16900-08

Digital Titrator

Model 16900

jk/dk March 2013 25 ed

TABLE OF CONTENTS

ACID-BASE

ACIDITY

ALKALINITY

AMMONIA, HIGH RANGE (Ammonium Hydroxide)

CARBON DIOXIDE

CHELANT, FREE

CHELANT, TOTAL

TABLE OF CONTENTS, continued

CHLORIDE

CHLORINE, FREE AND TOTAL

CHLORINE, TOTAL

CHLORINE, FREE

CHLORINE, TOTAL

CHLORINE, TOTAL

CHROMATE

HARDNESS, CALCIUM

HARDNESS, TOTAL

HARDNESS, TOTAL, SEQUENTIAL

HYPOCHLORITE (Bleach)

IRON

NITRITE

TABLE OF CONTENTS, continued

OXYGEN, DISSOLVED

SALINITY

SULFITE

TURBIDITY STANDARDS

VOLATILE ACIDS

APPENDIX A

SPECIFICATIONS

Digital Titrator

Delivery: 800 digits/mL or 0.00125 mL/digit

Accuracy*: ± 1% for readings over 100 digits. (Uncertainty of readings is 1 digit. Most samples require more than 100 digits.)

Weight: 132 g (4.7 oz.)

Cartridges for the Digital Titrator

Volume: 13 mL

Number of tests: Most reagents are formulated to provide 100 typical titrations; the number may vary depending on sample concentration.

Weight (full): 56.75 g (2 oz.)

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* Overall method accuracy includes, in addition to the Digital Titrator, other sources of error controlled by the analyst. The other sources of error include: sampling, sample volume, dilution (if required), end point detection, reagent quality, and interferences.

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.

DANGER

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les Fiches de Données de Sécurité des Produits (FDSP) et se familiariser avec toutes les procédures de sécurité avant de manipuler tous les produits chimiques.

PELIGRO

La manipulación de muestras químicas, estándares y reactivos puede ser peligrosa. Revise las fichas de seguridad de materiales y familiarícese con los procedimientos de seguridad antes de manipular productos químicos.

GEFAHR

Das Arbeiten mit chemischen Proben, Standards und Reagenzien ist mit Gefahren verbunden. Es wird dem Benutzer dieser Produkte empfohlen, sich vor der Arbeit mit sicheren Verfahrensweisen und dem richtigen Gebrauch der Chemikalien vertraut zu machen und alle entsprechenden Materialsicherheitsdatenblätter aufmerksam zu lesen.

PERIGO

A manipulação de amostras, padrões e reagentes químicos pode ser perigosa. Reveja a folha dos dados de segurança do material e familiarize-se com todos os procedimentos de segurança antes de manipular quaisquer produtos químicos.

GENERAL DESCRIPTION

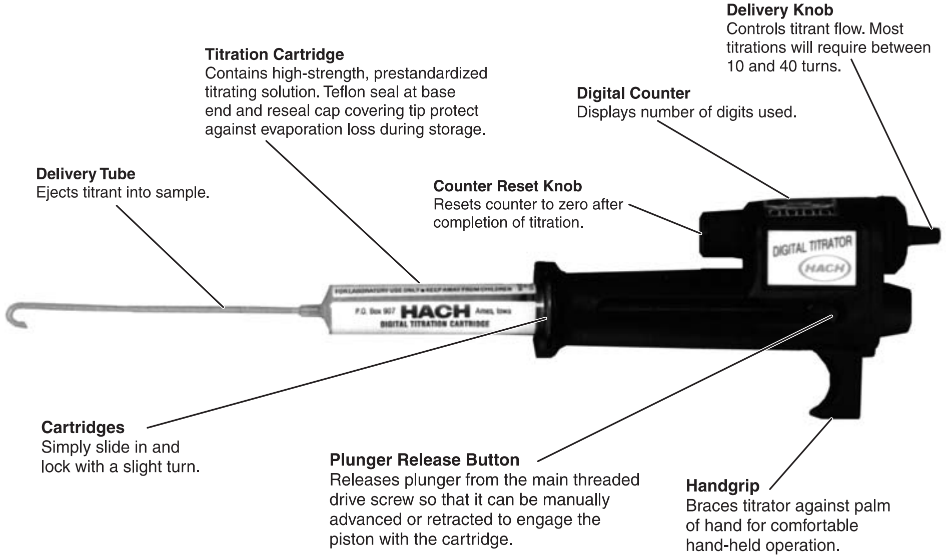
1.1 Introduction

Hach's Digital Titrator is a new concept in titrimetric analysis. It is a precision dispensing device fitted with compact cartridges that contain concentrated titrants. Accurate titrations are made without the bulk and fragility of conventional burets.

A main drive screw in the Digital Titrator controls a plunger which forces the concentrated titrant from a titration cartridge in a carefully regulated flow. The titrator body is constructed of precision-molded, heavy-duty, chemical- and impact-resistant acetal plastic. Accuracy is rated at ± 1% or better for a titration of more than 100 digits. For titrations less than 100, accuracy is ± 1 digit.

Titration solutions (titrants) are packaged in disposable polypropylene or Kynar® containers with Teflon-covered neoprene seals and polyethylene resealable closures to cover the cartridge tips. Each cartridge contains approximately 13 mL of titrating solution, enough for 50–100 average titrations. Titrant solutions are typically controlled to ± 0.5% concentration with normality and tolerances listed on the label. Titrant concentrations are designed for titrations of 10 to 40 turns (100 to 400 digits) of the delivery knob. For the most commonly used concentration ranges, the digits appearing in the counter window correspond to the sample concentration.

Figure 1 Hach Digital Titrator



Both portable and fixed-position titrations are possible with the Digital Titrator. The instrument has a grip for hand-held operation or it can be clamped to a TitraStir® Stir Plate or laboratory stand for stationary setups. See *Figure 1*.

Each Digital Titrator comes with five delivery tubes and a methods manual, which covers the most commonly tested parameters and the corresponding titrant cartridges. Right-angle (ninety-degree) delivery tubes for stationary setups are available as an optional accessory.

1.1.1 Following a Procedure for the First Time

Each method is divided into five sections: Procedure, Accuracy Check, Interferences, Summary of Method, and Reagents and Apparatus. For more information about how to select a procedure or for answers to chemical questions, see Hach's *Water Analysis Handbook* (literature 8376). For more information about chlorine measurement, also see the technical booklet titled, *Current Technology of Chlorine Analysis for Water and Wastewater* (literature 7019).

The **Procedure** details how to perform the method step-by-step. To select the appropriate sample volume and titration cartridge based on expected sample concentration, use the tables provided in each procedure. If the expected sample concentration is not known, start with one of the smaller sample volumes and determine its approximate concentration. Retest with the appropriate sample size.

The ranges in the table overlap to offer more flexibility. In most procedures, the number of digits used for each concentration range will be 100 to 400 digits.

To determine the actual concentration of the sample, use the correct digit multiplier for the sample volume and titration cartridge used.

Throughout the procedure, the notes will provide additional information.

The **Accuracy Check** provides a way to verify the results and determine if interferences are present. It also provides a method for checking the performance of reagents, the Digital Titrator and the operator's technique. Further information is provided in *Appendix A, Accuracy Check and Standard Additions*.

The **Interferences** section identifies common interferences causing inaccurate results and describes how to eliminate their effects. The interference levels are based on the sample volume that has 1.0 as the digit multiplier. Higher interference levels may be tolerated if a smaller sample is used.

The **Summary of Method** section discusses the chemical reaction taking place and information that applies to the entire procedure.

The **Reagents and Apparatus** list concludes the procedure. All the items required to perform the test are listed first and are available from Hach. The items listed in the notes or interferences sections are included in the optional listings.

1.2 Step-By-Step

1. Select a sample volume and titration cartridge corresponding to the expected sample concentration from the table given in each procedure.

   If the expected sample concentration is not known, start with one of the smaller sample volumes and determine its approximate concentration. Retest with the appropriate sample size.

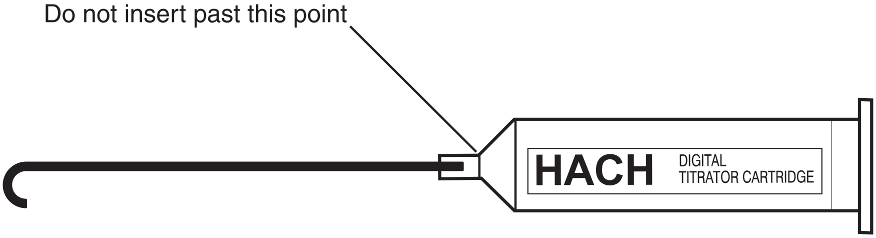
2. Slide the cartridge into the titrator receptacle and lock in position with a slight turn. See *Figure 2.*

Figure 2 **Sliding the Cartridge into Place**

3. Remove the polyethylene cap and insert a clean delivery tube into the end of the cartridge until it is tight. See *Figure 3.* Use a straight tube with a hook at the end for hand-held titrations; use a 90° tube with a hook at the end for stationary setups.

   Do not insert tube past cartridge extension; see illustration below. In some instances, it might be necessary to remove a small burr on the leading edge of the tube before insertion.

Figure 3 **Inserting the Delivery Tube**



4. For stationary titrations, use a TitraStir Stir Plate or a clamp holder and clamp to attach the titrator to a laboratory stand. See *Figure 4* and *Figure 5.*

   The TitraStir Stir Plate holds the Digital Titrator during the titration and also stirs the sample at a constant speed, leaving the analyst free to detect the end point.

When a TitraStir Stir Plate is used, substitute or add the following Optional Apparatus.

APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	1	5/pkg	41578-00
Flask, Erlenmeyer, 125 mL	1	each	505-43
Flask, Erlenmeyer, 250 mL	1	each	505-46
Stir Bar, 28.6 x 7.9 mm	1	each	20953-52
TitraStir® Stir Plate, 115 Vac	1	each	19400-00
TitraStir® Stir Plate, 230 Vac	1	each	19400-10

5. To start titrant flowing and flush the delivery tube, hold the tip of the cartridge up. Advance the plunger release button to engage the piston with the cartridge (push the button in and toward the cartridge). Do not expel solution when pushing the piston toward the cartridge. Turn the delivery knob until air is expelled and several drops of solution flow from the tip. As you turn the knob a drive screw pushes a piston against the cartridge seal and forces liquid out through the delivery tube. Then use the counter reset knob to turn the digital counter back to zero and wipe the tip. The tip can be rinsed with deionized water rather than wiped, if desired.

Figure 4 Using the TitraStir® Stir Plate

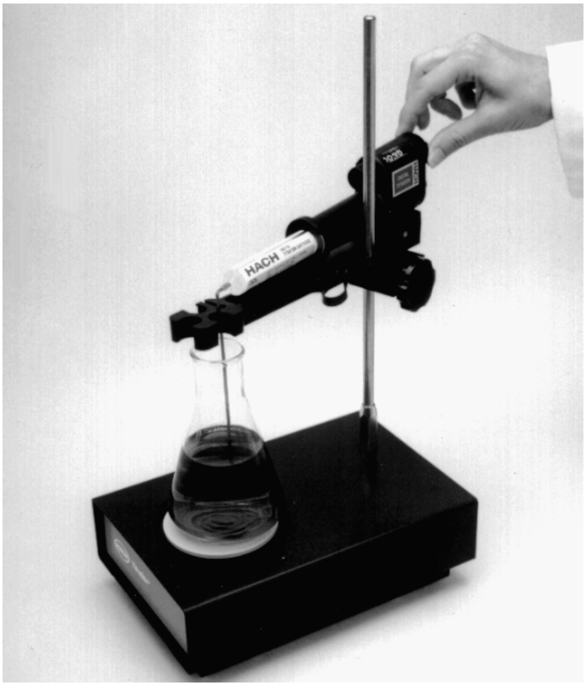


Figure 5 Using a Laboratory Stand

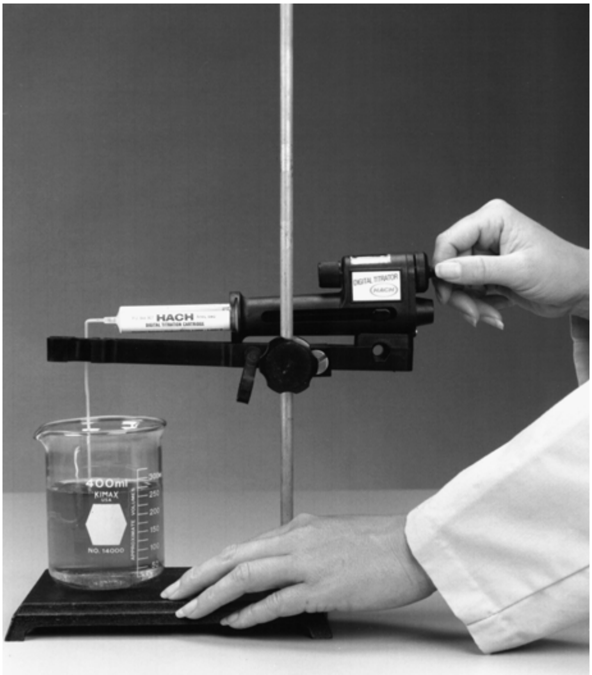


Figure 6 Titrating the Sample

6. Use the smallest appropriate graduated cylinder or pipet to measure the sample volume from the given table. Transfer the sample into a 125-mL or 250-mL Erlenmeyer flask. Dilute to the appropriate total volume with deionized water if necessary.

Note: *Sample volume measurements and dilutions (if required) must be made accurately. However, final total volume of titrated solution is not critical.*

7. Add the necessary reagents to the sample and swirl to mix.

8. Immerse the delivery tube tip in the solution and swirl the flask while titrating. Titrate by turning the delivery knob. Keep turning the knob and swirling the sample until the end point is reached. Record the number of digits that appear in the digital counter window. See *Figure 6*.

Note: *The number of digits required will usually range from 100 to 400. In nearly all of the procedures if the digits required is less than 100 or more than 400, an alternate sample volume or titrant cartridge should be used.*

Note: *Inaccurate results will occur if the delivery tube tip is held out of the solution rather than under the solution surface.*

9. Calculate the concentration of your sample by using the following formula:

Digits Required × Digit Multiplier = Sample Concentration

Where:

Digits Required = the number that appeared in the digital counter window in Step 8.

Digit Multiplier = the number from the table given in the procedure. It takes into account the sample dilution and titrant strength.

10. After completing testing for the day, press the plunger release button and manually retract the plunger into the body of the titrator. Remove the cartridge. Remove the delivery tube and reseal the cartridge with the polyethylene cap. See *Figure 7.*

Figure 7 **Retracting the Plunger**

11. Discard or clean the delivery tube immediately after use. To clean, force water, then air, into the tube opening with a syringe or wash bottle.

1.3 Helpful Hints

1.3.1 To Reuse a Partially Emptied Cartridge

1. With the plunger fully retracted, attach cartridge to the titrator.
2. Press the plunger release; then manually push the plunger against the cartridge seal.
3. Attach a delivery tube. Hold the tip of the cartridge up. Eject air and a few drops of titrant, zero the counter, and wipe the tip.
4. Titrate as usual.

1.3.2 To Calculate Titrant Volume Used

Normalities of many Hach titration cartridge solutions have been designed so that the number of digits used in a titration corresponds to the sample concentration in mg/L. To determine the volume used in mL, divide the Digital Titrator reading by 800.

1.3.3 To Fill Your Own Titration Cartridges

Cartridges may be cleaned and refilled, or new empty cartridges, Cat. No. 14495-01, can be purchased from Hach Company. See *Figure 8*. When preparing to refill old cartridges, push the cartridge seal out of the cartridge with air pressure applied through the tip. Cap the tip, fill with solution and reinsert the cartridge seal using care to avoid wrinkling the Teflon sheath. Filling also can be accomplished at the tip with a syringe.

Figure 8 Digital Titrator Cartridges

1.3.4 Verifying Technique

Whenever procedures are changed or new equipment is used, it is helpful to run a sample of known concentration. This technique will confirm the operator is following the procedure correctly and the new equipment is working properly. One objective important to Hach Company is making our tests self-verifying. This means Hach makes the tools available so the operator can check their own work for accurate results without relying on an outside lab or chemist.

For most of the tests in this manual, *Table 1* on page *21* lists each procedure, the suggested standard, the volume of standard needed, the titration cartridge used, and the number of expected digits when the test is performed correctly. The suggested standards are Voluette® or PourRite™ Ampules whenever possible because of their superior accuracy and stability.

To use titration standards follow these steps:

1. Select the procedure of interest and order the appropriate standard. Use the given catalog numbers.
2. Measure the volume of standard to be used as the sample in the procedure using a TenSette® Pipet or Class A pipet.
3. Perform the procedure as written, adding deionized water as necessary.

4. After titrating, the required number of digits should approximately equal the expected digits.

Call Hach Technical and Customer Service (1-800-227-4224) for additional help.

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Table 1 Titration Standards

Procedure (Parameter)	Standard Description (Cat. No.)	Volume of Standard (mL)	Titration Cartridge (Cat. No.)	Expected Digits
Acid-Base: Acid	0.500 N H_2SO_4 (2121-26)	1.0	1.600 N NaOH (14379-01)	250
		5.0	8.00 N NaOH (14381-01)	250
Base	0.500 N Na_2CO_3 (14278-10)	1.0	1.600 N H_2SO_4 (14389-01)	250
		5.0	8.00 N H_2SO_4 (14391-01)	250
Acidity	0.500 N H_2SO_4 (2121-26)	0.1	0.1600 N NaOH (14377-01)	250
		1.0	1.600 N NaOH (14379-01)	250
Alkalinity	0.500 N Na_2CO_3 (14278-10)	0.1	0.1600 N H_2SO_4 (14388-01)	250
		1.0	1.600 N H_2SO_4 (14389-01)	250
Calcium*: mg/L $CaCO_3$	10,000 mg/L $CaCO_3$ (2187-10)	0.1	0.0800 M EDTA (14364-01)	100
		1.0	0.800 M EDTA (14399-01)	100
G.d.h.	10,000 mg/L $CaCO_3$ (2187-10)	0.2	0.1428 M EDTA (14960-01)	112
		1.0	0.714 M EDTA (14959-01)	112
Carbon Dioxide	10,000 mg/L CO_2 (14275-10)	0.2	0.3636 N NaOH (14378-01)	100
		2.0	3.636 N NaOH (14380-01)	

GENERAL DESCRIPTION, continued

Table 1 Titration Standards (Continued)

Procedure (Parameter)	Standard Description (Cat. No.)	Volume of Standard (mL)	Titration Cartridge (Cat. No.)	Expected Digits
Chloride	12,500 mg/L Cl (14250-10)	0.1	0.2256 N $Hg(NO_3)_2$ (14393-01)	125
		0.1	0.2256 N $AgNO_3$ (14396-01)	125
		1.0	1.128 N $AgNO_3$ (14397-01)	250
		1.0	2.256 N $Hg(NO_3)_2$ (921-01)	125
Chlorine	~50 mg/L Cl_2 (14268-20) (see certificate)	2.0	0.02256 N $Na_2S_2O_3$ (24091-01)	varies**
	~25 mg/L Cl_2 (26300-20)	0.5	0.00564 N FEAS (22923-01)	varies***
Chromate	1000 mg/L Cr (2231 mg/L CrO_4) (14664-42)	1.0	0.2068 N $Na_2S_2O_3$ (22676-01)	223
Hardness: mg/L $CaCO_3$	10,000 mg/L $CaCO_3$ (2187-10)	0.1	0.0800 M EDTA (14364-01)	100
		0.1	0.0800 M CDTA (14402-01)	100
		1.0	0.800 M EDTA (14399-01)	100
		1.0	0.800 M CDTA (14403-01)	100
G.d.h.	10,000 mg/L $CaCO_3$ (2187-10)	0.2	0.1428 M EDTA (14960-01)	112
		1.0	0.714 M EDTA (14959-01)	112
Iron	50 mg/L Fe (14254-10)	10.0	0.0716 M TitraVer (20817-01)	200
	1000 mg/L Fe (2271-42)	10.0	0.716 M TitraVer (20818-01)	100
Oxygen, Dissolved****	10 mg/L as DO (401-11)	100	0.2000 N $Na_2S_2O_3$ (22675-01)	500
		200	2.00 N $Na_2S_2O_3$ (14401-01)	100
Sulfite	5000 mg/L SO_3 (22674-10)	1.0	0.3998 N KIO_3–KI (14961-01)	250

* One to two drops of Magnesium Standard Solution (10 g/L as $CaCO_3$) must be added to get a sharp end point. These added drops will not change the results.

** The expected digits equal the volume of standard times the concentration on the certificate (e.g., 2 mL x 50 mg/L = 100 digits).
*** The expected digits equals the volume of standard times the concentration on the certificate times the constant, 4. (Example: 0.5 mL x 50 mg/L x 4 = 100 digits)
**** Add one Sulfamic Acid Powder Pillow to the volume of standard and follow Steps 10 to 12 in the Dissolved Oxygen Procedure. It is not necessary to add the first two reagents.

1.4 Adapting a Buret Titration to the Digital Titrator

Adapt any standard titration procedure using a buret to the Digital Titrator by using the following procedure.

1. Determine the approximate number of digits required. The Digital Titrator dispenses 1 mL per 800 digits on the counter. Using the following equation, determine the digits required for your buret method.

$$\text{Digits Required} = \frac{N_t \times mL_t \times 800}{N_c}$$

Where:

N_t = Normality of buret titrant
mL_t = milliliters of buret titrant required for an average titration
N_c = Normality of Digital Titrator cartridge

2. If the number of digits required is within the range of 70 to 350, you can use the procedure as written, substituting the Digital Titrator directly for the buret. Or, if the number of digits is outside of this range, make the following modifications:
    - **a.** If the number of digits required is more than 350, reduce the sample size to save titrant.
    - **b.** If the number of digits required is less than 70, increase the sample size to increase precision.
    - **c.** If the sample size is altered, adjust the amount of buffering or indicating reagents by the same proportion.
3. When using the Digital Titrator for your buret method, note the number of digits required for a sample titration.

