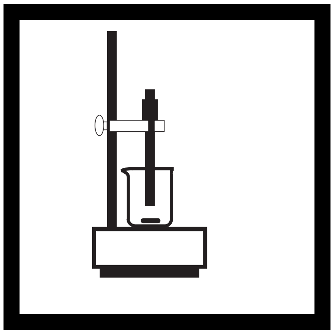
2. Use a graduated cylinder to measure 200 mL sample into a 250-mL beaker.



3. Add the contents of one Potassium Iodide Powder Pillow. Swirl to dissolve. Place a 50-mm stir bar into the beaker.



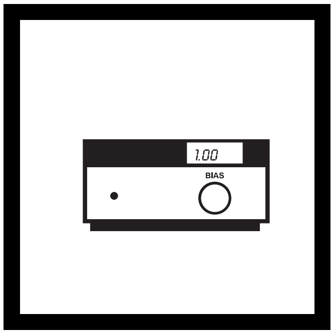
4. Add 1.0 mL of pH 4 Acetate Buffer Solution to make the prepared sample.



5. Place the beaker of prepared sample on the TitraStir Stir Plate and turn on the stirring motor. Immerse the tip of the probe in the prepared sample. The platinum wires must be submerged.

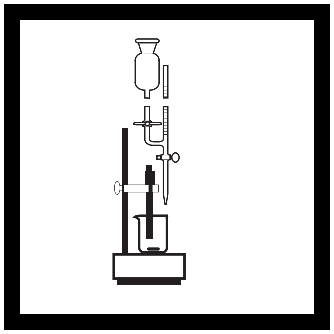
Note: *If a stir plate other than the TitraStir Stir Plate is used, set the speed for moderate mixing-do not adjust the speed after this point.*

Note: *If the probe is new or has not been used recently, condition the probe as described in the instrument manual.*

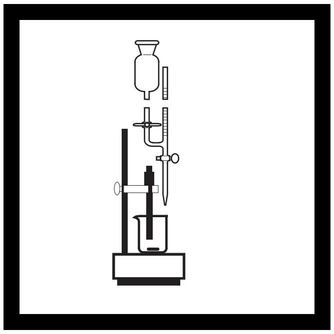


6. Note the LED reading on the Amperometric Titrator. Using the BIAS control, adjust the LED reading to about 1.00.

Note: *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. A precise adjustment is not required.*



7. Dispense the titrant into the beaker in small increments while observing the downward readings on the Amperometric Titrator.



8. Continue dispensing slowly. At the end point of the titration is approached, record the LED reading along with the corresponding total volume of titrant added to the nearest 0.01 mL. Add a small amount of titrant; wait a few seconds for a stable reading and record.

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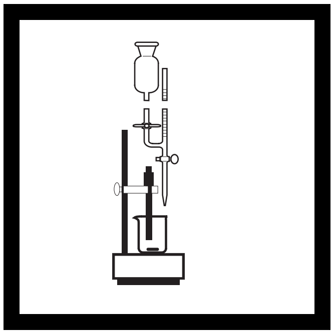
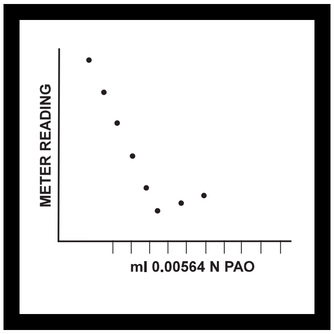
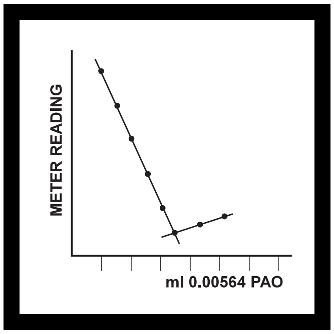
* Adapted from *Standard Methods for the Examination of Water and Wastewater,* 18th edition, 4500-C1 D.



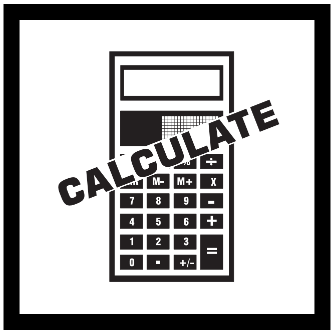
9. Continue the titration by recording at least three points on the downward sloping curve and at least three points after the end point has been reached. The latter points will indicate little change in the meter readings.



10. Construct a graph of the titration by plotting the readings obtained from the Amperometric Titrator display on the vertical axis and the corresponding volume of titrant used on the horizontal axis.