To convert the digits required to the equivalent number of milliliters if the buret method was used, calculate:

$$\text{Equivalent Buret Milliliters} = \text{Digits Required} \times \frac{N_c}{800 \text{ x } N_t}$$

If the sample size was changed, adjust the equivalent buret milliliters accordingly. If the sample size was increased, reduce the equivalent buret milliliters; if the sample size was reduced increase the equivalent buret milliliters. Multiply the equivalent buret milliliters by any normally used factors to calculate concentration in oz/gal, g/L, etc.

Example: Adapt a buret procedure, which normally requires about 20 mL of a 0.4 N titrant, to the Digital Titrator. Try an 8.0 N titration cartridge. The first equation above gives:

$$\text{Digits Required} = \frac{0.4 \times 20 \times 800}{8.0} = 800 \text{ digits}$$

Because this would use excessive titrant, reduce the sample size to one fourth its normal size to reduce the digits required to 200, well within the recommended range.

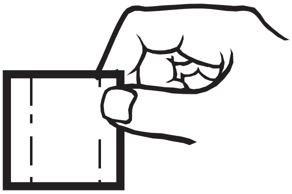
Upon completion of the titration using the smaller sample size, calculate the equivalent buret milliliters by the second equation above. If 205 were the digits required:

$$\text{Equivalent Buret Milliliters} = \frac{205 \times 8.0}{800 \times 0.4} = 5.13 \text{ mL}$$

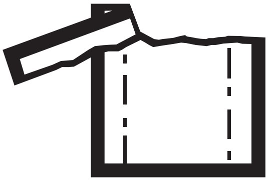
Multiply the 5.13 mL by 4 to account for the reduction in sample size to give the true equivalent buret milliliters of 20.5 mL. If the buret method called for multiplying the number of milliliters of titrant by a factor to calculate the concentration of a sample component, then multiply 20.5 by that factor.

1.5 Using PermaChem® Powder Pillows

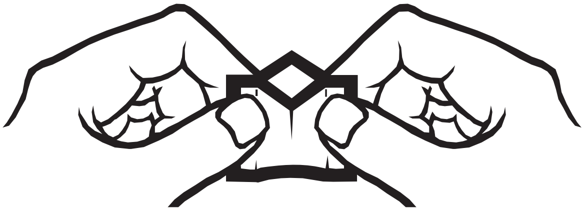
1. **Tap** the PermaChem on a hard surface to collect the powdered reagent in the bottom.



2. **Tear** across on the dotted pillow line marked “TEAR” holding the pillow away from your face.



3. Using two hands, **Push** both sides toward each other until thumbs and forefingers form a diamond. Make sure to **Crease** the foil pack, so that it forms a spout.



4. **Pour** the pillow contents into the sample. The polyfilm lining is specially formulated to deliver all the powder necessary for accurate results (no tapping on the vessel edge is necessary).

1.6 Safety

Safety is the responsibility of each individual when performing analysis procedures, and the analyst must develop and maintain good safety habits. Because many of the procedures in this methods handbook use potentially hazardous chemicals and apparatus, it is important that the analyst practice good laboratory techniques to minimize accidents. The following paragraphs present several techniques applicable to water analysis in the laboratory and in the field. They are not all inclusive, of course, nor do they apply only to the procedures provided in this handbook. They are general in nature but emphasize practices that are often key factors in personal injury incidents.

- Read labels carefully. Never remove the label from a reagent container. When preparing a reagent or standard solution, be sure to label the container clearly and date it.
- A Material Safety Data Sheet (MSDS) comes with each reagent. This sheet contains helpful information on first aid, spill and disposal procedures, and precautionary measures and should be read before using the product.
- Warning labels also appear on some of the apparatus used with the test procedures.
- Wear protective clothing when handling chemicals that cause irritation or burns. Eye protection in particular is important to guard against spattering and splashes from accidental spills when caustic materials are being used.
- Use tongs or finger cots when transferring apparatus that is hot.
- Use mechanical pipetters: Mouth pipetting could result in accidentally ingesting dangerous chemicals. Make a habit of using mechanical pipet fillers for all pipetting. This will avoid mistakes that could cause serious injury.
- Use special care with dangerous chemicals and apparatus.
- Follow the test procedure steps carefully and observe all precautionary measures. It is good practice to read the entire procedure carefully before beginning the procedure. Use safety equipment, such as pipet fillers, protective clothing, and ventilating hoods, appropriate for the test being conducted. Wipe up all spills promptly. Do not smoke or eat in an area where toxic or irritating chemicals are used. Use reagents and apparatus only as they were meant to be used and use them only as

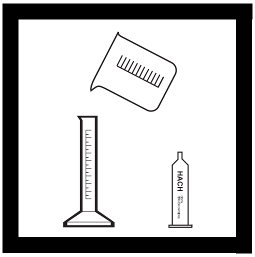
directed in the test procedure. Do not use damaged labware and malfunctioning equipment.

TITRATION PROCEDURES

Method 8200

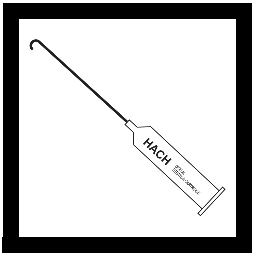
ACID-BASE (10 to 4000 mg/L as meq/L)

Acid Determination

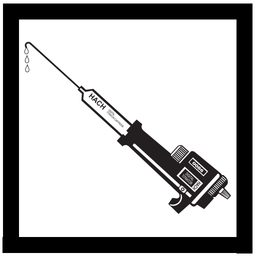


1. Select the sample volume corresponding to the expected acid concentration in milliequivalents (meq)/L or normality (N) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

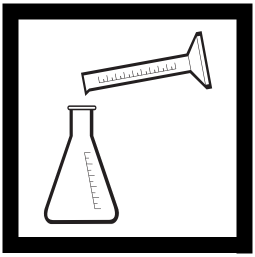


2. Insert a clean delivery tube into the appropriate Sodium Hydroxide Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions.



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

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. The solution should be colorless.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*

6. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium hydroxide until a light pink color forms and persists for 30 seconds. Record the number of digits required.

Digits Required x Digit Multiplier

= Milliequivalents/L of Acid

7. Calculate:

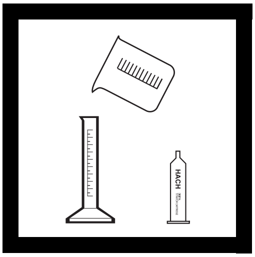
Digits Required x Digits Multiplier = Milliequivalents per Liter of Acid

Note: *To determine the normality of the sample, divide the milliequivalents per liter obtained by 1000.*

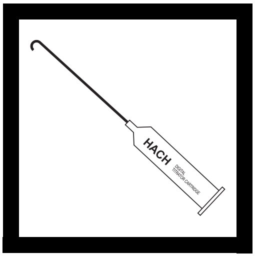
Table 1

Range meq/L	Range N	Sample Volume (mL)	Titration Cartridge	Catalog Number	Digit Multiplier
1-4	0.001-0.004	100	1.6 N NaOH 1.6 N H_2SO_4	14379-01 14389-01	0.02
4-10	0.004-0.01	50	1.6 N NaOH 1.6 N H_2SO_4	14379-01 14389-01	0.04
10-40	0.01-0.04	100	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	0.1
20-80	0.02-0.08	50	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	0.2
50-200	0.05-0.2	20	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	0.5
100-400	0.1-0.4	10	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	1.0
200-800	0.2-0.8	5	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	2.0
500-2000	0.5-2	2	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	5.0
1000-4000	1-4	1	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	10.0

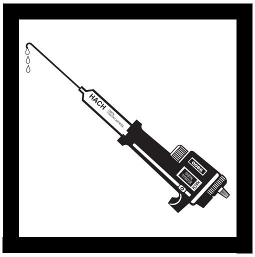
Base Determination



1. Select the sample volume corresponding to the expected base concentration in milliequivalents/L or normality from *Table 1*.

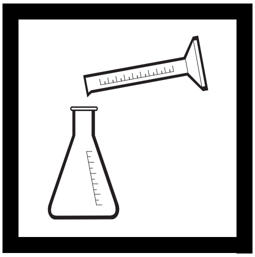


2. Insert a clean delivery tube into the appropriate Hydrochloric Acid or Sulfuric Acid Titration Cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step,* for assembly instructions, if necessary.



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

***Note:** For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. The solution should be a pink color.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*

6. Titrate with 8.00 N hydrochloric acid or sulfuric acid until the solution is colorless. Record the number of digits required.

Digits Required x Digit Multiplier

= Milliequivalents/L of Base

7. Calculate:

Digits Required x Digit Multiplier = Milliequivalents per Liter of Base

Note: *To determine the normality of the sample, divide the milliequivalents per liter obtained by 1000.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Minimize agitation or prolonged exposure to air. Sample may be stored at least 24 hours by cooling to 4 °C (39 °F) or below if they cannot be analyzed immediately. Warm to room temperature before analyzing.

Accuracy Check

Using a clean Class A 20.00 mL pipet, transfer 20.00 mL 0.100 N NaOH Standard Solution (for base determination) or 20.00 mL 0.100 N Sulfuric Acid Standard Solution (for acid determination) to a clean 250-mL Erlenmeyer flask. Dilute to about 100 mL with deionized water.

Follow the procedure for base determination using 8.00 N HCl or H_2SO_4 Titration Cartridge or for acid determination using 8.00 N NaOH Titration Cartridge. About 200 digits of titrant should be required.

Interferences

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.

Summary of Method

A measured amount of sample is treated with a colorimetric indicator and then titrated with a strong acid or base. The amount of titrant used is directly proportional to the milliequivalents of acid or base in the sample. These titrations also can be performed using a pH meter instead of a colorimetric indicator. In this case, titrate to pH 7 or to the pH required.

REQUIRED REAGENTS

(varies with sample characteristics)

Description	Cat. No.
Acid Determination Reagent Set (about 100 tests)	
1-10 meq/L includes: (1) 942-99, (1) 14379-01	24459-00
10-4,000 meq/L includes: (1) 942-99, (1) 14381-01	24460-00

REQUIRED REAGENTS, continued

Description	Unit	Cat. No.
Hydrochloric Acid Titration Cartridge, 8.00 N	each	14390-01
Phenolphthalein Indicator Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 1.600 N	each	14379-01
Sodium Hydroxide Titration Cartridge, 8.00 N	each	14381-01
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 8.00 N	each	14391-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 5-mL	each	508-37
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Phenolphthalein Indicator Solution, 5 g/L	100 mL*	162-32
Sodium Hydroxide Standard Solution, 0.100 N	1000 mL	191-53
Sulfuric Acid Standard Solution, 0.100 N	1000 mL*	202-53

OPTIONAL APPARATUS

Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong, extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, volumetric, Class A, 1-mL	each	14515-35
Pipet, volumetric, Class A, 2-mL	each	14515-36
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

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* Contact Hach for larger sizes.

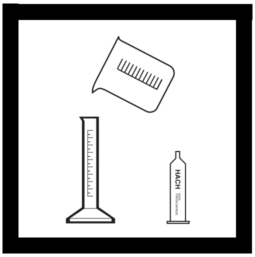
Methods 8201 and 8202

ACIDITY (10 to 4000 mg/L as $CaCO_3$)

Methyl Orange and Phenolphthalein (Total) Methods

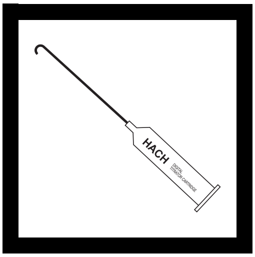
Methyl Orange Method

Method 8201

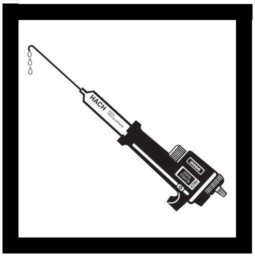


1. Select a sample volume and a Sodium Hydroxide (NaOH) Titration Cartridge corresponding to the expected acidity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

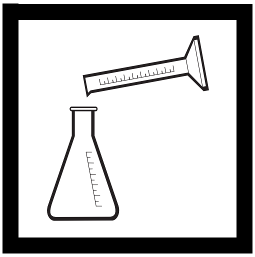


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

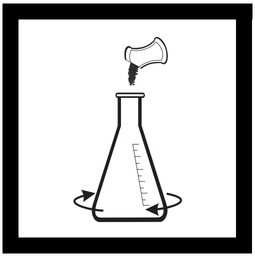


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Note: *Minimize agitation because dissolved gases in the sample such as carbon dioxide, hydrogen sulfide and ammonia may be lost and cause inaccurate results.*

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14377-01	0.1
40-160	25	0.1600	14377-01	0.4
100-400	100	1.600	14379-01	1.0
200-800	50	1.600	14379-01	2.0
500-2000	20	1.600	14379-01	5.0
1000-4000	10	1.600	14379-01	10.0



5. Add the contents of one Bromphenol Blue Indicator Powder Pillow and swirl to mix.

Note: *Six drops of Bromphenol Blue Indicator Solution may be substituted in this step.*

6. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium hydroxide from yellow to blue-violet (pH 3.7). Record the number of digits required.

Note: *A solution of one pH 3.7 Buffer Powder Pillow and one Bromphenol Blue Indicator Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*

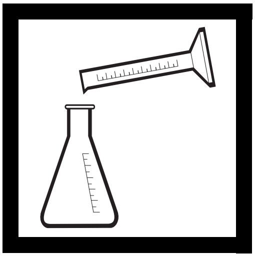
Digits Required x Digit Multiplier
= mg/L as $CaCO_3$ Methyl Orange Acidity

7. Calculate:

Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Methyl Orange Acidity

Phenolphthalein (Total) Method

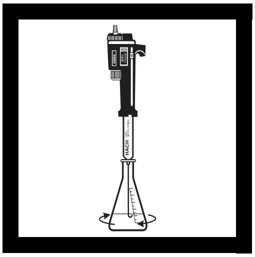
Method 8202



1. Measure a second portion of the sample selected from *step 1 on page 39* into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

2. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

***Note:** Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*



3. Titrate with sodium hydroxide from colorless to a light pink color that persists for 30 seconds. Record the number of digits required.

***Note:** A solution of one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*

Digits Required x Digit Multiplier
= mg/L as $CaCO_3$ Phenolphthalein Acidity

4. Calculate:

Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Phenolphthalein Acidity

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Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Minimize agitation or prolonged exposure to air. Samples may be stored at least 24 hours by cooling to 4 °C
(39 °F) or below if they cannot be analyzed immediately. Warm to room temperature before analyzing.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Acidity Voluette® Ampule Standard, 0.500 N.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 6* for methyl orange acidity or *step 3* for phenolphthalein acidity. Resume titration back to the same end point. Note the number of digits required.

3. Repeat using two more additions of 0.1 mL. Titrate to the end point after each addition.

4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.

- Chlorine may interfere with the indicators. Add one drop of 0.1 N Sodium Thiosulfate to eliminate this effect.

- To determine the phenolphthalein acidity of samples containing hydrolyzable metals such as iron, manganese or aluminum, use the following procedure:

  a. Adjust the sample in *step 1* for phenolphthalein acidity to pH 4.0 or less (if necessary) by using the Digital Titrator with an acid titration cartridge of identical normality to the Sodium Hydroxide Titration Cartridge used. Record the number of digits of acid added to lower the pH.

  b. Add five drops of 30% Hydrogen Peroxide Solution and boil the solution for 2-5 minutes.

  c. Cool to room temperature. Titrate following the Phenolphthalein Procedure *steps 2* and *3*. Subtract the number of digits of acid added to lower the pH from the number of digits required in *step 3* of the Phenolphthalein Procedure. Continue with *step 4*.

Summary of Method

Bromphenol blue (pH 3.7) or phenolphthalein (pH 8.3) indicator is used to titrate the sample with sodium hydroxide to a colorimetric end point. Bromphenol blue gives a better end point than methyl orange indicator. Titration to pH 3.7 determines strong mineral acidity (also referred to as methyl orange acidity), whereas the pH 8.3 phenolphthalein end point includes weaker acid species as well, and represents the total acidity. The results are expressed in mg/L as calcium carbonate ($CaCO_3$) at a specified pH.

REQUIRED REAGENTS

(varies with sample characteristics)

Description	Unit	Cat. No.
Acidity Reagent Set (about 100 tests)		22728-00
Includes: (1) 942-99, (1) 14377-01, (1) 14379-01, (1) 14550-99		
Bromphenol Blue Powder Pillows	100/pkg	14550-99
Phenolphthalein Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.1600 N	each	14377-01
Sodium Hydroxide Titration Cartridge, 1.600	each	14379-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Description	Unit	Cat. No.
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated 25-mL	each	508-40
Cylinder, graduated 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Acidity Standard Solution, Voluette® Ampules, 0.500 N H_2SO_4, 10 mL	16/pkg	14330-10
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32

ACIDITY, continued

Buffer Powder Pillows, pH 3.7	25/pkg	14551-68
Buffer Powder Pillows, pH 8.3	25/pkg	898-68
Hydrogen Peroxide Solution, 30%	200 mL MDB	144-45
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB*	323-32

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Hot Plate, 3½-inch circular, 115 V	each	12067-01
Hot Plate, variable control, 4-inch circular, 230 V	each	12067-02
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion***™***1*** Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-0

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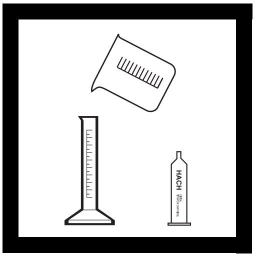
* Contact Hach for larger sizes.

Method 8203

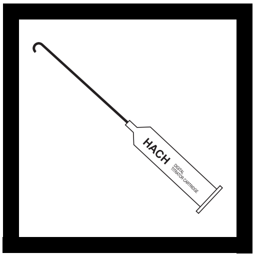
ALKALINITY (10 to 4000 mg/L as $CaCO_3$)

Phenolphthalein and Total Method

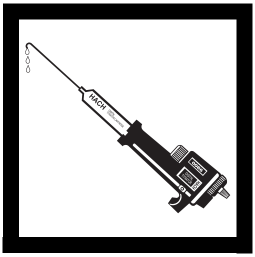


1. Select the sample volume and Sulfuric Acid (H_2SO_4) Titration Cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

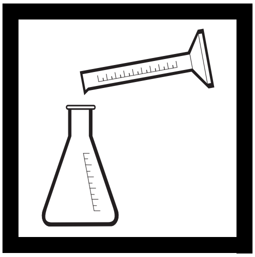


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

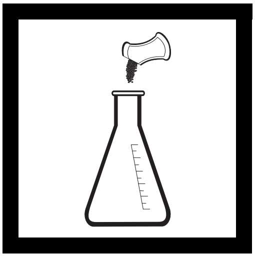
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (H_2SO_4)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14388-01	0.1
40-160	25	0.1600	14388-01	0.4
100-400	100	1.600	14389-01	1.0
200-800	50	1.600	14389-01	2.0
500-2000	20	1.600	14389-01	5.0
1000-4000	10	1.600	14389-01	10.0



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

Note: *A solution of one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*

6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

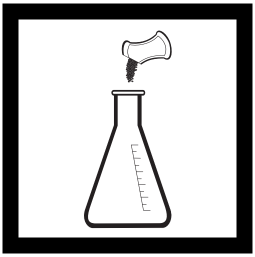
Note: *If the solution is colorless before titrating with sulfuric acid, the Phenolphthalein (P) Alkalinity is zero; proceed with step 8.*

Digits Required x **Digit Multiplier**

= mg/L as $CaCO_3$ P Alkalinity

7. Calculate:

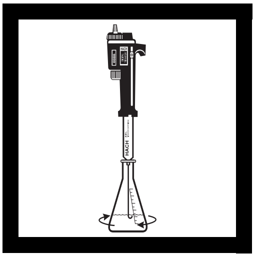
Digits Required x Digit Multiplier = mg/L $CaCO_3$ P Alkalinity



8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix.

Note: *Four drops of Methyl Purple Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow. Titrate from green to a gray end point (pH 5.1).*

Note: *Four drops of Bromcresol Green-Methyl Red Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.*



9. Continue the titration with sulfuric acid to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) color, as required by the sample composition; see *Table 2.* Record the number of digits required.

Note: *A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pillow of the appropriate pH buffer in 50 mL of deionized water is recommended as a comparison for judging the proper end point color. If the pH 3.7 end point is used, use a Bromphenol Blue Powder Pillow instead of a Bromcresol Green-Methyl Red and titrate to a green end point.*

Total Digits Required x Digit Multiplier
= mg/L as $CaCO_3$ Total (T or M) Alkalinity

10. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CaCO3 Total (T or M) Alkalinity

Note: *Carbonate, bicarbonate and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.*

Note: *meq/L Alkalinity = mg/L as $CaCO_3$ ÷ 50.*

Table 2

Sample Composition	End Point
Alkalinity about 30 mg/L	pH 4.9
Alkalinity about 150 mg/L	pH 4.6
Alkalinity about 500 mg/L	pH 4.3
Silicates or Phosphates present	pH 4.5
Industrial waste or complex system	pH 4.5

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity is equal to:	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one half of Total Alkalinity	0	Total Alkalinity	0

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity is equal to:	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
5	Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use the table follow these steps:

a. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

b. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

c. Multiply the phenolphthalein alkalinity by 2.

d. Select Row 3, 4, or 5 based on comparing the result of *step c* with the total alkalinity.

e. Perform the required calculations in the appropriate row, if any.

f. Check your results. The sum of the three alkalinity types will equal the total alkalinity.

For example:
A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see *step a*.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see *step b*.

The phenolphthalein alkalinity multiplied by 2 = 340 mg/L, see *step c*.

Because 340 mg/L is greater than 250 mg/L, select Row 5, see *step d*.

The hydroxide alkalinity is equal to: (see *step e*).

340 – 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

250 – 170 = 80
80 x 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity equals 0 mg/L.

Check: (see *step f*).

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L

The above answer is correct; the sum of each type equals the total alkalinity.

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Standard Solution Voluette® Ampule, 0.500 N.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in Steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.
- Chlorine may interfere with the indicators. Add one drop of 0.1 N Sodium Thiosulfate to eliminate this interference.

Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide.

REQUIRED REAGENTS

(varies with sample characteristics)

Description	Unit	Cat. No
Alkalinity Reagent Set (about 100 tests)		22719-00
Includes: (1) 942-99, (1) 943-99, (1) 14388-01, (1) 14389-01		
Bromcresol Green-Methyl Red Powder Pillows	100/pkg	943-99
Phenolphthalein Powder Pillows	100/pkg	942-99
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N	each	14388-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Description	Unit	Cat. No
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Description	Unit	Cat. No
Alkalinity Standard Solution Voluette® Ampules, 0.500 N Na_2CO_3, 10-mL	16/pkg	14278-10
Bromcresol Green-Methyl Red Indicator Solution	100 mL MDB	23292-32
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Bromphenol Blue Powder Pillows	100/pkg	14550-99
Buffer Powder Pillows, pH 3.7	25/pkg	14551-68
Buffer Powder Pillows, pH 4.5	25/pkg	895-68
Buffer Powder Pillows, pH 4.8	25/pkg	896-68
Buffer Powder Pillows, pH 5.1	25/pkg	897-68
Buffer Powder Pillows, pH 8.3	25/pkg	898-68
Methyl Purple Indicator Solution	100 mL MDB	21934-32
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32

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* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette® 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™**1*** Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

Method 10222

AMMONIA, HIGH RANGE (Ammonium Hydroxide)

5 to 35% (50 to 350 g/L) as NH_3 or 5 to 60% (50 to 600 g/L) as NH_4OH

Acid Titration Method

For use with Digital Titrator Test Kit, Model NI-HRDT (Cat. No. 29304-00)

Scope and Application: For determining high levels of aqua ammonia (ammonium hydroxide) in solutions used for chloramination of drinking water, for determining aqua ammonia feed pump rates or applications requiring the determination of high concentrations (g/L) of aqua ammonia.

CAUTION:

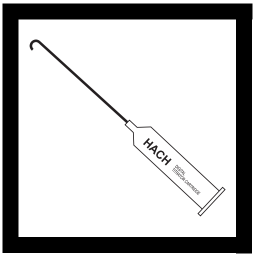
Handling chemical samples, standards, and reagents can be dangerous. Review the Material Safety Data Sheets before handling chemicals. Wear eye protection and protective gloves when sampling.

Measuring Hints and General Test Information

- Wash all labware between tests. Contamination may alter test results. Rinse with clean water (preferably deionized water).
- Hach recommends that reagent accuracy and analyst technique be checked using a standard solution. Use the Ammonium Hydroxide solution listed on page *59* and follow the procedure in the Accuracy Check section on page *58*.

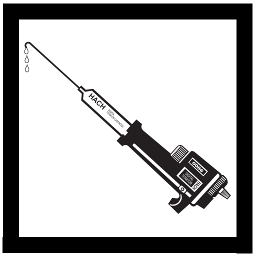
Ammonia Titration Procedure

To ensure accurate results, read carefully before proceeding.



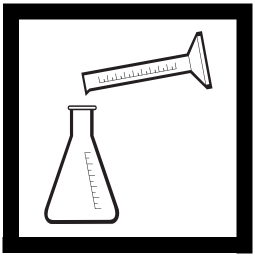
1. Insert a clean delivery tube into the 8.00 N Sulfuric Acid Titration Cartridge. Attach the cartridge to the titrator body.

Note: *See section 1.2 on page 13 for assembly instructions.*



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

Note: *For added convenience use the TitraStir® Stir Plate. See section 1.2, step 4 on page 14.*

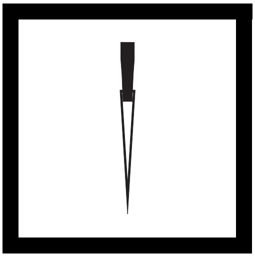


3. Fill a clean 125-mL Erlenmeyer flask to about the 75-mL mark with deionized water.

Select sample volume

4. Select a sample volume for the expected concentration range from *Table 1–Table 4* on page *57*.

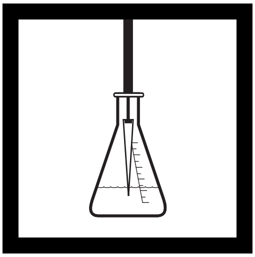
Note: *See Sampling and Storage following these steps.*



5. Attach a clean tip to the pipettor and collect 100-µL (0.100 mL) of the aqua ammonia sample.

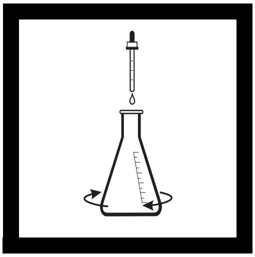
__Note:__ Alternatively, use a TenSette® Pipet (Cat. No. 19700-01) with a clean tip.

__Note:__ Review the instructions supplied with the 100-µL pipettor before using. Depress the plunger to the first stop and release to fill with sample.



6. Dispense the sample below the liquid level in the flask. Dispense another 100 µL of sample into the flask (200 µL sample size). For other sample sizes, repeat until the required sample volume from *step 4* has been added.

__Note:__ Review the instructions supplied with the 100-µL pipettor before using. Depress the plunger to the first stop to fill; depress the plunger completely to dispense.



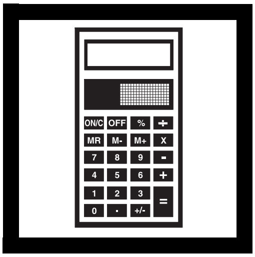
7. Add 1 mL (one full dropper) of Wide Range pH Indicator Solution to the flask.

8. Swirl to mix. The solution will turn purple.

9. Place the delivery tube tip into the solution. Swirl the flask while titrating with the sulfuric acid titrant until the solution color changes from purple to orange-red. Record the number of digits used.

Find Digit Multiplier

10. Find the digit multiplier from *Table 1–Table 4* on page *57*.



11. Calculate:

Digits Used x
Digits Multiplier =
concentration.

__Note:__ See example on page 57.

Example

A bulk solution of aqua ammonia was delivered to a facility and was expected to have a concentration of 19 percent (19% NH_3). A portion of the sample was titrated to confirm the concentration.

The sample volume from *Table 1* was found to be 0.2 mL (200 µL). The acid titration procedure was followed and 218 digits were used to reach the endpoint. The digit multiplier from *Table 1* was found to be 0.085. The concentration of ammonia was found to be 18.5 percent:

$$\% \ NH_3 = 218 \text{ digits} \times 0.085$$
$$\% \ NH_3 = 18.5\%$$

Tables for Sample Volume and Digit Multiplier

Find the expected sample concentration from one of the tables for ammonia (% or g/L) or ammonium hydroxide (% or g/L) and then find the corresponding sample volume and Digit Multiplier:

Table 1 Ammonia (Percent)

Expected % NH_3	Sample Volume (mL)	Digit Multiplier
5–15	0.5	0.034
10–35	0.2	0.085

Table 2 Ammonia (g/L)

Expected g/L NH_3	Sample Volume (mL)	Digit Multiplier
50–150	0.5	0.34
100–350	0.2	0.85

Table 3 Ammonium Hydroxide (Percent)

Expected % NH_4OH	Sample Volume (mL)	Digit Multiplier
5–15	1	0.035
10–30	0.5	0.070
25–60	0.2	0.175

Table 4 Ammonium Hydroxide (g/L)

Expected g/L NH_4OH	Sample Volume (mL)	Digit Multiplier
50–150	1	0.35
100–300	0.5	0.70
250–600	0.2	1.75

Sampling and Storage

Collect samples in clean glass bottles and cap tightly. Store in a cool place. Analyze as soon as possible.

Interferences

Other strong bases such as sodium hydroxide and potassium hydroxide will cause a positive interference in the test. Other alkaline substances, such as carbonates, will also react with the strong acid titrant. The amounts of these compounds should be insignificant in aqua ammonia solutions, however, and will not affect test results. High levels of alkalinity in the dilution water will cause high results. Be sure to use deionized water in *step 3*.

Accuracy Check

1. Fill an Erlenmeyer flask with approximately 75 mL of deionized water.

2. Use a Class A 1.0-mL pipet to transfer 1.0 mL of a 10% ammonium hydroxide solution to the flask.

3. Add 1 mL (one full dropper) of Wide Range pH Indicator Solution to the flask. The solution will turn a purple color.

4. Titrate the sample using the Digital Titrator to the red-orange endpoint with 8.00 N sulfuric acid. The titration should use 270–300 digits of 8.00 N sulfuric acid to reach the endpoint.

Note: *If the number of digits used to reach the endpoint does not fall within the 270–300 digit range, make sure that the dilution water does not contain excess alkalinity and that the 1.0 mL of ammonium hydroxide is measured accurately. Ammonium hydroxide solutions that are left open to the atmosphere will lose ammonia over time and will give low results. Store the solutions in tightly-capped bottles.*

Precision

In a single laboratory using an ammonium hydroxide solution of 9.71%, a single operator obtained a standard deviation of ± 0.1% as NH_4OH.

Summary of Method

Ammonia exists in water as ammonium hydroxide. The hydroxide ions are titrated with sulfuric acid to a colorimetric end point corresponding to a pH value between 4.4 and 6.2. The hydroxide concentration is directly proportional to the volume of acid titrant used.

REQUIRED REAGENTS

Description		Cat. No.
HR Aqua Ammonia Reagent Set (about 100 tests)		29305-00
Includes: (1) 14391-01, (1) 23293-32		
Sulfuric Acid Titration Cartridge, 8.00 N	each	14391-01
Wide Range pH Indicator Solution	100 mL	23293-32
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Description		Cat. No.
Digital Titrator Assembly	each	16900-01
Delivery Tubes, J hook	5/pkg	17205-00
Flask, Erlenmeyer, 125-mL	each	505-43
Pipettor, 100 µL	each	22753-00
Pipettor Tips, for 22753-00	10/pkg	22754-10

OPTIONAL REAGENTS AND APPARATUS

Description		Cat. No.
Ammonium Hydroxide Solution, 10%	500 mL	14736-49
Bottle, sampling, square glass 118 mL	3/pkg	21631-03
Bottle, wash, poly, 500-mL	each	620-11
Demineralizer Bottle, 473-mL	each	21846-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Gloves, chemical resistant, size 9–9½*	pair	24101-04
Goggles, safety	each	25507-00
Hypochlorite, HR (Bleach) Digital Titrator Kit	each	26871-00
Notebook, field	each	20918-00
Pipet, TenSette, 0.1–1.0 mL	each	19700-01
Pipet, volumetric, Class A, 1.0 mL	each	14515-35
Pipet Bulb	each	14651-00
Pipet Tips, for TenSette Pipet 19700-01	50/pkg	21856-96
Tech Board with built-in calculator	each	27473-00
TitraStir® Stir Plate, 115 VAC	each	19400-00
TitraStir® Stir Plate, 230 VAC	each	19400-10
Pipettor Tips, for 22753-00	1000/pkg	22754-00

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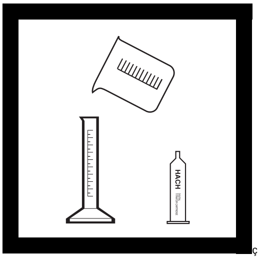
* Other sizes available.

Method 8205

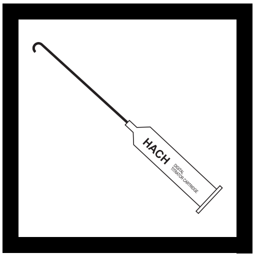
CARBON DIOXIDE (10 to 1000 mg/L as CO_2)

Using Sodium Hydroxide

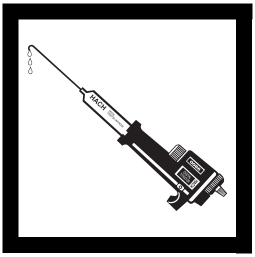


1. Select a sample size and a Sodium Hydroxide (NaOH) Titration Cartridge corresponding to the expected carbon dioxide (CO_2) concentration; see *Table 1*.

Note: *See Sampling and Storage following these steps.*



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

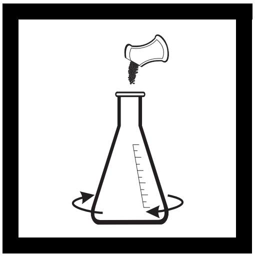
4. Collect a water sample directly into the titration flask by filling to the appropriate mark.

Note: *Minimize agitation because carbon dioxide may be lost.*

Note: *For most accurate results, check the calibration of the Erlenmeyer flask by measuring the proper volume in a graduated cylinder. Mark the proper volume on the flask with a permanent marker.*

Table 1

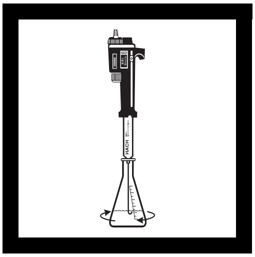
Range (mg/L as CO_2)	Sample Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
10-50	200	0.3636	14378-01	0.1
20-100	100	0.3636	14378-01	0.2
100-400	200	3.636	14380-01	1.0
200-1000	100	3.636	14380-01	2.0



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and mix.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*

Note: *If a pink color forms, no carbon dioxide is present.*



6. Place the delivery tube tip into the solution and swirl the flask gently while titrating with sodium hydroxide from colorless to a light pink color that persists for 30 seconds. Record the number of digits required.

Digits Required x **Digit Multiplier**

= mg/L as CO_2

7. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CO2

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples as soon as possible after collection. If immediate analysis is not possible, the samples may be stored for at least 24 hours by cooling to 4 °C (39 °F) or below. Before analysis, warm the samples to room temperature.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Carbon Dioxide Standard Solution Voluette® Ampule, 10,000 mg/L CO_2.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 6*. If using 0.3636 N titrant, use 1.0 mL of standard. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 mL and 0.3 mL (2.0 and 3.0). Titrate to the same end point after each addition.
4. Each addition of standard should require 50 additional digits of titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Other acid components in the sample will be titrated and interfere directly in this determination.
- Sodium hydroxide standard solutions tend to lose strength slowly with age and should be checked periodically by titrating a known standard. Check the solution frequently (monthly) by titrating 50 mL of Potassium Acid Phthalate Standard Solution, 100 mg/L CO_2, using Phenolphthalein Indicator Solution. The titration should require 5.00 mL of titrant. If the volume required for this titration is greater than 5.25 mL, discard the sodium hydroxide and replace it with a fresh supply.

Summary of Method

Acidity due to carbon dioxide in a sample is titrated with sodium hydroxide to a phenolphthalein end point. Strong acids are assumed to be absent or of insignificant concentration. Request Hach’s *Water Analysis Handbook,* Publication 8376, to obtain additional information on carbon dioxide determinations.

CARBON DIOXIDE, continued

REQUIRED REAGENTS

(varies with sample characteristics)

Description	Unit	Cat. No.
Carbon Dioxide Reagent Set (about 100 tests)		22727-00
Includes: (1) 942-99, (1) 14378-01, (1) 14380-01		
Phenolphthalein Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.3636 N	each	14378-01
Sodium Hydroxide Titration Cartridge, 3.636 N	each	14380-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Description	Unit	Cat. No.
Digital Titrator	each	16900-01
Select one or more based on sample concentration:		
Flask, Erlenmeyer, 250 mL	each	505-46
Flask, Erlenmeyer, 125 mL	each	505-43

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Carbon Dioxide Standard Solution Voluette® Ampules, 10,000 mg/L as CO$_2$, 10 mL	16/pkg	14275-10
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Potassium Acid Phthalate Standard Solution, 100 mg/L as CO$_2$	100 mL	2261-42
Potassium Acid Phthalate Standard Solution, 400 mg/L as CO$_2$	500 mL	1885-49

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet Filler, safety bulb	each	14651-00
sension™*1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

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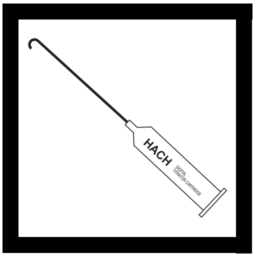
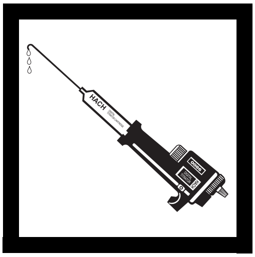
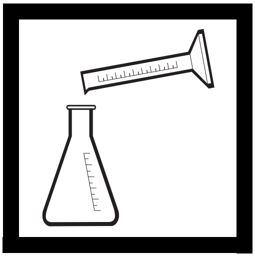
* Contact Hach for larger sizes.

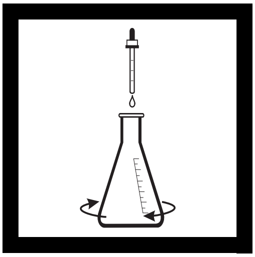
CHELANT, FREE (0 to 20.0 mg/L as $CaCO_3$)

Using Magnesium Chloride









1. Insert a clean delivery tube into the Magnesium Chloride Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-By-Step,* for assembly instructions.

2. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

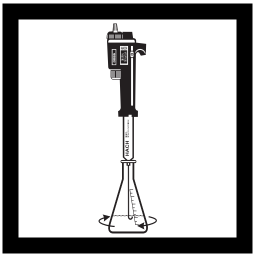
3. Use a graduated cylinder to measure the 100 mL of sample into a 125-mL Erlenmeyer flask.

Note: *Filter sample if necessary. If sample is boiler water or highly alkaline, refer to Interferences following these steps.*

4. Using the 1-mL calibrated dropper, add
2 mL of Hardness 1 Buffer Solution to the flask and swirl to mix.

5. Add the contents of one ManVer® 2 Hardness Indicator Powder Pillow to the flask and swirl to mix. If the solution turns blue, free chelant is present. Proceed to *step 6*. If the solution turns red, a deficiency of chelant exists.

Note: *Four drops of ManVer Hardness Indicator Solution or a 0.1 g scoop of ManVer 2 Hardness Indicator Powder may be substituted in this step.*



6. Place the delivery tube tip into the solution. While swirling the flask, titrate until a red-violet color appears. Record the number of digits required.

Digits Required x Digit Multiplier

= mg/L as $CaCO_3$ Free Chelant

7. Calculate:

Digits Required x 0.10 = mg/L Free Chelant (as $CaCO_3$)

Note: *The results may be expressed as mg/L tetra-sodium EDTA (digits required x 0.38 = mg/L as Na_4 EDTA).*

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Use a TenSette® Pipet to add 0.4 mL of 0.035 N EDTA Standard Solution to the solution titrated in *step 6*. Resume titration back to the same end point. Record the number of digits required.
2. Each 0.4 mL addition of standard should require 70 additional digits of 0.0800 M titrant. If this increase does

not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- If chelant residual in boiler water is being analyzed, adjust the pH before adding the Hardness 1 Buffer Solution as follows:
  - **a.** To another 100-mL sample, add 2 drops of Phenolphthalein Indicator Solution.
  - **b.** Counting the drops, add 5.25 N Sulfuric Acid Standard Solution one drop at a time until the solution changes from pink to colorless. Discard this sample.
  - **c.** To the actual 100-mL sample, add the same number of drops of 5.25 N Sulfuric Acid Standard Solution before adding the buffer in *step 4*.
- Orthophosphate causes a slow end point. Polyphosphate must be absent for accurate results.
- All apparatus must be scrupulously clean and rinsed frequently with acid and deionized water to remove any hardness present on the plastic or glass.
- Run reagent blanks occasionally, using deionized or distilled water in place of the sample. Subtract the value of the blank from the sample value before recording the final answer.

Summary of Method

Chelant residual is determined by titration with a standard solution of magnesium chloride at pH 10. The end point is determined by a color change from blue to red-violet.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Hardness 1 Buffer Solution	100 mL MDB	424-32
ManVer® 2 Hardness Indicator Powder Pillows	100/pkg	851-99
Magnesium Chloride Titration Cartridge, 0.0800 M	each	20625-01

REQUIRED APPARATUS

Description	Unit	Cat. No.
Cylinder, graduated, 100-mL	each	508-42
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43

OPTIONAL REAGENTS

Description	Unit	Cat. No.
EDTA Standard Solution, 0.035 N	100 mL MDB	23499-32
ManVer® 2 Hardness Indicator Powder	113 g	280-14
ManVer® 2 Hardness Indicator Solution	100 mL MDB*	425-32
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Clippers (shears), 7.25 inch	each	23694-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, Erlenmeyer, 250 mL	each	505-46
Funnel, analytical, poly, 65 mm	each	1083-67
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Spoon, measuring, 0.5 gram	each	907-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

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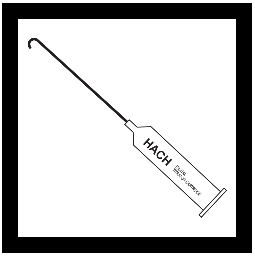
* Contact Hach for larger sizes.

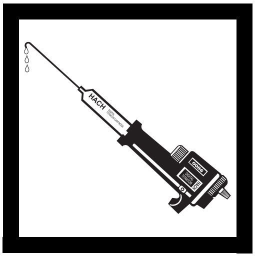
Method 8350

CHELANT, TOTAL (0 to 40.0 mg/L as Na_4EDTA)

Using Bismuth Nitrate

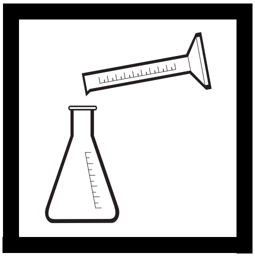


1. Insert a clean delivery tube into the Bismuth Nitrate Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-By-Step,* for assembly instructions.



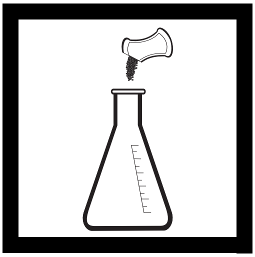
2. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



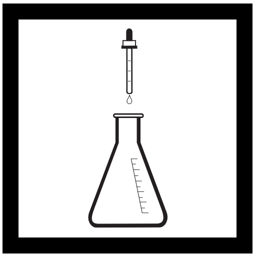
3. Use a graduated cylinder to measure the 50 mL of clear sample into a 125-mL Erlenmeyer flask.