11. Draw the two best intersecting lines through the points plotted as shown above. Determine the volume of titrant used to the nearest 0.01 mL at the intersection of the 2 lines. This is the mL Titrant at End Point.



12. Determine the total chlorine concentration:

mL Titrant at End Point

= mgL Total Chlorine Cl_2

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinty influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

Do not use the same sample containers for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to separate, dedicated sample containers for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. Perform the chlorine analysis immediately.

Interferences

Refer to *SECTION 5* on page *19* for a discussion of sources of errors and interferences using the amperometric methods.

Summary of Method

Total chlorine is determined by adding potassium iodide to the sample and titrating at pH 4 with PAO to the amperometric end point. Refer to *Section 1.1.1* on page *3* for more information.

REQUIRED REAGENTS

	Cat. No.
Chloride Reagent Set (about 200 tests)	24607-00

Includes: (2) 14909-37, (1) 1999-16, (2) 1077-99

Description	**Quantity Required Per Test**	**Unit**	**Cat. No.**
Acetate Buffer Solution, pH 4	1 mL	100 mL MDB	14909-32
Phenylarsine Oxide Solution, 0.00564 N	varies	1 L	1999-53
Potassium Iodide Powder Pillows	1 pillow	100/pkg	1077-99

REQUIRED APPARATUS

Select one based on available voltage:

Amperometric Buret Titrator System (115 Vac)	each	19300-10
Includes: 14909-37, 1999-16, 1077-99, 19299-00, 20550-37, 328-00, 508-46, 19300-08, 20953-55, 563-00, 19400-00, 500-46, 21553-32		
Amperometric Buret Titrator System (230 Vac)	each	19300-12
Includes:14909-37, 1999-16, 1077-99, 19299-00, 20550-37, 328-00, 508-46, 19300-08, 20953-55, 563-00, 19400-10, 500-46, 21553-32		
Beaker, 150 mL	each	500-44

OPTIONAL APPARATUS

Buret, automatic, 5 mL	each	20550-37
Buret Clamp	each	328-00
Cylinder, graduated, 250 mL	each	508-46
Instruction Manual, Amperometric Titrator	each	19300-08
Microscribe Strip Chart Recorder	each	24080-00
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, 50 mm	each	20953-55
Support Stand	each	563-00
TitraStir Stir Plate, 115 Vac	each	19400-00
TitraStir Stir Plate, 230 Vac	each	19400-10

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With that in mind, we have compiled the following information for your convenience.

REPLACEMENT PARTS AND REAGENTS

APPARATUS

Description	**Cat. No.**
Beaker, 250-mL	500-46
Buret, automatic, 5-mL	20550-37
Buret Holder	328-00
Circuit Board, display	19205-01
Circuit Board, main	19309-00
Cylinder, graduated, 250-mL	508-46
Delivery Tubes, 90° with hook, 5/pkg	41578-00
Digital Titrator	16900-01
Electronic Schematic Drawing	19318-00
Fl Fuse, 1/8-A, 3AG,for 115 V operation	11601-24
Fl Fuse, 1/16-A, 3 AG, for 230 V operation	11603-24
Manual, Amperometric Titrator	19300-08
R3 Potentiometer, bias control, 10K, ½ W, 10%	12365-18
Power Cord, Probe	18010-00
Assembly, amperometric titrator	19390-00
Recorder Plug, 3-conductor, 1/4-inch	16084-00
Stirring Bar, 50-mm	20953-55
Support Stand	563-00
S1 Switch, power, SPDT	19254-00
TitraStir Titration Stand, 115 V	19400-00
TitraStir Titration Stand, 230 V	19400-10
Titrator/Electrode Holder Assembly	19401-00

REAGENTS

Acetate Buffer Solution, pH 4, 100 mL MDB*	14909-32
Nitric Acid Solution, 1:1 , 500 mL	2540-49
PAO (Phenylarsine Oxide) Standard Solution, 0.00564 N, 100 mL	1999-42
PAO (Phenylarsine Oxide) Titration Cartridge, 0.0451 N	21420-01
PAO (Phenylarsine Oxide) Titration Cartridge, 0.00564 N	1999-01
Phosphate Buffer Solution, pH 7, 100 mL MDB	21553-32
Potassium lodide Powder Pillows, 100 pillows	1077-99
Sodium Thiosulfate Standard Solution, 0.00564 N, 100 mL	24088-42
Standard Iodine Titrant Cartridge, 0.0282 N	23333-01

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* Marked dropping bottle

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