Note: *Filtration is required for turbid samples.*



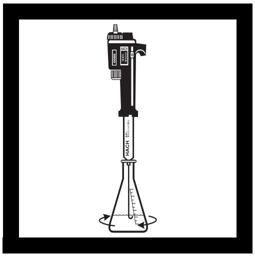
4. Add the contents of one Ascorbic Acid Powder Pillow to the flask and swirl to mix.

5. Add the contents of one Methylthymol Blue Powder Pillow to the flask and swirl to mix.



6. If the solution in the flask is yellow, add one drop of 5.25 N Sulfuric Acid Standard Solution.

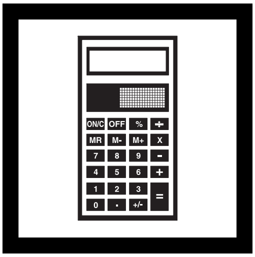
If the solution is blue, add 5.25 N Sulfuric Acid Standard Solution dropwise until the solution changes to yellow. Add one additional drop.



7. Place the delivery tube tip into the solution. While swirling the flask, titrate with the Bismuth Nitrate until the color changes from yellow to blue-green. Record the number of digits required.

Note: *Titrate slowly as the end point is approached.*

Note: *For best results, determine a reagent blank. Use 50 mL of deionized water in step 3. Subtract the number of digits required for the reagent blank from the number of digits required for titrating the sample.*



8. Calculate the final concentration:

Digits Required x 0.188 = Total Chelant (as mg/L Na_4EDTA)

Interferences

Interference from ferric iron (Fe^{3+}) is minimized by adding ascorbic acid. The end point should by approached slowly in samples containing ferric iron because the iron decreases the sharpness of the color change.

Summary of Method

Total chelant is determined by titrating an acid sample with bismuth nitrate the presence of methylthymol blue indicator.

The end point is signaled by a color change from yellow to blue-green.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Ascorbic Acid Powder Pillows	100/pkg	14577-99
Bismuth Nitrate Titration Cartridge, 0.0200 M	each	24345-01
Methylthymol Blue Indicator Powder Pillows	50/pkg	22847-99
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

REQUIRED APPARATUS

Cylinder, graduated, poly, 100 mL	each	1081-42
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Stir Bar, analytical, Teflon-coated, 50 mm	each	20953-55
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Water, deionized	4 L	272-56

OPTIONAL APPARATUS

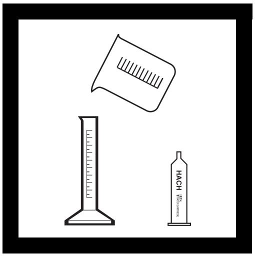
Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Clippers (shears), 7.25 inch	each	23694-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Filter paper, folded, 12.5 cm	100/pkg	1894-57
Flask, Erlenmeyer, 250 mL	each	505-46
Funnel, analytical, poly, 65 mm	each	1083-67

Methods 8206 and 8207

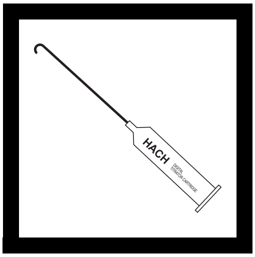
CHLORIDE

Mercuric Nitrate and Silver Nitrate Methods

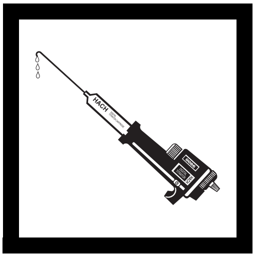
Mercuric Nitrate Method (10 to 8000 mg/L as Cl^-) Method 8206



1. Select the sample volume and Mercuric Nitrate Titration Cartridge corresponding to the expected chloride concentration from *Table 1*.

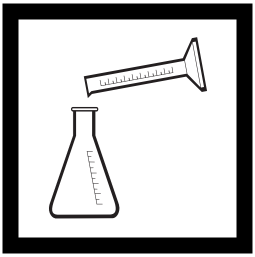


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step,* for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

***Note:** For added convenience use the TitraStir® Stir Plate. See General Description, step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

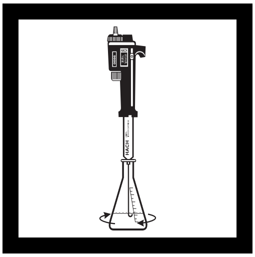
***Note:** See following these steps.*

Table 1

Range (mg/L as Cl^-)	Sample Volume (mL)	Titration Cartridge (N $Hg(NO_3)_2$)	Catalog Number	Digit Multiplier
10-40	100	0.2256	14393-01	0.1
40-160	25	0.2256	14393-01	0.4
100-400	100	2.256	921-01	1.0
200-800	50	2.256	921-01	2.0
500-2000	20	2.256	921-01	5.0
1000-4000	10	2.256	921-01	10.0
2000-8000	5	2.256	921-01	20.00

5. Add the contents of one Diphenylcarbazone Powder Pillow and swirl to mix.

Note: *Results will still be accurate if a small amount of the powder does not dissolve.*



6. Place the delivery tube tip into the solution and swirl the flask while titrating with mercuric nitrate from a yellow to light pink color.
Record the number of digits required.

Digits Required x **Digit Multiplier**

= mg/L Chloride

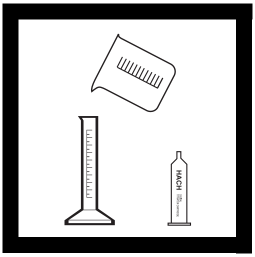
7. Calculate:

Digits Required x Digit Multiplier = mg/L Chloride

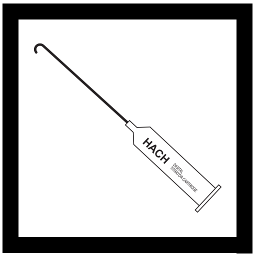
Note: *Results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.*

Note: *meq/L Chloride = mg/L* Cl^- *÷ 35.45.*

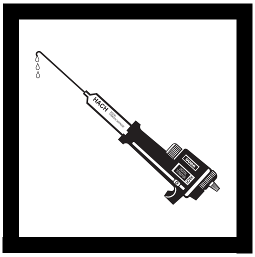
Silver Nitrate Method (10 to 10000 mg/L as Cl^-) Method 8207



1. Select the sample volume and Silver Nitrate Titration Cartridge corresponding to the expected chloride concentration from *Table 2*.

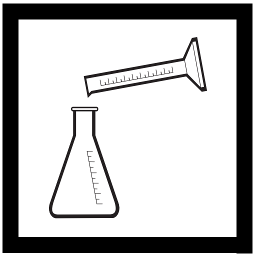


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step,* for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

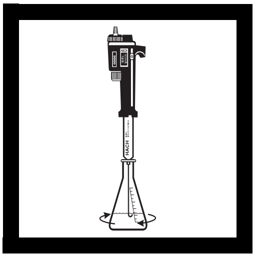
Note: *See following these steps.*

Table 2

Range (mg/L as Cl^-)	Sample Volume (mL)	Titration Cartridge (N $AgNO_3$)	Catalog Number	Digit Multiplier
10-40	100	0.2256	14396-01	0.1
25-100	40	0.2256	14396-01	0.25
100-400	50	1.128	14397-01	1.0
250-1000	20	1.128	14397-01	2.5
1000-4000	5	1.128	14397-01	10.0
2500-10000	2	1.128	14397-01	25.0

5. Add the contents of one Chloride 2 Indicator Powder Pillow and swirl to mix.

Note: *Results will still be accurate if a small amount of the powder does not dissolve.*



6. Place the delivery tube tip into the solution and swirl the flask while titrating with silver nitrate from a yellow to red-brown color.
Record the number of digits required.

Digits Required x **Digit Multiplier**

= mg/L Chloride

7. Calculate:

Digits Required x
Digit Multiplier =
mg/L Chloride

Note: *Results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.*

Note: *meq/L Chloride = mg/L Cl^- ÷ 35.45.*

Sampling and Storage

Collect at least 100 to 200 mL of sample in a clean glass or polyethylene container. Samples may be stored up to 7 days before analysis.

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Chloride Standard Solution Voluette® Ampule, 12,500 mg/L Cl^-.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample after titration in *step 6*. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 and 0.3 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 12.5 additional digits of 2.256 N titrant, 25 digits of 1.128 N titrant, or 125 digits of 0.2256 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences Using the Mercuric Nitrate Method

- Chromate, ferric iron, and sulfite in excess of 10 mg/L interfere with this method.
- Eliminate sulfite interference by adding three drops of hydrogen peroxide, 30%, in *step 4*.
- Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 mL of sample, mixing for one minute, and filtering through a folded filter paper.
- Iodide and bromide interfere directly and titrate as chloride.
- Neutralize strongly alkaline or acid samples to a pH of 2 to 7 with 5.25 N Sulfuric Acid Standard Solution or 5.0 N Sodium Hydroxide Standard Solution. Determine the

amount of acid or base necessary in a separate sample because pH electrodes will introduce chloride into the sample.

Interferences Using the Silver Nitrate Method

- Iron in excess of 10 mg/L masks the end point.
- Orthophosphate in excess of 25 mg/L will precipitate the silver.
- Sulfite in excess of 10 mg/L interferes. Eliminate sulfite interference by adding three drops of 30% hydrogen peroxide in *step 4*.
- Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 mL of sample, mixing for one minute, and filtering through a folded filter paper.
- Cyanide, iodide, and bromide interfere directly and titrate as chloride.
- Neutralize strongly alkaline or acid samples to a pH of 2 to 7 with 5.25 N Sulfuric Acid Standard Solution or 5.0 N Sodium Hydroxide Standard Solution. Determine the amount of acid or base necessary in a separate sample because pH electrodes will introduce chloride into the sample.

Summary of the Mercuric Nitrate Method

When using Mercuric Nitrate Standard Solution, the sample is titrated under acid conditions in the presence of diphenylcarbazone indicator. Upon addition of a slight excess of mercuric ion, a pink-purple complex is formed with the indicator, signaling the end point.

Summary of the Silver Nitrate Method

The sample is titrated with Silver Nitrate Standard Solution in the presence of potassium chromate (from the Chloride 2 Indicator Powder). The silver nitrate reacts with the chloride present to produce insoluble white silver chloride. After all the chloride has been precipitated, the silver ions react with the excess chromate present to form a red-brown silver chromate precipitate, marking the end point of the titration.

Request Hach's *Water Analysis Handbook,* Publication 8376, to obtain additional information on chloride determinations.

REQUIRED REAGENTS FOR THE MERCURIC NITRATE METHOD

Description	**Unit**	**Cat. No.**
Mercuric Nitrate Chloride Reagent Set (about 100 tests)		22726-00
Includes: (2) 836-46, (1) 921-01, (1) 14393-01		
Diphenylcarbazone Reagent Powder Pillows	100/pkg	836-99
Mercuric Nitrate Titration Cartridge, 0.2256 N	each	14393-01
Mercuric Nitrate Titration Cartridge, 2.256 N	each	921-01
Water, deionized	4 L	272-56

REQUIRED REAGENTS FOR THE SILVER NITRATE METHOD

Silver Nitrate Chloride Reagent Set (about 50 tests)		22880-00
Includes: (2) 1057-66, (1) 14396-01, (1) 14397-01		
Chloride 2 Indicator Powder Pillows	50/pkg	1057-66
Silver Nitrate Titration Cartridge, 0.2256 N	each	14396-01
Silver Nitrate Titration Cartridge, 1.128 N	each	14397-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS FOR THE MERCURIC NITRATE METHOD AND SILVER NITRATE METHOD

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Chloride Standard Solution, 1000 mg/L Cl^-	500 mL	183-49
Chloride Standard Solution Voluette® Ampules, 12,500 mg/L Cl^-, 10-mL	16/pkg	14250-10
Hydrogen Peroxide, 30%, ACS	200 mL	144-45
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32

CHLORIDE, continued

Sulfide Inhibitor Powder Pillows	100/pkg	2418-99
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

OPTIONAL APPARATUS

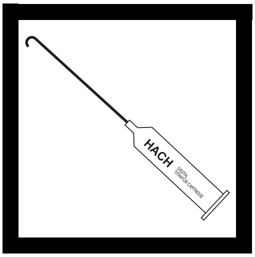
Description	Unit	Cat. No.
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Funnel, poly, 65-mm	each	1083-67
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2-mL	each	14515-36
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens***ion**™***1*** Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

Method 8210

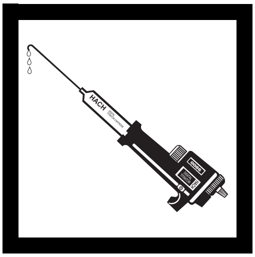
CHLORINE, FREE AND TOTAL (0 to 3.00 mg/L as Cl_2)

DPD-FEAS Method

Note: *This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.*

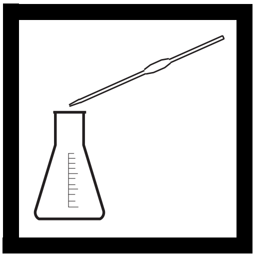


1. Insert a clean delivery tube into a 0.00564 N Ferrous Ethylenediammonium Sulfate (FEAS) Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.



2. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

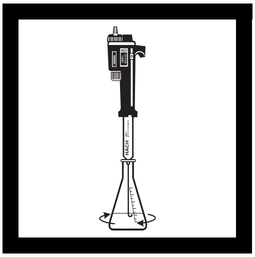


3. Pipet 25.0 mL of sample into a 50-mL Erlenmeyer flask.

4. Add the contents of a DPD Free Chlorine Powder Pillow to the sample and swirl to mix.

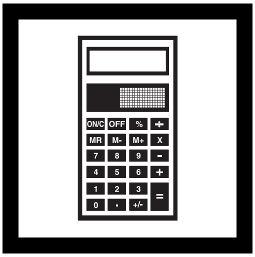
Note: *Accuracy is unaffected if a small portion is undissolved.*

Note: *See Sampling and Storage following these steps.*



5. Place the delivery tube tip into the solution and swirl the flask while immediately titrating with FEAS to a colorless end point. Record the number of digits required.

Note: *Complete the titration rapidly.*



6. Calculate:

Digits Required x 0.01 = mg/L Free Chlorine

mg/L Total Chlorine
- mg/L Free Chlorine
mg/L Combined Chlorine

7. If total residual chlorine is desired, return to *step 3* and substitute a DPD Total Chlorine Powder Pillow in *step 4*. Wait three minutes before titrating. Continue with *step 5*. The results will be expressed as mg/L total chlorine.

mg/L Total Chlorine -
mg/L Free Chlorine =
mg/L Combined Chlorine

Sampling and Storage

Chlorine in water is easily lost. Therefore, start chlorine determinations immediately after sampling, avoiding excessive light and agitation. Do not store samples.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when the analyst suspects interferences or to verify analytical technique.

1. Snap the neck off a Chlorine Standard Solution PourRite™ Ampule.
2. Use a TenSette® Pipet to add 0.10 mL, 0.20 and 0.30 mL of standard, respectively, to three 25-mL samples. Mix each well.
3. Analyze each sample as described in the procedure.

4. Each 0.1-mL addition of standard should require approximately 20 digits. Check the certificate enclosed with the PourRite Ampules to obtain the exact concentration. To determine the exact number of digits required for each
0.2-mL addition, multiply the exact concentration times the volume of the addition in mL times four. (Example: 50 mg/L x 0.1 mL x 4 = 20 digits.) If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

Higher room temperatures tend to lead to higher free chlorine residual due to reaction of chloramines. Higher room temperatures also result in increased color fading. If the sample contains more than 250 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$, the sample may not develop the full amount of color or it may instantly fade. To overcome this interference, adjust the pH of a separate 25-mL sample to a 6 to 7 pH by adding 1 N Sulfuric Acid Standard Solution or 1 N Sodium Hydroxide Standard Solution in small increments and using a pH meter. Record the amount of acid or base required. Add this amount of acid or base to the sample to be tested and proceed with *step 4*.

Bromine, iodine, ozone, and oxidized forms of manganese and chromium will also react and read as chlorine. To compensate for the effects of manganese, Mn^{4+}, or chromium, Cr^{6+}, add three drops of Potassium Iodide, 30 g/L to 25 mL of sample. Mix and wait one minute. Add three drops of Sodium Arsenite, 5 g/L and mix. Analyze this solution as described above. (If chromium is present, allow exactly the same reaction period in *step 7* with the DPD for both analyses.) Subtract the result from the original analysis to correct for the interference.

Summary of Method

The DPD-FEAS method provides a titrimetric procedure for determining free available chlorine and for estimating free and combined chlorine fractions present together. The magenta species, resulting from the oxidation of DPD by chlorine, is destroyed quantitatively by titration with ferrous ethylenediammonium sulfate and the volume of titrant required to reach a colorless end point is proportional to the chlorine concentration. Total residual chlorine may also be determined by this test.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Free and Total Chlorine Reagent Set (about 100 tests) Includes: (1) 14064-99, (1) 14070-99, (1) 22923-01		24453-00
DPD Free Chlorine Powder Pillows, 25 mL	100/pkg	14070-99
DPD Total Chlorine Powder Pillows, 25 mL	100/pkg	14064-99
Ferrous Ethylenediammonium Sulfate Titration Cartridge, 0.00564 N	each	22923-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 50-mL	each	505-41
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet Filler, safety bulb	each	14651-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite™ Ampules, 50-75 mg/L Cl_2, 2-mL	20/pkg	14268-20
Potassium Iodide Solution	100 mL MDB	343-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL MDB	1270-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL MDB	1045-32
Sodium Arsenite Solution	100 mL MDB	1047-32

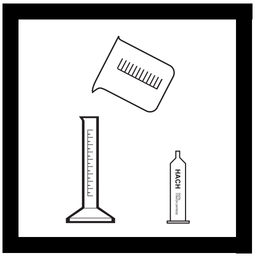
OPTIONAL APPARATUS

Clamp, 2-prong, extension	each	21145-00
Clamp Holder	each	326-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
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
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

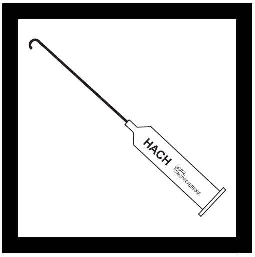
Method 8209

CHLORINE, TOTAL

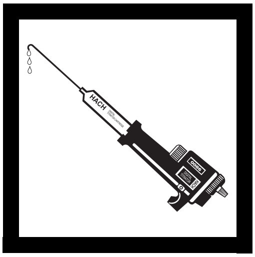
Iodometric Method (1 to 400 mg/L as Cl_2 Using Sodium Thiosulfate)



1. Select the sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected chlorine concentration from *Table 1*.

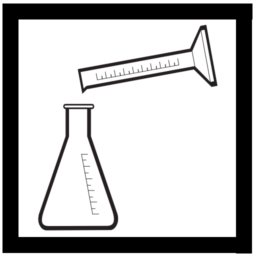


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



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

***Note:** For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



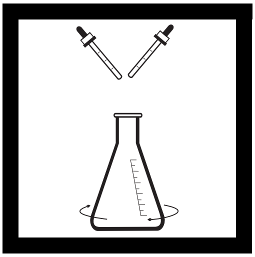
4. Use a clean graduated cylinder to take a water sample. Pour sample into a clean 125- or 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water.

***Note:** See Sampling and Storage following these steps.*

Table 1

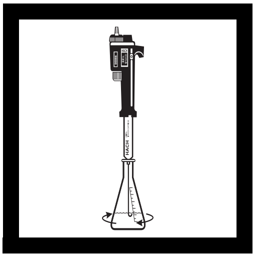
Range (mg/L Cl_2)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
1-4	100	0.02256	24091-01	0.01
2-8	50	0.02256	24091-01	0.02
5-20	20	0.02256	24091-01	0.05
10-40	10	0.02256	24091-01	0.10
20-80	5	0.02256	24091-01	0.20
50-200	2	0.02256	24091-01	0.50
100-400	1	0.02256	24091-01	1.00

CHLORINE, TOTAL, continued

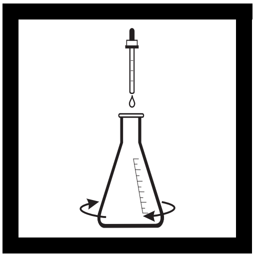


5. Add 2 Droppers (2 mL) Acetate Buffer Solution, pH 4 and swirl to mix.

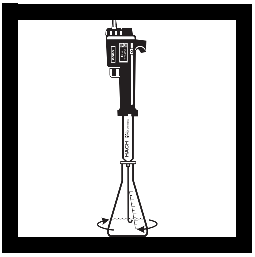
6. Clip open the end of one Potassium Iodide Powder Pillow. Add the contents to the flask. Swirl to mix.



7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate until the solution is a pale yellow.



8. Add one dropper of starch indicator solution and swirl to mix. A dark blue color will develop.



9. Continue the titration until the solution changes from dark blue to colorless. Record the number of digits required.

Digits Required x **Digit Multiplier**

= mg/L Total Chlorine (Cl_2)

10. Calculate:

Digits Required x Digit Multiplier = mg/L Total Chlorine (Cl2)

Note: *These procedures can be used to check iodine and bromine concentrations if chlorine is not present. Multiply the test result (in mg/L chlorine) by 3.58 or 2.25, respectively, to accurately express the iodine or bromine content of your sample.*

Sampling and Storage

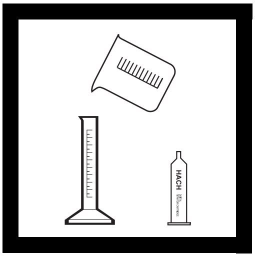
Collect at least 200 mL of sample in a clean glass or polyethylene container. Analyze on site or as soon as possible after collection.

Accuracy Check

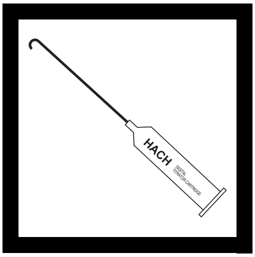
Standard Additions Method
Perform this accuracy check when you suspect interferences or to verify analytical technique.

1. Snap the neck off a Chlorine Standard Solution PourRite™ Ampule.
2. Use a TenSette® Pipet to add 0.2 mL, 0.4 mL, and 0.6 mL of standard to three aliquots of sample of the same volume as used in the procedure.
3. Analyze each sample as described in the procedure.
4. Each 0.2-mL addition of standard should require approximately 10 digits of the titration cartridge solution. Check the certificate enclosed with the PourRite Ampules to obtain the exact concentration. To determine the exact number of digits required for each 0.2-mL addition, multiply the exact concentration times the volume of the addition in mL. (Example: 50 mg/L x 0.2 mL = 10 digits.) If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

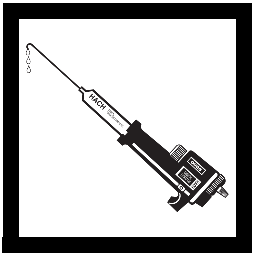
Iodometric Method (20 to 70,000 mg/L as Cl_2 Using Sodium Thiosulfate)



1. Select the sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected chlorine concentration from *Table 2*.

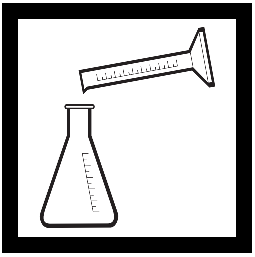


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



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

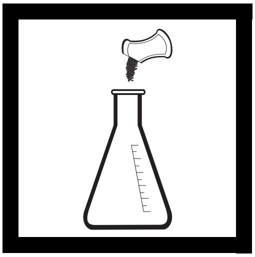
Note: *For added convenience use the TirtaStir® stirring apparatus. See General Description, Step 3 of Step-by-Step.*



4. Use a pipet or graduated cylinder to measure the sample volume from *Table 2*. Transfer the sample into a 125-mL Erlenmeyer flask and dilute to about the 50-mL mark with deionized water.

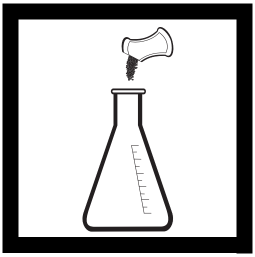
Table 2

Range (mg/L Cl_2)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
20-80	25	0.113	22673-01	0.2
50-200	10	0.113	22673-01	0.5
100-400	5	0.113	22673-01	1
250-1000	2	0.113	22673-01	2.5
500-2000	1	0.113	22673-01	5
2000-9000 (0.2-0.9%)	4	2.00	14401-01	22.2
5000-18,000 (0.5-1.8%)	2	2.00	14401-01	44.3
10,000-35,000 (1.0-3.5%)	1	2.00	14401-01	88.7
20,000-70,000 (2.0-7.0%)	0.5	2.00	14401-01	177



5. Add the contents of one Dissolved Oxygen 3 Powder Pillow.

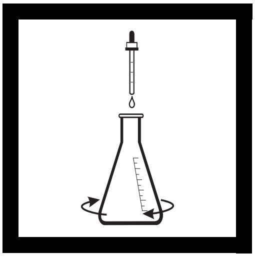
Note: *Normally the addition of the powder pillow will lower the pH to 4 or less. If the sample size is large and highly alkaline, verify the solution pH is 4 or less with a pH meter or pH paper before proceeding.*



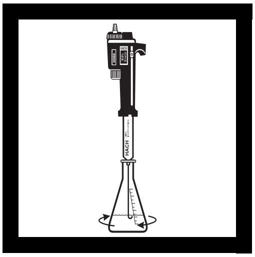
6. If you are using the 2.00 N titration cartridge, add the contents of one Potassium Iodide Powder Pillow (Cat. No. 20599-96) to the flask and swirl to mix.

If you are using the 0.113 N titration cartridge, add the contents of one Potassium Iodide Powder Pillow (Cat. No. 1077-99) to the flask and swirl to mix.

7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate until the solution is a pale yellow.



8. Add one dropperful of starch indicator solution and swirl to mix. A dark blue color will develop.



9. Continue the titration until the solution changes from dark blue to colorless. Record the number of digits required.

Digits Required x **Digit Multiplier**

= mg/L Total Chlorine (Cl_2)

10. Calculate:

Digits Required x Digits Multiplier = mg/L Total Chlorine (Cl2)

To convert the above results to the equivalent percent chlorine (Cl_2), divide by 10,000.

Accuracy Check

Standard Additions Method
This accuracy check is applicable **only for the 0.113 N titration cartridge**. Perform it when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Chlorine Standard Solution PourRite Ampule.
2. Use a TenSette Pipet (or glass pipet) to add 1.0 mL, 2.0 mL, and 3.0 mL of standard to three samples of the same volume as used in the procedure.
3. Analyze each sample as described in the procedure.
4. Each 1.0-mL addition of standard should require approximately 10 digits of the 0.113 N titration cartridge. Check the certificate enclosed with the PourRite Ampules to obtain the exact concentration. To determine the exact number of digits required for each 1.0-mL addition, multiply the exact concentration times the volume of the addition in mL. Divide this by five. For example: (50 mg/L x 1.0 mL) ÷ 5 = 10 digits. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Summary of Method

Total chlorine concentration equals the concentration of the free and the combined forms of chlorine. Free chlorine reacts readily with ammonia to form combined chlorine such as monochloramines. When potassium iodide is added to a sample containing chlorine at a pH less than 8, free iodine is liberated in direct proportion to the amount of total chlorine present. The iodine is then titrated with sodium thiosulfate.

REQUIRED REAGENTS (For Using the 0.02256 N Titration Cartridge)

Description	Unit	Cat. No.
Acetate Buffer Solution, pH 4	100 mL MDB	14909-32
Potassium Iodide Powder Pillows	100/pkg	1077-99
Starch Indicator Solution	100 mL MDB*	349-32
Sodium Thiosulfate Titration Cartridge, 0.02256 N	each	24091-01

REQUIRED REAGENTS (For Using the 0.113 N Titration Cartridge)

Chlorine Reagent Set, 20-2,000 mg/L (about 100 tests)		22725-00
Includes: (1) 349-32, (1) 987-99, (1) 1077-99, (1) 22673-01		
Dissolved Oxygen 3 Powder Pillows	100/pkg	987-99
Potassium Iodide Powder Pillows	100/pkg	1077-99
Sodium Thiosulfate Titration Cartridge, 0.113 N	each	22673-01
Starch Indicator Solution	100 mL MDB*	349-32
Water, deionized	4 L	272-56

REQUIRED REAGENTS (For Using the 2.00 N Titration Cartridge)

Chlorine Reagent Set, 2,000-70,000 mg/L (about 100 tests)		24448-00
Includes: (1) 349-32, (1) 987-99, (2) 14401-01, (2) 20599-96		
Dissolved Oxygen 3 Powder Pillows	100/pkg	987-99
Potassium Iodide Powder Pillows	50/pkg	20599-96
Sodium Thiosulfate Titration Cartridge, 2.00 N	each	14401-01
Starch Indicator Solution	100 mL MDB*	349-32
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Pipet Filler, 3-valve	each	12189-00
Select one or more based on sample concentration:		
Pipet, serological, 1 mL	each	532-35
Pipet, volumetric, Class A, 1 mL	each	14515-35
Pipet, volumetric, Class A, 2 mL	each	14515-36
Pipet, volumetric, Class A, 4 mL	each	14515-04
Pipet, volumetric, Class A, 5	each	14515-37
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 25 mL	each	14515-40

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* Contact Hach for larger sizes.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite™ Ampules, 50-75 mg/L as Cl_2, 2 mL	20/pkg	14268-20

OPTIONAL APPARATUS

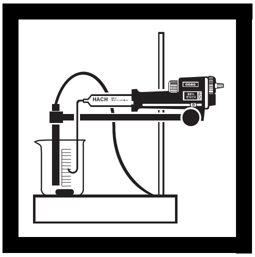
Description	Unit	Cat. No.
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Cylinder, graduated, 5 mL	each	508-37
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
pH Paper, 1-11 pH	5 rolls/pkg	391-33
PourRite™ Ampule Breaker	each	24846-00
*sens**ion**™**1*** Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

Method 10024

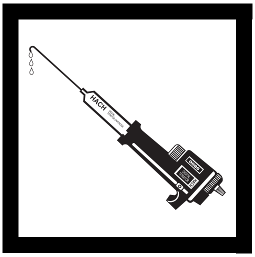
CHLORINE, FREE (0 to 1000 µg/L as Cl_2)

Amperometric Forward Titration

USEPA Accepted for Reporting*



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

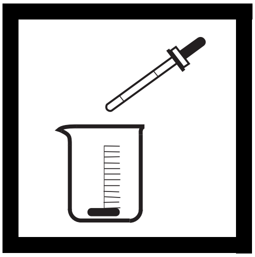


2. Install the 0.00564 N Phenylarsine Oxide (PAO) cartridge. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

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 the Amperometric Titrator Instruction Manual.*

3. With minimum 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, instability of 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.*

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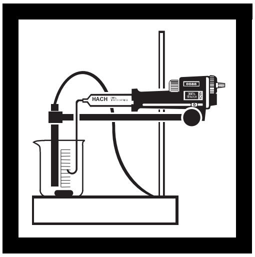
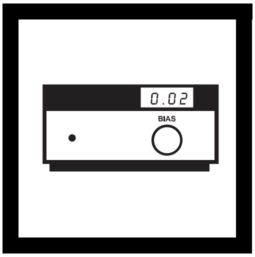
* Procedure is equivalent to *Standard Methods for the Examination of Water and Wastewater* (18th ed.) 4500 Cl D for drinking water.

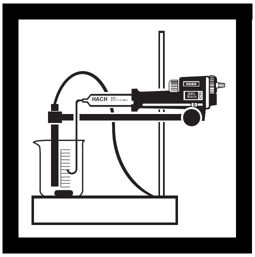


5. Place the beaker on the TitraStir® Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



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.

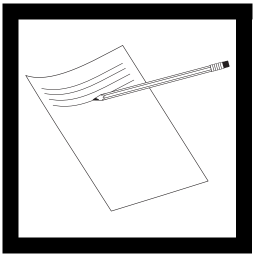
Note: *The bias adjustment controls the slope of the titration curve. The actual instrument reading is not important; but rather the change in the readings as the titration proceeds. The adjustment need not be precise.*



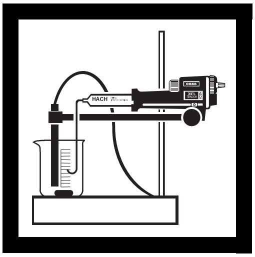
7. Using the Digital Titrator delivery knob, dispense the PAO titrant Solution in 5-10 digit increments while noting the LED reading.

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.*

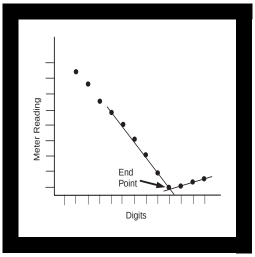
Note: *If excess reductant such as sulfite, bisulfite or sulfur dioxide is present in the sample, the LED readings will not decrease and may even increase. This indicates that no free chlorine is present in the sample*



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 have 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 1*. Determine the number of digits at the intersection of the lines; this is the end point.

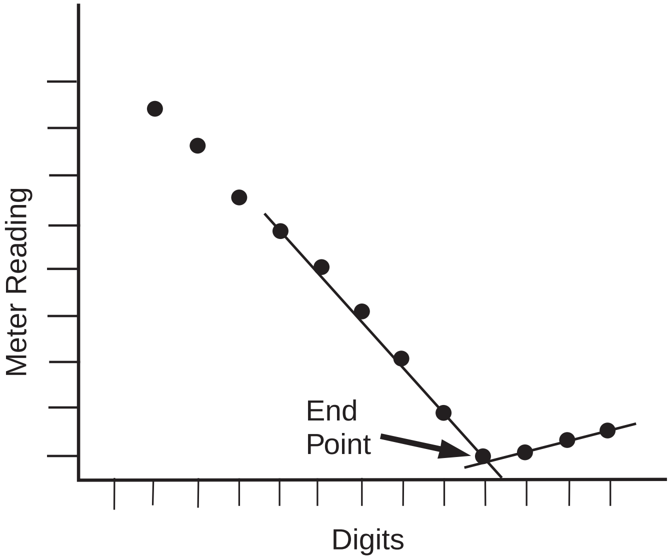
Digits at End Point x 1.25

= µg/L Free Clorine as Cl_2

11. Calculate the µg/L free chlorine:

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

Figure 1
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 chlorine concentration of each.
5. Calculate the theoretical concentration of the spiked sample:

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

Where:

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

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

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

6. Calculate the percent spiked recovery:

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

Example:

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

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

Volume Sample (V_u) = 200 mL

Volume Standard (V_s) = 0.2 mL

Chlorine Standard (C_s) = 68.1 mg/L

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

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

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

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.

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 been 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™ Ampules, 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
Standard Methods for the Examination of Water and Wastewater, 19th edition	each	22708-00

Method 10025

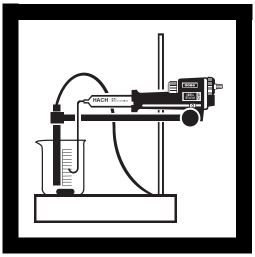
CHLORINE, TOTAL (6 to 1000 µg/L as Cl_2)

For wastewater

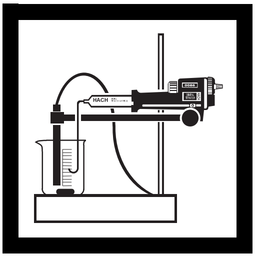
Amperometric Back Titration

USEPA Accepted for Reporting*

Phase 1: Adjusting the Electrode Response Slope

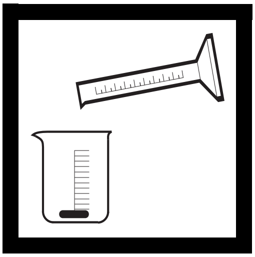


1. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.



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 the Amperometric Titrator Instruction Manual.*



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.

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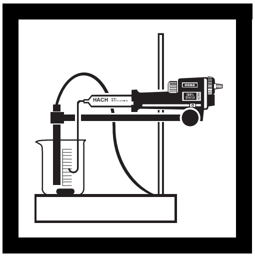
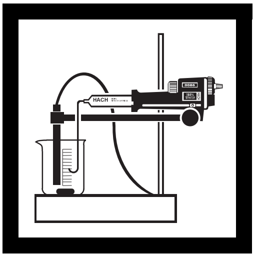
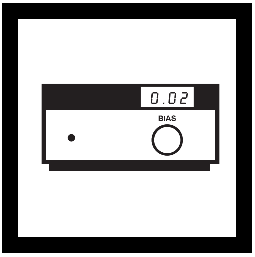
* Procedure is equivalent to USEPA method 330.2 and *Standard Methods for the Examination of Water and Wastewater* (17th ed.) 4500-Cl C for wastewater.



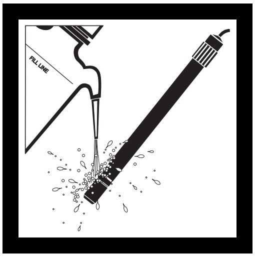
5. Place the beaker on the TitraStir® Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



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

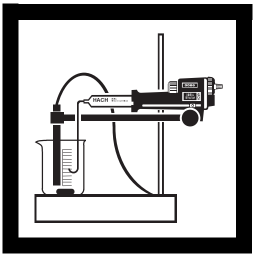


7. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control and adjust the BIAS control knob until a stable reading between 0.50-0.60 is obtained. Lock the BIAS control.



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

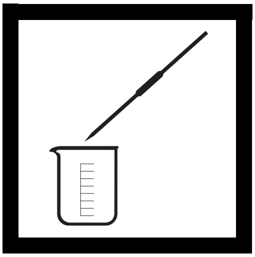
Phase 2: Standardization of the Iodine Titrant



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.

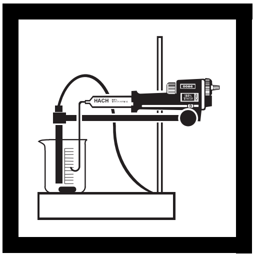
Note: *An improper size of stirring bar can result in volatilization of iodine, instability of readings and loss of sensitivity.*



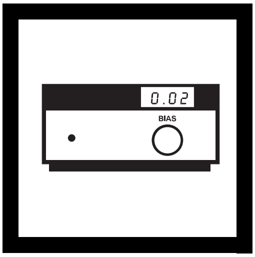
3. Using a Class A pipet, transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the beaker. Swirl to mix.

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

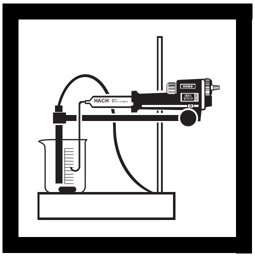
4. Add 1 mL of pH 4 Acetate Buffer Solution and the contents of one Potassium Iodide Powder Pillow.



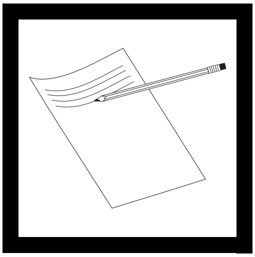
5. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



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

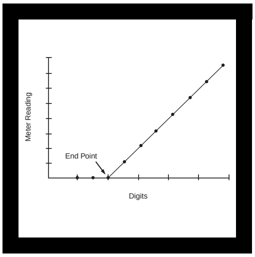


7. Using the Digital Titrator delivery knob, dispense 100 digits of Standard Iodine Titrant Solution and note the LED reading.

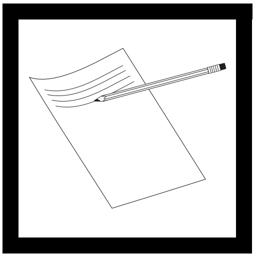


8. Continue dispensing titrant in 5-10 digit increments while noting the LED reading. Record at least 3 points (null current values and Digital Titrator reading), before the end point is reached. After the end point of the titration (nominal 160 digits), record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter. Add 5-10 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 1*. 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, which relates to 160 digits needed to titrate 1.00 mL of 0.00564 N Thiosulfate. If the calculated end point is greater than 160 digits, this indicates 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.*

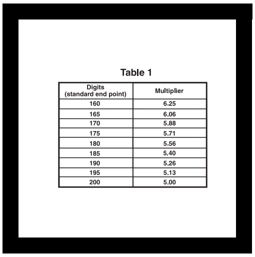
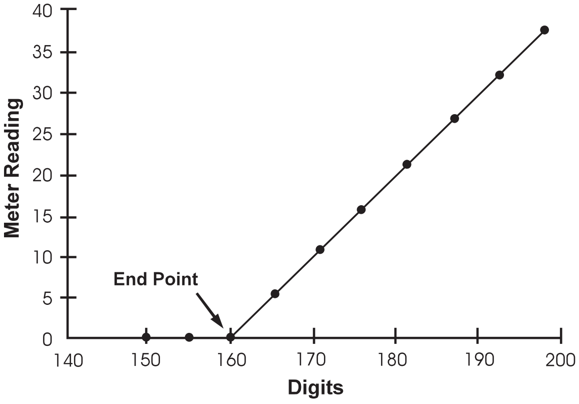


Table 1

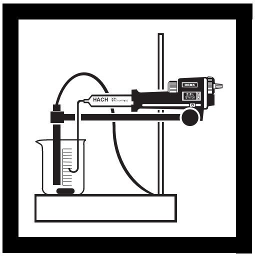
Digits (standard end point)	Multiplier
160	6.25
165	6.06
170	5.88
175	5.71
180	5.56
185	5.40
190	5.26
195	5.13
200	5.00

11. Locate the appropriate multiplier based on the standard end point in *Table 1* on page 109. The multiplier is used in *Phase 3: Titration of Sample for Total Residual Chlorine*. Interpolation between values in the table is not necessary.

Figure 1
Back Amperometric Titration Graph



Phase 3: Titration of Sample for Total Residual Chlorine



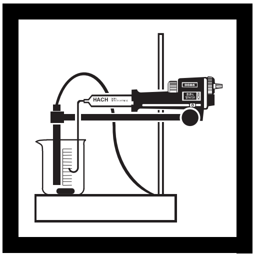
1. Set-up the Amperometric Digital Titrator System as in *Phase 1: Adjusting the Electrode Response Slope* if it has not already been done. Reset the Digital Titrator counter to zero and wipe the tip.

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.*

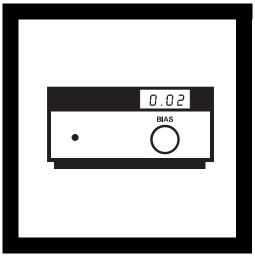
3. With minimum agitation, measure 200 mL sample with a clean graduated cylinder and transfer the sample to the beaker. Swirl to mix the reagents with sample.

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.*

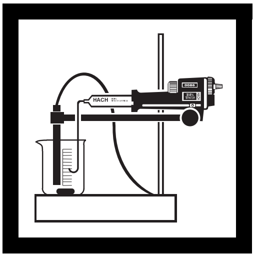


4. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.

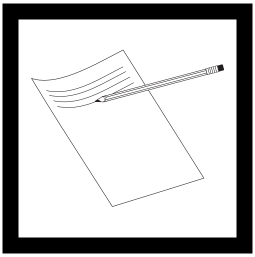
5. Add the contents of one pillow of Potassium Iodide Reagent to the beaker and allow the powder to dissolve.



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

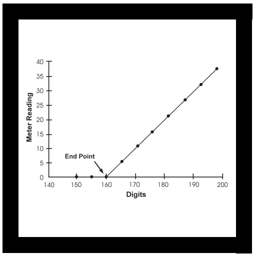


7. Using the Digital Titrator delivery knob, dispense the Standard Iodine Titrant Solution in 5-10 digit increments while noting the LED reading. Record at least 3 points (null current values and Digital Titrator reading), before end point is reached.

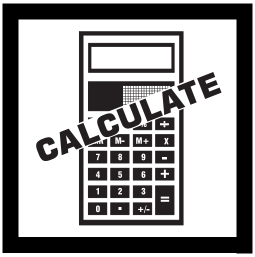


8. After the end point of the titration is reached, record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter. Add 5-10 digits of titrant; wait a few seconds for a stable reading and record. Stop the titrant addition when the LED readings exceed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

Note: *LED readings above 0.60 will be excessively noisy. With samples containing excess de-chlorinating agents, such as sulfur dioxide, sulfite or bisulfite, the titration end point (number of digits) will be greater than the number of digits obtained during the standardization. It is not necessary to continue the titrant addition if the number of digits used in the sample titration exceeds that calculated for the standardization end point. This indicates that no free or combined chlorine is present in the sample.*



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 1* on page 106. 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.*

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

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 *Phase 3: Titration of Sample for Total Residual Chlorine*. 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*.
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

5. Calculate the percent spiked recovery:

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

---

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

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

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

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, 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™ Ampules, 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

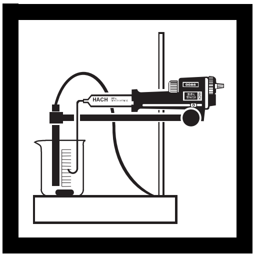
Method 10026

CHLORINE, TOTAL (0 to 1000 µg/L as Cl_2)

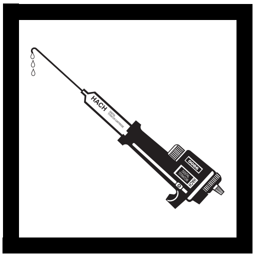
For drinking water or wastewater

Amperometric Forward Titration

USEPA Accepted for Reporting*



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

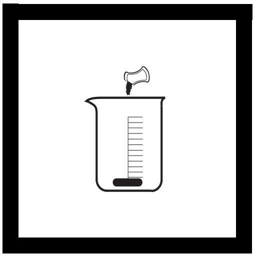


2. Install the Phenylarsine Oxide (PAO), 0.00564 N Cartridge. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

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 the Amperometric Titrator Instruction Manual.*

3. With minimum 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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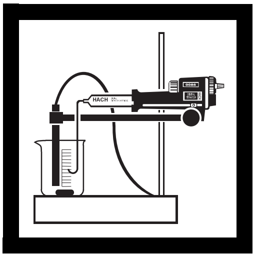
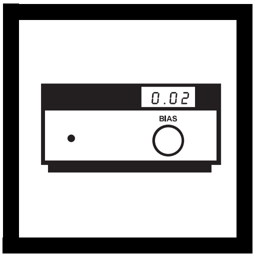
* Procedure is equivalent to USEPA method 330.1 and 330.3, *Standard Methods for the Examination of Water and Wastewater* (18th ed.) 4500-Cl D for drinking water and *Standard Methods* (17th ed.) 4500-Cl D for wastewater.

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

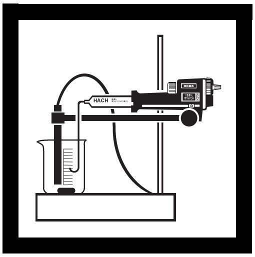


6. Place the beaker on the TitraStir® Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



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.

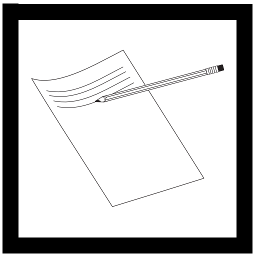
***Note:** The bias adjustment controls the slope of the titration curve. The actual instrument reading is not important; but rather the change in the readings as the titration proceeds. The adjustment need not be precise.*



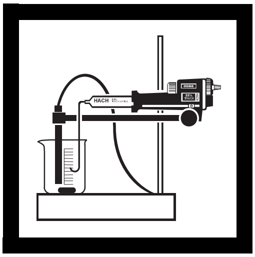
8. Using the Digital Titrator delivery knob, dispense the PAO titrant Solution in 5-10 digit increments while noting the downward reading.

***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.*

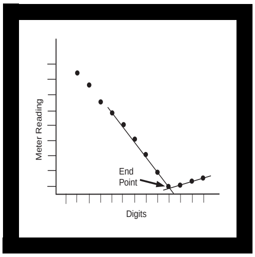
***Note:** If excess reductant, such as sulfite, bisulfite, or sulfur dioxide is present in the sample, the LED readings will not decrease and may even increase. This indicates that no free chlorine or chloramines are present in the sample.*



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 have 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 1*. Determine the number of digits at the intersection of the lines; this is the end point.

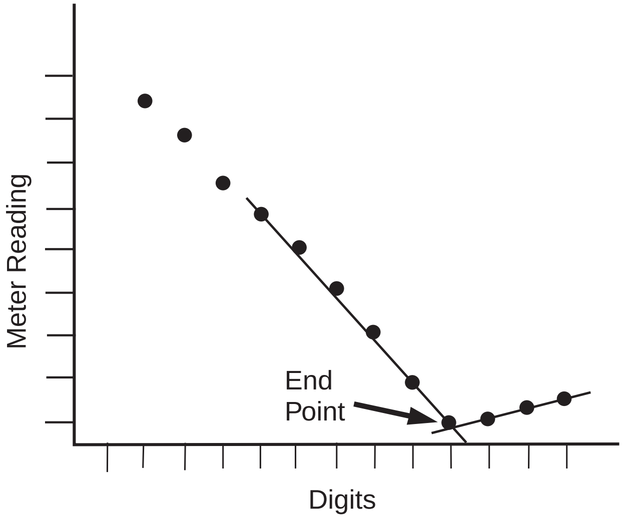
Digits at End Point x **1.25**

= µg/L Total Chlorine as Cl_2

12. Calculate the µg/L total chlorine:

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

Figure 1
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:

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

---

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

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

6. Calculate the percent spiked recovery:

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

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

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

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.

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™ Ampules, 50-75 mg/L Cl_2, 2-mL	20/pkg	14268-20
Water, deionized	4 L	272-56

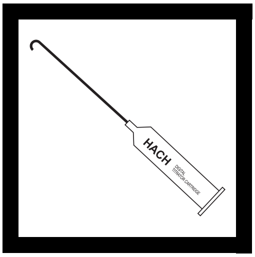
OPTIONAL APPARATUS

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
Standard Methods for the Examination of Water and Wastewater, 19th edition	each	22708-00

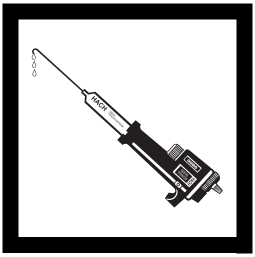
Method 8211

CHROMATE (20 to > 400 mg/L as CrO_4^{2-})

Using Sodium Thiosulfate

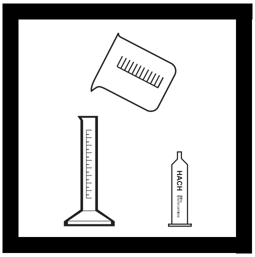


1. Insert a clean delivery tube into the Sodium Thiosulfate titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



2. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

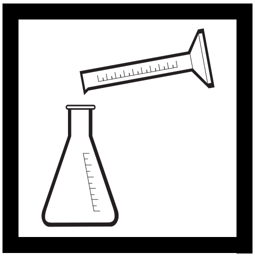
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



3. Select a sample volume corresponding to the expected chromate (CrO_4^{2-}) concentration from *Table 1*.

Note: *Collect 200 to 300 mL of sample in an acid-washed glass or polyethylene container.*

Note: *See Sampling and Storage following these steps.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample to a clean 125-mL Erlenmeyer flask. Dilute to about the 50-mL mark with deionized water.

Table 1

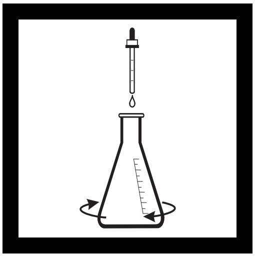
Range (mg/L as CrO_4^{2-})	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
20-80	50	0.2068 N	22676-01	0.2
50-200	20	0.2068 N	22676-01	0.5
100-400	10	0.2068 N	22676-01	1.0
> 400	5	0.2068 N	22676-01	2.0

5. Add the contents of one Potassium Iodide Powder Pillow and swirl to mix.

6. Add the contents of one Dissolved Oxygen 3 Reagent Powder Pillow and swirl to mix. Wait at least three minutes but not more than 10 minutes before completing *steps 7 to 9*.

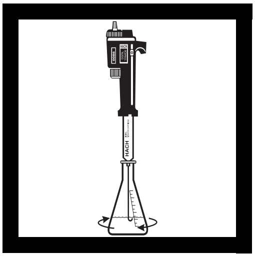
Note: *A yellow or brown color indicates the presence of chromate.*

7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate to a straw-yellow color.



8. Add one dropper of Starch Indicator Solution and swirl to mix.

Note: *A blue color will form.*



9. Continue titrating until the solution turns from blue to colorless. Record the number of digits required.

Digits Required x **Digit Multiplier**

= mg/L Chromate (CrO_4^{-2})

10. Calculate:

Total Digits Required x Digit Multiplier = mg/L chromate (CrO_4^{2-})

Note: *Results may be expressed as mg/L sodium chromate (Na_2CrO_4) or chromium (Cr) by multiplying the mg/L chromate by 1.4 or 0.448, respectively.*

Sampling and Storage

Collect 200 to 300 mL of sample in an acid-washed glass or polyethylene container. If sample cannot be analyzed immediately add 1 mL concentrated sulfuric acid and swirl to mix.

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Use a TenSette® Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of Hexavalent Chromium Standard Solution, 1000 mg/L to three samples of the same volume as that titrated in the procedure.
2. Analyze each as described in the procedure.
3. Each 0.1 mL addition of standard should require 22 additional digits of titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Standard Preparation

A standard solution equivalent to 67 mg/L chromate (30 mg/L Cr) can be prepared by diluting 3.0 mL of Hexavalent Chromium Standard Solution, 1000 mg/L Cr to 100 mL in a volumetric flask. Titrate a 20-mL or 50-mL sample as described in the procedure.

Interferences

Substances capable of oxidizing iodide to iodine under acidic conditions (such as ferric iron and copper) will interfere to give high results. The effects of iron and copper may be masked by dissolving a Magnesium CDTA Powder Pillow, followed by two 1.0-gram measuring spoons of Sodium Acetate in the sample between *steps 6 and 7*.

Summary of Method

Chromate in the sample reacts with iodide under acidic conditions to form iodine as triiodide. Addition of starch indicator produces a blue color complex with the iodine. This complex is titrated with sodium thiosulfate to a colorless end point. The volume of titrant used is proportional to the chromate concentration.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Chromate Reagent Set (about 100 tests)		22724-00
Includes: (1) 349-32, (1) 987-99, (1) 20599-96, (1) 22676-01		
Dissolved Oxygen 3 Reagent Powder Pillows	100/pkg	987-99
Potassium Iodide Powder Pillows	50/pkg	20599-96
Sodium Thiosulfate Titration Cartridge, 0.2068 N	each	22676-01
Starch Indicator Solution	100 mL MDB	349-32
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125-mL	each	505-43
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41

OPTIONAL REAGENTS

Chromium, Hexavalent, Standard Solution, 1000 mg/L	100 mL	14664-42
Magnesium CDTA Powder Pillows	100/pkg	14080-99
Sodium Acetate, trihydrate, ACS	100 g	178-26

OPTIONAL APPARATUS

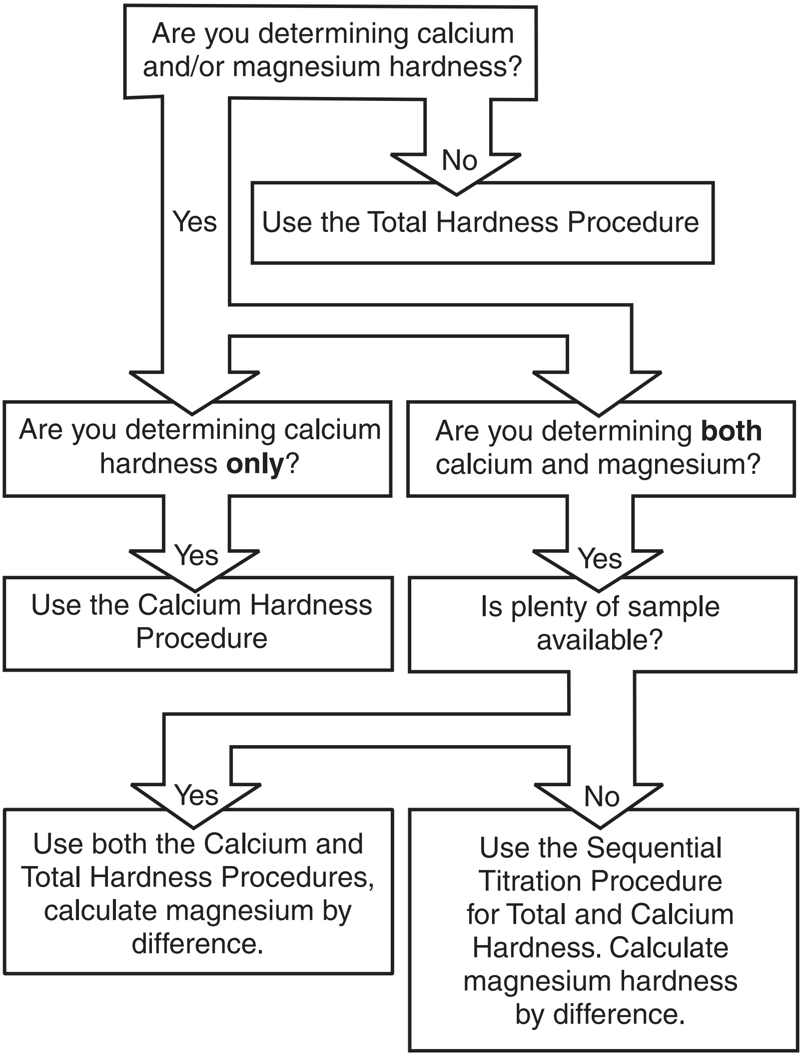
Clamp, 2-prong, extension	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Flask, volumetric, Class B, 100 mL	each	547-42
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01

OPTIONAL APPARATUS, continued

Description	Unit	Cat. No.
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 3-mL	each	14515-03
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet Filler, safety bulb	each	14651-00
Spoon, measuring, 1.0-gram	each	510-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

HARDNESS DECISION TREE

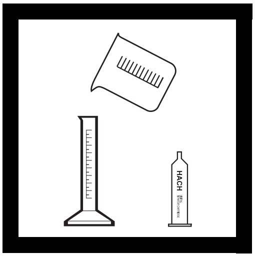
There are several hardness procedures presented in this manual.
Use the following decision tree to select the appropriate procedure for your application.



Method 8204

HARDNESS, CALCIUM (10 to 4000 mg/L as $CaCO_3$)

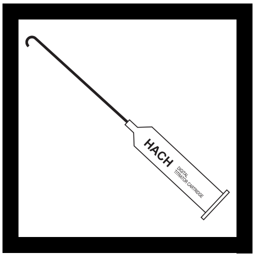
Using EDTA



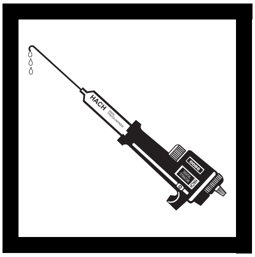
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected calcium as calcium carbonate ($CaCO_3$) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: *One German degree hardness equals 17.9 mg/L hardness as $CaCO_3$.*

Note: *If sample cannot be analyzed immediately, add 1.5 mL Nitric Acid per liter of sample to preserve the sample and to prevent adsorption of the calcium to the container walls. Store in a refrigerator. Samples preserved in this manner are stable for one week. Neutralize to pH 7 before running the test.*

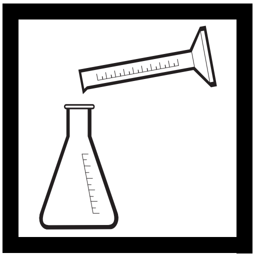


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

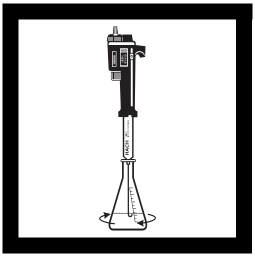
5. Add 2 mL of 8 N Potassium Hydroxide Standard Solution and swirl to mix.

Note: *For samples of 50 mL or less, 1 mL may be added.*

Note: *Magnesium is not included in the results but must be present for a sharp end point. If it is known to be absent, add one to two drops of Magnesium Standard Solution, 10 g/L as* $CaCO_3$.

6. Add the contents of one CalVer® 2 Calcium Indicator Powder Pillow (Cat. No. 852-99) and swirl to mix.

Note: *A 0.1-gram scoop of CalVer 2 Calcium Indicator Powder (Cat. No. 281-14) may be substituted here.*



7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from pink to blue. Record the number of digits required.

Note: *Titrate slowly near the end point, because the reaction is slow, especially in cold samples.*

Total Digits Required x **Digit Multiplier**

= mg/L Calcium Hardness as $CaCO_3$

8. Calculate the sample concentration using one of the formulas below:

Total Digits Required x Digit Multiplier (*Table 1*) = mg/L Calcium Hardness as $CaCO_3$

Total Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

Hardness Relationships

mg/L Ca = Ca Hardness, mg/L as $CaCO_3$ x 0.40

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Hardness Standard Solution Voluette® Ampule, 10,000 mg/L as $CaCO_3$.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the solution titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 10 additional digits of 0.800 N titrant or 100 digits of 0.0800 N titrant (11 digits of 0.714 M or 56 digits of 0.1428 M titrant). If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

WARNING: Potassium cyanide is toxic. Always add it after the potassium hydroxide. Excess potassium cyanide does not affect results. All cyanide wastes should be disposed of by adding an excess of strongly alkaline sodium hypochlorite solution (bleach) with stirring. Use good ventilation. Allow to stand for 24 hours before disposal.

- Some transition and heavy metals complex the indicators and prevent the color change at the end point. Adding a 0.5-g scoop of potassium cyanide (KCN) after the addition of potassium hydroxide removes interference from the following metals at the levels listed (in an undiluted 100-mL sample), see *Table 3*.

Table 3

Metal	Max. Tolerance Level* with KCN	Max. Tolerance Level* without KCN present
Cobalt	20 mg/L	none
Copper	100 mg/L	0.10 mg/L
Nickel	200 mg/L	0.5 mg/L
Zinc	100 mg/L	5 mg/L

* Proportionally higher levels of these elements are tolerable in smaller sample sizes since their effect is diluted when bringing the volume to 100 mL. Because Tables 1 and 2 have sample volumes of 10-100 mL, the interference concentrations may be greater in your sample and have no effect because of sample dilution.

- Iron interferes above 8 mg/L in undiluted samples. Above this level, it causes a red-orange to green end point which is sharp and usable up to 20 mg/L iron.
- Manganese interferes above 5 mg/L.
- Aluminum causes a slow end point, but up to 200 mg/L can be tolerated by allowing enough time for color change.

- Magnesium interference up to 200 mg/L is prevented by formation of magnesium hydroxide at the high test pH, but higher levels prevent a distinct end point.
- Orthophosphate causes a slow end point, but does not interfere if the calcium phosphate that forms is allowed enough time to redissolve during the titration. Polyphosphate must be absent for accurate results.
- Barium and strontium are titrated with calcium but seldom present in natural waters in significant amounts.
- Acidity and alkalinity at 10,000 mg/L as $CaCO_3$ do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
- Samples at about 20 °C (68 °F) or colder should be titrated slowly near the end point to allow enough time for the color change.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

The sample is made alkaline (pH 12-13) with potassium hydroxide to precipitate magnesium as magnesium hydroxide. CalVer 2 Indicator is added and combines with any calcium to form a pink-red color. As EDTA is added, it reacts with the free calcium ions present. When no free calcium ions remain, the EDTA then removes the calcium complexed with the indicator, causing a color change to blue.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Calcium Hardness Reagent Sets (about 100 tests)		
1-16 G.d.h. includes: (1) 282-32, (1) 852-99, (1) 14960-01		24473-00
10-100+ G.d.h. includes: (1) 282-32, (1) 852-99, (1) 14959-01		24474-00
10-160 mg/L includes: (1) 282-32, (1) 852-99, (1) 14364-01		24472-00
100-4,000 mg/L includes: (1) 282-32, (1) 852-99, (1) 14399-01		24475-00

CalVer® 2 Indicator Powder Pillows	100/pkg	852-99
Potassium Hydroxide Standard Solution, 8.00 N	100 mL MDB*	282-32
Water, deionized	4 L	272-56

Select one or more based on sample concentration:

EDTA Titration Cartridge, 0.0800 M	each	14364-01
EDTA Titration Cartridge, 0.1428 M	each	14960-01
EDTA Titration Cartridge, 0.714 M	each	14959-01
EDTA Titration Cartridge, 0.800 M	each	14399-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46

Select one or more based on sample concentration:

Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 100 mL	each	508-42

OPTIONAL REAGENTS

Calcium and Magnesium Total Hardness Reagent Set (about 100 tests)		22721-00
Includes: (2) 282-32, (1) 424-32, (1) 851-99, (1) 947-99, (1) 14364-01, (1) 14399-01		

Description	Unit	Cat. No.
Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$	1000 mL	121-53
CalVer® 2 Calcium Indicator Powder	113 g	281-14
Calcium Standard Solution Voluette® Ampules, 10,000 mg/L as $CaCO_3$, 10-mL	16/pkg	2187-10
Magnesium Standard Solution, 10 g/L $CaCO_3$	29 mL SCDB	1022-33
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Potassium Cyanide, ACS	125 g	767-14

OPTIONAL APPARATUS

Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong, extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01

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* Marked Dropper Bottle (MDB). Contact Hach for larger sizes.

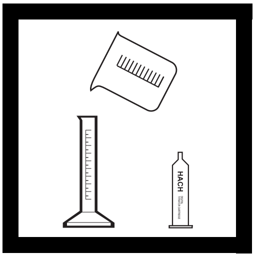
HARDNESS, CALCIUM, continued

Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion***™***1*** Basic Portable pH Meter with electrode	each	51700-10
Spoon, measuring, 0.1-gram	each	511-00
Spoon, measuring, 0.5-gram	each	907-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

Method 8213

HARDNESS, TOTAL (10 to 4000 mg/L as $CaCO_3$)

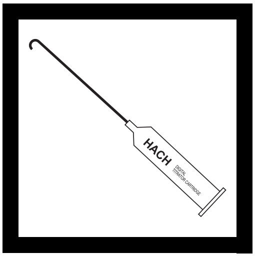
Using EDTA



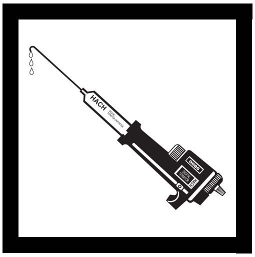
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected total hardness as calcium carbonate ($CaCO_3$) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: *One German degree hardness equals 17.9 mg/L hardness as* $CaCO_3$.

Note: *Collect at least 100 mL of sample in a glass or polyethylene container. Samples may be held up to seven days before analysis if stored at 4 °C and acidified to pH 2 with concentrated nitric acid. Neutralize acidified sample to pH 7 with ammonium hydroxide before testing.*

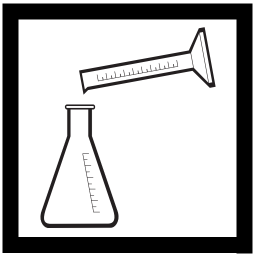


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

5. Add 2 mL of Hardness 1 Buffer Solution and swirl to mix.

6. Add the contents of one ManVer® 2 Hardness Indicator Powder Pillow (Cat. No. 851-99) and swirl to mix.

Note: *Four drops of ManVer Hardness Indicator Solution or a 0.1 g scoop of ManVer 2 Hardness Indicator Powder (Cat. No. 280-14) may be substituted for the powder pillow.*

7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from red to pure blue. Record the number of digits required.

Note: *Titrate slowly near the end point because the reaction is slow, especially in cold samples.*

Total Digits Required x Digit Multiplier

= mg/L Total Hardness as $CaCO_3$

8. Use one of the following formulas to calculate the final concentration:

Digits Required x Digit Multiplier (*Table 1*) = mg/L Total Hardness as $CaCO_3$

Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

Note: *The magnesium concentration may be determined by subtracting the results of the calcium determination from total hardness.*

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

Hardness Relationships

mg/L Total Hardness as Ca = mg/L Total Hardness as $(CaCO_3) \times 0.400$

mg/L Total Hardness (as $CaCO_3$) =
mg/L Ca (as $CaCO_3$) + mg/L Mg (as $CaCO_3$)

Accuracy Check

Standard Additions Method
To verify analytical technique, use 20 mL of the Calcium Standard Solution, 1000 mg/L as $CaCO_3$. Perform the procedure as described above. This solution will read 1000 mg/L or 55.9 G.d.h.

Perform this accuracy check when interferences are suspected.

1. Snap the neck off a Hardness Standard Solution Voluette® Ampule, 10,000 mg/L as $CaCO_3$.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 10 additional digits of 0.800 M titrant, 100 digits of 0.0800 M titrant, 11 digits of 0.714 M, or 56 digits of 0.1428 M titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results.
- Some transition and heavy metals complex the indicator and prevent the color change at the end point.

- Iron does not interfere up to 15 mg/L. Above this level it causes a red-orange to green end point which is sharp and usable up to 30 mg/L iron. Substitute a 0.0800 M CDTA or 0.800 M CDTA titration cartridge for the 0.0800 M EDTA or 0.800 M EDTA titration cartridges, respectively, if iron interference is probable.
- Manganese titrates directly up to 20 mg/L but masks the end point above this level. Adding a 0.1-gram scoop of hydroxylamine hydrochloride monohydrate raises this level to 200 mg/L manganese.

WARNING
Potassium cyanide is toxic. Always add it after the potassium hydroxide. Excess potassium cyanide does not affect results. All cyanide wastes should be disposed of by adding an excess of strongly alkaline sodium hypochlorite solution (bleach) with stirring. Use good ventilation. Allow to stand for 24 hours before disposal.

- Copper and aluminum interfere at levels above 0.10 and 0.20 mg/L, respectively. Cobalt and nickel interfere at all levels and must be absent or masked. A 0.5-gram scoop of potassium cyanide removes interference from up to 100 mg/L copper, 100 mg/L zinc, 100 mg/L cobalt, and 100 mg/L nickel. It raises the permissible aluminum level to 1 mg/L. Metals masked with cyanide will not be included in the hardness result.
- Orthophosphate causes a slow end point and polyphosphate must be absent for accurate results.
- Acidity and alkalinity at 10,000 mg/L (as $CaCO_3$) do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
- Adding the contents of one CDTA Magnesium Salt Powder Pillow removes metal interferences at or below the levels shown in *Table 3*.

Table 3

Metal	CDTA Removes Interference Below This Level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Manganese	200 mg/L

Table 3

Metal	CDTA Removes Interference Below This Level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

- If more than one metal is present at or above the concentrations shown above, an additional CDTA Magnesium Salt Powder Pillow may be required.

Results obtained by this procedure include the hardness contributed by the metals. If the concentration of each metal is known, a correction can be applied to obtain the calcium and magnesium hardness concentration. The hardness (in mg/L as $CaCO_3$) contributed by each mg/L of metal is listed below, and can be subtracted from the total hardness value obtained above to determine the calcium and magnesium hardness. See *Table 4*.

Table 4

Metal	Hardness as $CaCO_3$ Contributed by Each mg/L of Metal
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

- Barium, strontium and zinc titrate directly.

- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

After the sample is buffered to pH 10.1, ManVer 2 Hardness Indicator is added, and forms a red complex with a portion of the calcium and magnesium in the sample. EDTA titrant reacts first with the free calcium and magnesium ions, then with those bound to the indicator, causing it to change to a blue color at the end point.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Total Hardness Reagent Sets (about 100 tests)		
1-16 G.d.h. includes: (1) 424-32, (1) 851-99, (1) 14960-01		24478-00
10-100+ G.d.h. includes: (1) 424-32, (1) 851-99, (1) 14959-01		24479-00
10-160 mg/L includes: (1) 424-32, (1) 851-99, (1) 14364-01		24480-00
100-4,000 mg/L includes: (1) 424-32, (1) 851-99, (1) 14399-01		24481-00
Hardness 1 Buffer Solution	100 mL MDB	424-32
ManVer® 2 Hardness Indicator Powder Pillow	100/pkg	851-99
Water, deionized	4 L	272-56
Select one or more based on sample concentration:		
EDTA Titration Cartridge, 0.0800 M	each	14364-01
EDTA Titration Cartridge, 0.1428 M	each	14960-01
EDTA Titration Cartridge, 0.714 M	each	14959-01
EDTA Titration Cartridge, 0.800 M	each	14399-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Ammonium Hydroxide, 10%	100 mL MDB*	14736-32
Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$	1000 mL	121-53
CDTA Magnesium Salt Powder Pillows	100/pkg	14080-99
CDTA Titration Cartridge, 0.0800 M	each	14402-01

CDTA Titration Cartridge, 0.800 M	each	14403-01
Calcium Standard Solution Voluette® Ampules, 10,000 mg/L as $CaCO_3$, 10-mL	16/pkg	2187-10
Hydroxylamine Hydrochloride, Monohydrate, ACS	113 g	246-14
ManVer® 2 Hardness Indicator Powder	113 g	280-14
ManVer® Hardness Indicator Solution	100 mL MDB*	425-32
Nitric Acid Solution, 1:1	500 mL	2540-49
Nitric Acid, ACS	500 mL	152-49
Potassium Cyanide, ACS	125 g	767-14

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, poly, 500-mL	each	620-11
Clamp 2-prong, extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™**1*** Basic Portable pH Meter with electrode	each	51700-10
Spoon, measuring, 0.1-gram	each	511-00
Spoon, measuring, 0.5-gram	each	907-00
Spoon, measuring, 1.0-gram	each	510-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

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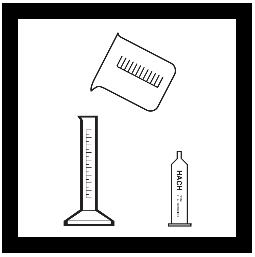
* Contact Hach for larger sizes.

Method 8329

HARDNESS, TOTAL, SEQUENTIAL (10 to 4000 mg/L as $CaCO_3$)

Sequential Titration Procedure (Limited Sample)

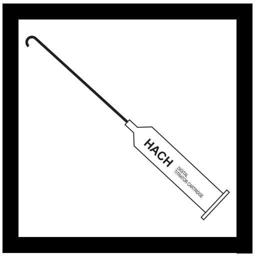
Scope and Application: To determine total and calcium hardness in samples with limited sample size, follow this procedure. Calculate magnesium hardness by difference.



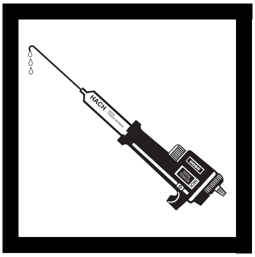
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected calcium as calcium carbonate ($CaCO_3$) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: *One German degree hardness equals 17.9 mg/L hardness as* $CaCO_3$.

Note: *If sample cannot be analyzed immediately, add 1.5 mL Nitric Acid per liter of sample to preserve the sample and to prevent adsorption of the calcium to the container walls. Store in a refrigerator. Samples preserved in this manner are stable for one week. Neutralize to pH 7 before running the test.*

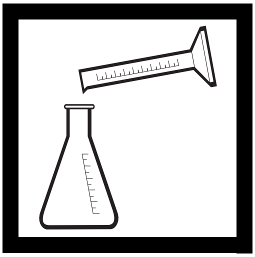


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience, use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

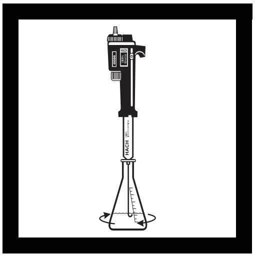
5. Add 2 mL of 8 N Potassium Hydroxide Standard Solution and swirl to mix.

Note: *For samples of 50 mL or less, 1 mL may be added.*

Note: *Magnesium is not included in the results but must be present for a sharp end point. If it is known to be absent, add 1–2 drops of Hardness Standard Solution.*

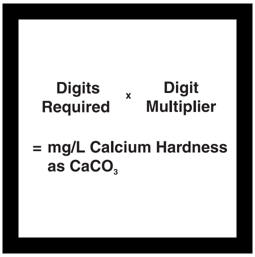
6. Add the contents of one CalVer® 2 Calcium Indicator Powder Pillow (Cat. No. 947-99) and swirl to mix.

Note: *Do not use potassium cyanide to eliminate interferences or toxic gas will form in subsequent steps.*



7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from pink to blue. Record the number of digits required.

Note: *Titrate slowly near the end point, because the reaction is slow, especially in colder samples.*

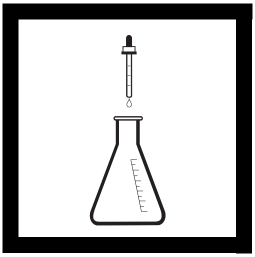


8. Calculate the sample concentration of calcium hardness by using one of the formulas below:

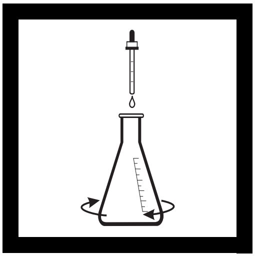
Digits Required x Digit Multiplier (*Table 1*) = mg/L Calcium Hardness as CaCO3

Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

Note: *Do not reset the counter to zero.*



9. After completing the calcium titration, add 1 mL of 5.25 N Sulfuric Acid Standard Solution. Add additional acid dropwise and swirl the solution until the color changes from pure blue to purple, then to blue and finally to red. Swirl the flask to ensure that all precipitated magnesium hydroxide has re-dissolved.



10. Add 2 mL of Hardness 1 Buffer Solution and swirl to mix.

11. Add the contents of one ManVer® 2 Hardness Indicator Powder Pillow (Cat. No. 928-99) or 4 drops of Hardness 2 Test Solution (Cat. No. 425-32). Swirl to mix.

12. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from red to pure blue. Record the number of digits required.

Note: *Titrate slowly near the end point because the reaction is slow, especially in colder samples.*

Digits Required x Digit Multiplier

= mg/L Total Hardness as $CaCO_3$

Total Hardness (mg/L $CaCO_3$)

- Ca Hardness (mg/L $CaCO_3$)

= Mg Hardness (mg/L $CaCO_3$)

13. Use the appropriate formula below to calculate the final concentration based on sample size and cartridge used:

Digits Required x Digit Multiplier (*Table 1*) = mg/L Total Hardness as $CaCO_3$

Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

14. The first titration gives the mg/L calcium hardness and the second gives the mg/L total hardness. The difference between the values is the mg/L magnesium hardness as $CaCO_3$.

Total Hardness (mg/L $CaCO_3$) - Ca Hardness (mg/L $CaCO_3$) = Mg Hardness (mg/L $CaCO_3$)

Note: *See below for conversion factors.*

Hardness Relationships

mg/L Mg Hardness as $CaCO_3$
= mg/L Total Hardness as $CaCO_3$ – mg/L Ca Hardness as $CaCO_3$

mg/L $MgCO_3$ = mg/L Mg Hardness as $CaCO_3 \times 0.842$

mg/L Mg = mg/L $MgCO_3 \times 0.29$

Interferences

WARNING:
Do not use potassium cyanide to eliminate interferences because it will generate deadly hydrogen cyanide gas when the sulfuric acid solution is added in step 9.

- Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results.
- Some transition and heavy metals complex the indicator and prevent the color change at the end point.
- Iron does not interfere up to 15 mg/L. Above this level it causes a red-orange to green end point which is sharp and usable up to 30 mg/L iron. Substitute a 0.0800 M CDTA or 0.800 M CDTA titration cartridge for the 0.0800

M EDTA or 0.800 M EDTA titration cartridges, respectively, if iron interference is probable. For results in G.d.h., divide the mg/L result by 17.9.

- Manganese titrates directly up to 20 mg/L but masks the end point above this level. Adding a 0.1-gram scoop of hydroxylamine hydrochloride raises this level to 200 mg/L manganese.
- Copper interferes at levels of 0.10 and 0.20 mg/L. Cobalt and nickel interfere at all levels and must be absent or masked.
- Orthophosphate causes a slow end point and polyphosphate must be absent for accurate results.
- Acidity and alkalinity at 10,000 mg/L (as $CaCO_3$) do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
- Adding the contents of one CDTA Magnesium Salt Powder Pillow removes metal interferences at or below the levels shown in *Table 3*.
- If more than one metal is present at or above the concentrations shown in *Table 3*, an additional CDTA Magnesium Salt Powder Pillow may be required.

- Results obtained by this procedure include the hardness contributed by polyvalent metal ions. If the concentration of each metal is known, a correction can be applied to obtain the calcium and magnesium hardness concentration. The hardness (in mg/L as $CaCO_3$) contributed by each mg/L of metal is listed in *Table 4*. Hardness contributed by metals can be subtracted from the total hardness value obtained in *step 13* to determine the calcium and magnesium hardness concentration.
- Barium, strontium and zinc titrate directly.

Table 3

Metal	CDTA Removes Interference Below this Level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

Table 4

Metal	Hardness as $CaCO_3$ Contributed by Each mg/L of Metal
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

REQUIRED REAGENTS*

Calcium and Magnesium Hardness Reagent Sets (about 100 tests each)

10-100+ G.d.h. includes: (1) 282-32, (1) 424-32, (1) 928-99, (1) 947-99, (1) 2449-32, (1) 14959-01	24485-00
10-160 mg/L includes: (1) 282-32, (1) 424-32, (1) 928-99, (1) 947-99, (1) 2449-32, (1) 14364-01	24486-00
100-4,000 mg/L includes: 282-32, (1) 424-32, (1) 928-99, (1) 947-99, (1) 2449-32, (1) 14399-01	24487-00

Description	Unit	Cat. No.
CalVer® 2 Indicator Powder Pillows	100/pkg	947-99
Hardness 1 Buffer Solution	100 mL MDB	424-32
ManVer® 2 Hardness Indicator Powder Pillows	100/pkg	928-99
Potassium Hydroxide Standard Solution, 8.00 N	100 mL MDB**	282-32
Sulfuric Acid, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56
Select one or more based on sample concentration:		
EDTA Titration Cartridge, 0.0800 M	each	14364-01
EDTA Titration Cartridge, 0.1428 M	each	14960-01
EDTA Titration Cartridge, 0.714 M	each	14959-01
EDTA Titration Cartridge, 0.800 M	each	14399-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 100 mL	each	508-42

OPTIONAL REAGENTS

CDTA Magnesium Salt Powder Pillows	100/pkg	14080-99
CDTA Titration Cartridge, 0.08 M	each	14402-01
CDTA Titration Cartridge, 0.8 M	each	14403-01
Hardness 2 Test Solution	100 mL MDB	425-32
Hardness Standard Solution, Voluette® Ampules, 10,000 mg/L as $CaCO_3$, 10 mL	16/pkg	2187-10
Hydroxylamine Hydrochloride	113 g	246-14
Nitric Acid, 70%	500 mL	152-49

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* Other reagents and apparatus are listed with the specific procedure.

** Marked Dropper Bottle (MDB). Contact Hach for larger sizes.

OPTIONAL APPARATUS

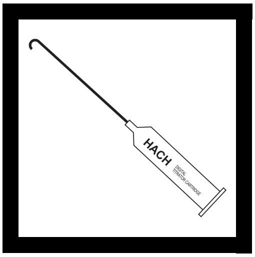
Description	Unit	Cat. No.
Bottle, wash, poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 20 mL	each	14515-20
Pipet, volumetric, Class A, 25 mL	each	14515-40
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pipet, volumetric, Class A, 100 mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™**1*** Basic Portable pH Meter with electrode	each	51700-10
Spoon, measuring, 0.1 gram	each	511-00
Spoon, measuring, 0.5 gram	each	907-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

Method 10100

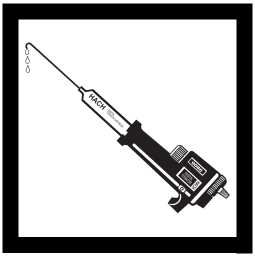
HYPOCHLORITE (Bleach) (50 to 150 g/L [5 to 15%] as Cl2)

Iodometric Method*

Scope and Application: For testing concentrated liquid bleach (sodium hypochlorite, soda bleach) used as a disinfectant in drinking water or wastewater treatment.



1. Insert a clean delivery tube into the 2.26 N Thiosulfate Titrant Solution cartridge. Attach the cartridge to the titrator body.

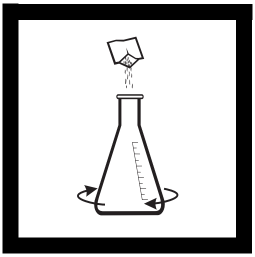


2. Flush the delivery tube by turning the deliver knob to eject a few drops of titrant. Reset the counter to zero and wipe off the tip.

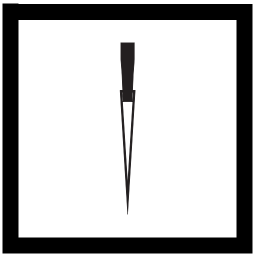
3. Fill a 125-mL Erlenmeyer flask to about the 75-mL mark with deionized or tap water.

Note: *The level of residual chlorine found in tap water will not interfere in the test.*

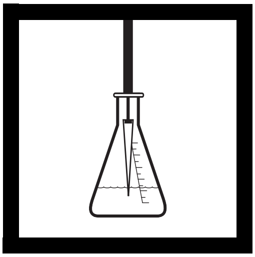
4. Add the contents of one Potassium Iodide Powder Pillow to the flask and swirl to mix.



5. Add the contents of one Acid Reagent Powder Pillow to the flask and swirl to mix.



6. Attach a clean tip to the TenSette® Pipet.



7. Use the pipet to dispense 0.2 mL of bleach sample below the solution level in the flask.

8. Swirl to mix. The solution will turn dark brown.

Note: *Proceed immediately with Step 9.*

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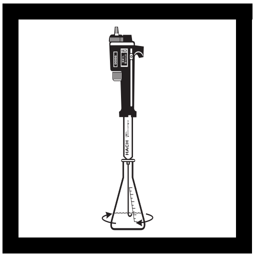
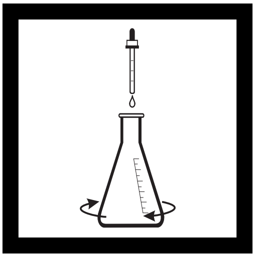
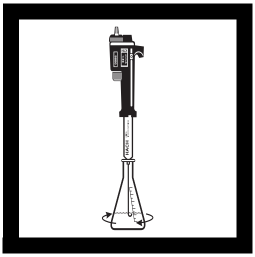
* Adapted from ASTM method D2022.



9. Place the delivery tube tip into the solution and swirl the flask while titrating with the thiosulfate titrant until the solution is pale yellow.



10. Add one dropper of Starch Indicator Solution to the flask and swirl to mix. A dark blue or green color will develop.



11. Continue the titration until the solution becomes colorless. Record the number of digits required.

g/L Chlorine
as Cl_2 =
Digits at End Point
x 0.5

12. Calculate the g/L chlorine:

g/L chlorine = Digits Required x 0.5

Note: *Divide the g/L chlorine by 10 to obtain the % (by volume) chlorine ("trade percent").*

Sample Collection, Preservation and Storage

Soda bleach solutions are relatively unstable. Avoid exposing the sample to heat or light. Collect samples in glass bottles and store in a cool, dark place until analyzed. Analyze as soon as practical.

Accuracy Check

Standard Solution Method

Hach strongly recommends that, for optimum test results, reagent accuracy be checked with each new lot of reagents. The strength of the Thiosulfate Standard Solution can be checked using Potassium Iodide-Iodate Standard Solution:

1. Use a Class A pipet to transfer 50.00 mL of 0.0125 N Potassium Iodide-Iodate Standard Solution to a clean 125-mL Erlenmeyer flask.
2. Add the contents of one Potassium Iodide Powder Pillow to the flask and swirl to mix.

3. Add the contents of three Acid Reagent Powder Pillows to the flask and swirl to mix. Swirl until all powder is dissolved.

4. Continue the titration starting at *step 9* of the procedure. It should take 217–227 digits of 2.26 N Thiosulfate Standard Solution to reach the end point.

Interferences

The iodometric method is relatively free of interferences. The test will determine chlorite ion (ClO_2^-) in addition to the hypochlorite ion (ClO^-). However, the amount of chlorite in commercial bleach is insignificant (typically less than 0.2%).

A large excess of caustic in the bleach sample may lead to low results. After adding the Acid Reagent Powder Pillow (*step 5*), check the pH of the solution with pH paper. The pH should be less than 3. If not, add additional Acid Reagent, one pillow at a time, until the pH drops below 3.

For most accurate results, the temperature of the dilution water (*step 3*) should be less than 20 °C (68 °F).

Precision

In a single laboratory, using a commercial bleach sample of 91.2 g/L (9.12%) Cl_2, a single operator obtained a standard deviation of ± 1.5 g/L (± 0.15%) Cl_2.

Summary of Method

Under acidic conditions, hypochlorite reacts with iodide to produce an equivalent amount of triiodide (I_3^-). The released I_3^- is titrated with standard thiosulfate solution to a colorless end point. The number of digits of thiosulfate required is proportional to the hypochlorite concentration in the original bleach sample.

REQUIRED REAGENTS

HR Hypochlorite (Bleach) Reagent Set (about 100 tests)	26870-00

Includes: (1) 349-32, (1) 1042-99, (1) 20599-96, (1) 26869-01

Description	Unit	Cat. No.
Acid Reagent Powder Pillows	100/pkg	1042-99
Potassium Iodide Powder Pillows	50/pkg	20599-96
Sodium Thiosulfate Standard Titrant Solution, 2.26 N	each	26869-01
Starch Indicator Solution	100 mL MDB*	349-32

REQUIRED APPARATUS

Clippers, large	each	968-00
Delivery Tubes, 180°	5/pkg	17205-00
Digital Titrator Assembly	each	16900-02
Flask, Erlenmeyer, 125-mL	each	505-43
Pipet, TenSette®, 0.1–1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96

OPTIONAL REAGENTS

Potassium Iodide-Iodate Standard Solution, 0.0125 N	1 L	14001-53

OPTIONAL APPARATUS

pH Paper, 1–11	5/pkg	391-33
Pipet, volumetric, Class A, 50.00 mL	each	14515-41

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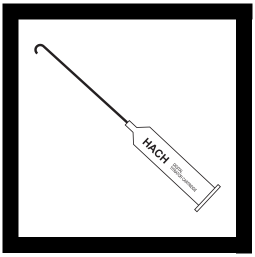
* Marked Dropping Bottle

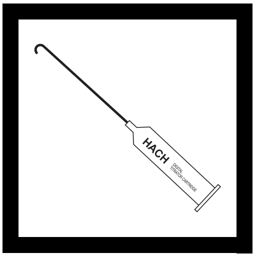
Method 8214

IRON (10 to 1000 mg/L as Fe)

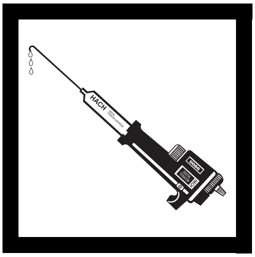
Using the TitraVer® Titration Cartridge



1. Select a sample volume and a TitraVer Titration Cartridge corresponding to the expected iron (Fe) concentration from *Table 1*.

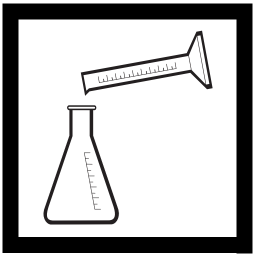


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

***Note:** For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder to measure the sample volume from *Table 1*. Transfer the sample into a clean 125-mL Erlenmeyer flask. Dilute to about the 50-mL mark with deionized water, if necessary.

Table 1

Range (mg/L as Fe)	Sample Volume (mL)	Titration Cartridge (M TitraVer)	Catalog Number	Digit Multiplier
10-40	50	0.0716	20817-01	0.1
25-100	20	0.0716	20817-01	0.25
100-400	50	0.716	20818-01	1.0
250-1000	20	0.716	20818-01	2.5

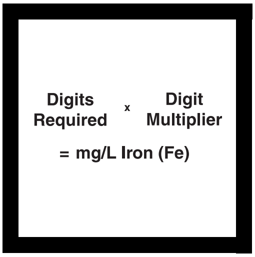
5. Add the contents of one Citrate Buffer Powder Pillow and swirl to mix.

6. Add the contents of one Sodium Periodate Powder Pillow and swirl to mix.

Note: *A yellow color indicates the presence of iron.*

7. Add the contents of one Sulfosalicylic Acid Powder Pillow and swirl to mix. A red color will develop if iron is present.

8. Place the delivery tube tip into the solution and swirl the flask while titrating the sample until the color changes from red to the original yellow. Record the number of digits required.



9. Calculate:

Digits Required x Digit Multiplier = mg/L Iron (Fe)

Accuracy Check

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Use a TenSette® Pipet to add 0.5 mL of 1000 mg/L as Fe standard to the sample in *step 7*. Resume titration back to the same end point. Record the number of additional digits required.
2. Repeat, using two more additions of 0.5 mL. Titrate to the end point after each addition.
3. Each 0.5-mL addition of standard should require 10 additional digits of 0.716 M titrant or 100 digits of 0.0716 M titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Summary of Method

Iron (Fe^{2+}) is oxidized by sodium periodate to the ferric ion (Fe^{3+}). When sulfosalicylic acid is present, the ferric ion forms a red complex, coloring the solution. The red complex is destroyed by titration with EDTA. Citric acid is used to buffer the solution and to stabilize the ferric ion in solution.

REQUIRED REAGENTS

(varies with sample characteristics)

Iron Reagent Sets (about 100 tests)

- **10-100 mg/L** includes: (1) 984-99, (1) 20815-99, (1) 20816-69, (1) 20817-0124492-00
- **100-1000 mg/L** includes: (1) 984-99, (1) 20815-99, (1) 20816-69, (1) 20818-01 24493-00

Description	**Unit**	**Cat. No.**
Citrate Buffer Powder Pillows	100/pkg	20815-99
Sodium Periodate Powder Pillows	100/pkg	984-99
Sulfosalicylic Acid Powder Pillows	100/pkg	20816-69
TitraVer® Standard Solution Titration Cartridge, 0.0716 M	each	20817-01
TitraVer® Standard Solution Titration Cartridge, 0.716 M	each	20818-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Select one or more based on sample concentration:		
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41

OPTIONAL REAGENTS

Iron Standard Solution, 1000 mg/L as Fe	100 mL	2271-42

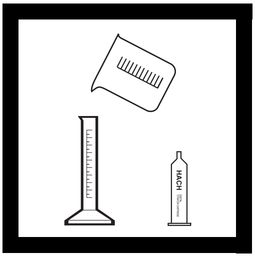
OPTIONAL APPARATUS

Bottle, wash, poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 25.0 mL	each	14515-40
Pipet, volumetric, Class A, 50.0 mL	each	14515-41
Pipet Filler, safety bulb	each	14651-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

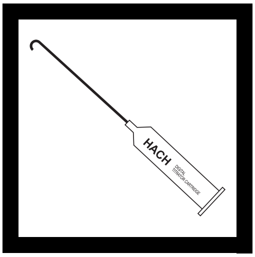
Method 8351

NITRITE (100 to 2500 mg/L as $NaNO_2$)

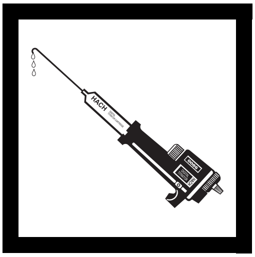
Using Ceric Standard Solution



1. Select the sample volume from *Table 1* which corresponds to the expected sample sodium nitrite concentration (as $NaNO_2$).

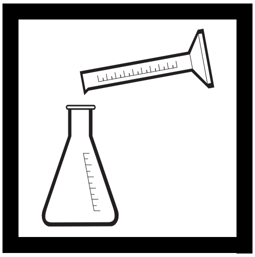


2. Insert a clean delivery tube into the Ceric Standard Solution Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



3. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.

***Note:** For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

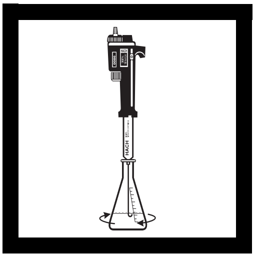


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample to a clean 125-mL Erlenmeyer flask. Add deionized water to about the 75-mL mark, if necessary.

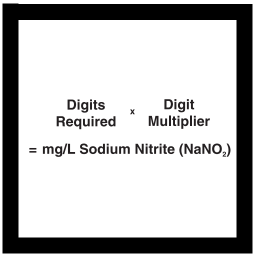
***Note:** A pipet is recommended for sample volumes less than 10 mL.*

5. Add five drops of 5.25 N Sulfuric Acid Standard Solution to the flask. Swirl to mix.

6. Add one drop of Ferroin Indicator Solution to the flask. Swirl to mix.



7. Place the delivery tip into the solution. While titrating with Ceric Standard Solution, swirl the flask until the solution color changes from orange to pale blue. Record the number of digits required.



8. Calculate:

Digits Required x Digit Multiplier = mg/L Sodium Nitrite ($NaNO_2$)

***Note:** See Standardization of Ceric Solution to verify the normality.*

Table 1

Expected Sample Concentration (as $NaNO_2$)	Sample Volume (mL)	Digit Multiplier
100-400	25	0.86
400-800	10	2.15
800-1500	5	4.31
1500-2500	2	10.78

Standardization of Ceric Solution

The normality of the Ceric Solution will sometimes decrease over time. Before use, verify the normality with the following procedure. This standardization should be done monthly.

1. Use a graduated cylinder or pipet to measure 50 mL of deionized water into a 125-mL Erlenmeyer flask.
2. Add 5 mL of 19.2 N Sulfuric Acid Standard Solution. Swirl to mix.
3. Insert a clean delivery tube into a Ceric Standard Titration Cartridge.
4. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.
5. Place the delivery tube tip into the solution. While swirling the flask, add 200 digits of Ceric Standard.
6. Insert a clean delivery tube into a 0.200 N Sodium Thiosulfate Titration Cartridge.
7. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.
8. Place the delivery tube tip into the solution. While swirling the flask, titrate with the sodium thiosulfate from

an intense yellow color to a faint yellow color. Record the number of digits required. This step should require about 400-450 digits of titrant.

9. Add one drop of Ferroin Indicator Solution. Swirl to mix. The solution will turn a faint blue.

10. Continue titrating the Ceric Standard Solution (using the 0.20 Sodium Thiosulfate Titration Cartridge) from a faint blue to orange color. Record the number of digits required.

11. Calculate the correction factor:

$$\text{Correction Factor} = \frac{\text{Digits Required}}{500}$$

12. Multiply the mg/L sodium nitrite from *step 8* of the nitrite titration procedure by the correction factor to obtain the correct sodium nitrite concentration.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Prompt analysis is recommended.

If prompt analysis is impossible, store samples for 24 to 48 hours at 4 °C (39 °F) or lower. Warm to room temperature before analysis. Do not use acid preservatives.

Accuracy Check

Dissolve 1.000 gram of fresh sodium nitrite in 100 mL of deionized water. Dilute to 1000 mL with deionized water to prepare a 1000 mg/L sodium nitrite standard solution. Use a 5.0 sample of the standard solution and start with *step 4* of the titration procedure. The analysis should yield 1000 mg/L for *step 8* of the titration procedure.

Summary of Method

Sodium nitrite is titrated with tetravalent cerium ion, a strong oxidant, in the presence of ferroin indicator. After the cerium oxidizes the nitrite, it oxidizes the indicator, causing a color change from orange to pale blue. The concentration of sodium nitrite is proportional to the amount of titrant used.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Ceric Standard Solution Titration Cartridge, 0.5 N	each	22707-01
Ferroin Indicator Solution	29 mL DB	1812-33
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Select one or more based on sample volume:		
Cylinder, graduated, 100 mL, poly	each	1081-42
Pipet, serological, 10 mL	25/pkg	20931-28

REQUIRED APPARATUS (Using Titrastir® Stir Plate Modification)

Delivery Tubes, 90° with hook	5/pkg	41578-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
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

Sodium Thiosulfate Titration Cartridge, 0.200 N	each	22675-01
Sodium Nitrite, ACS	454 g	2452-01
Sulfuric Acid Standard Solution, 19.2 N	100 mL	2038-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Balance, electronic, analytical	each	22310-00
Flask, volumetric, Class A, 50 mL	each	14547-41

OXYGEN, DISSOLVED (1 to greater than 10 mg/L as DO)

Azide Modification of Winkler Method

Using a 300-mL BOD Bottle

Method 8215

1. Collect a water sample in a clean 300-mL BOD Bottle.

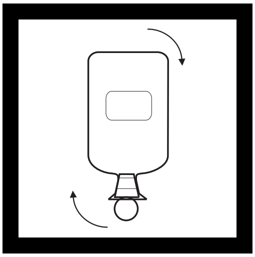
Note: *Allow the sample to overflow the bottle for 2-3 minutes to ensure air bubbles are not trapped.*

Note: *If samples cannot be analyzed immediately, see Sampling and Storage on page 172.*

2. Add the contents of one Manganous Sulfate Powder Pillow and one Alkaline Iodide-Azide Reagent Powder Pillow.

3. Immediately insert the stopper so air is not trapped in the bottle. Invert several times to mix.

Note: *A flocculent precipitate will form. It will be orange-brown if oxygen is present or white if oxygen is absent. The floc settles slowly in salt water and normally requires 5 additional minutes before proceeding to step 5.*

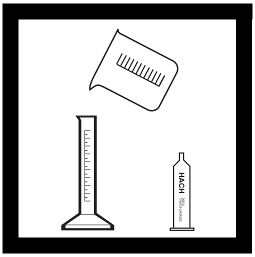


4. Wait until the floc in the solution has settled. Again invert the bottle several times and wait until the floc has settled.

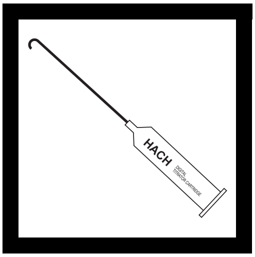
Note: *Waiting until floc has settled twice assures complete reaction of the sample and reagents.*

5. Remove the stopper and add the contents of one Sulfamic Acid Powder Pillow. Replace the stopper without trapping air in the bottle and invert several times.

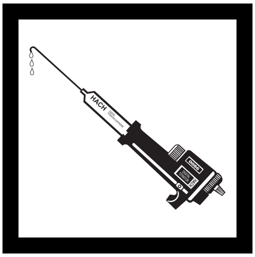
Note: *The floc will dissolve and leave a yellow color if oxygen is present.*



6. Select a sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected dissolved oxygen (D.O.) concentration from *Table 1*.

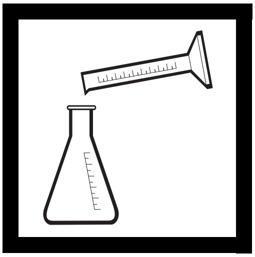


7. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.

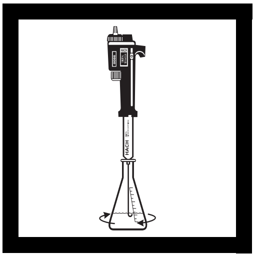


8. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

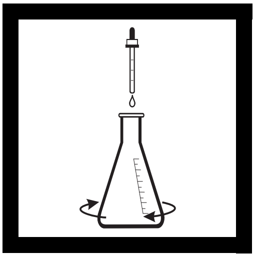
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



9. Use a graduated cylinder to measure the sample volume from *Table 1*. Transfer the sample into a 250-mL Erlenmeyer flask.

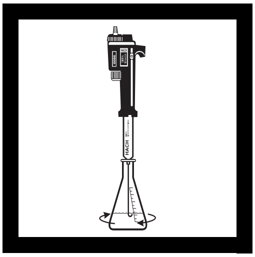


10. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate to a pale yellow color.



11. Add two 1-mL droppers of Starch Indicator Solution and swirl to mix.

Note: *A dark blue color will develop.*



12. Continue the titration to a colorless end point. Record the number of digits required.

Digits Required x Digit Multiplier
= mg/L Dissolved Oxygen

13. Calculate:

Digits Required x Digit Multiplier = mg/L Dissolved Oxygen

Table 1

Range (mg/L D.O.)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
1-5	200	0.200	22675-01	0.01
2-10	100	0.200	22675-01	0.02
>10	200	2.000	14401-01	0.1

Using a 60-mL BOD Bottle

Method 8332

1. Collect a water sample in a clean 60-mL glass-stoppered BOD Bottle.

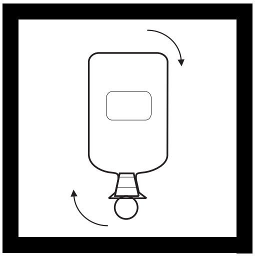
Note: *Allow the sample to overflow the bottle for 2-3 minutes to ensure air bubbles are not trapped.*

Note: *If samples cannot be analyzed immediately, see Sampling and Storage on page 172.*

2. Add the contents of one Dissolved Oxygen 1 Reagent Powder Pillow and one Dissolved Oxygen 2 Reagent Powder Pillow.

3. Immediately insert the stopper so air is not trapped in the bottle. Invert several times to mix.

Note: *A flocculent precipitate will form. It will be orange-brown if oxygen is present or white if oxygen is absent. The floc settles slowly in salt water and normally requires 5 additional minutes before proceeding to step 5.*

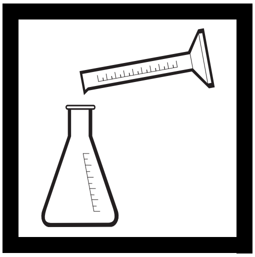


4. Wait until the floc in the solution has settled and the top half of the solution is clear. Again invert the bottle several times and wait until the floc has settled.

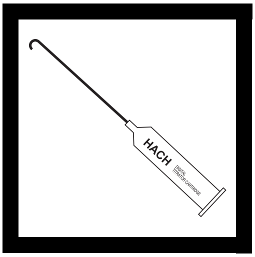
Note: *Results are not affected if the floc does not settle or if some of the reagent powder does not dissolve.*

5. Remove the stopper and add the contents of one Dissolved Oxygen 3 Powder Pillow. Replace the stopper without trapping air in the bottle and invert several times to mix.

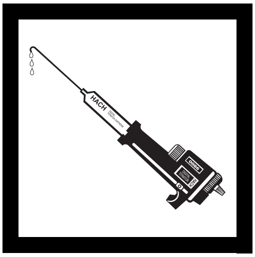
Note: *The floc will dissolve and leave a yellow color if oxygen is present.*



6. Accurately measure 20 mL of the prepared sample and transfer it to a 125-mL Erlenmeyer flask.

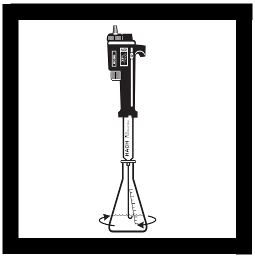


7. Attach a clean straight-stem delivery tube to a 0.2000 N Sodium Thiosulfate Titration Cartridge. Twist the cartridge onto the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary



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

Note: *For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.*



9. Titrate the prepared solution with 0.2000 N Sodium Thiosulfate until the sample changes from yellow to colorless. Record the number of digits.

Digits Required x **0.1**

= **mg/L Dissolved Oxygen**

10. Calculate:

Digits required x 0.1 = mg/L Dissolved Oxygen

Sampling and Storage

Sampling and sample handling are important in obtaining meaningful results. The dissolved oxygen content of the sample changes with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time, and other factors. A single dissolved oxygen test rarely reflects the over-all condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results.

Collect samples in clean BOD Bottles (see *step 1*). If storage is necessary, run steps 1-5 of the procedure and store in the dark at 10-20 °C. Seal the bottle with water by pouring a small volume of water into the flared lip area of a stopper bottle. Snap a BOD Bottle Cap over the flared lip. Samples preserved like this can be held 4-8 hours. Begin with *step 6* when analyzing.

Accuracy Check

Check the strength of the Sodium Thiosulfate Solution by using an Iodate-Iodide Standard Solution which is equivalent to 10 mg/L dissolved oxygen. For the 300-mL procedure, begin at *step 5* adding the Sulfamic Acid Powder Pillow. For the 60-mg/L procedure, begin the analysis at *step 5* adding the Dissolved Oxygen 3 Powder Pillow. The titration should take 10 mL. If more than 10.5 mL is required to reach the end point, replace the Sodium Thiosulfate Solution.

Interferences

Nitrite interference is eliminated by the azide in the reagents. Other reducing or oxidizing substances may interfere. If these are present, use an alternate method, such as the High Range Dissolved Oxygen Method (colorimetric) in this manual, or a dissolved oxygen electrode.

Summary of Method

Samples are treated with manganous sulfate and alkaline iodide-azide reagent to form an orange-brown precipitate. Upon acidification of the sample, this floc reacts with iodide to produce free iodine as triiodide in proportion to the oxygen concentration. The iodine is titrated with sodium thiosulfate to a colorless end point.

REQUIRED REAGENTS FOR 300-ML BOD BOTTLE

(Varies with sample characteristics)

Dissolved Oxygen Reagent Set (about 50 tests) 22722-00
Includes: (1) 349-32, (2) 1071-68, (2) 1072-68, (1) 22675-01, (2) 20762-68

Description	**Unit**	**Cat. No.**
Alkaline Iodide-Azide Powder Pillows	25/pkg	1072-68
Manganous Sulfate Powder Pillows	25/pkg	1071-68
Sodium Thiosulfate Titration Cartridge, 0.2000 N	each	22675-01
Sodium Thiosulfate Titration Cartridge. 2.00 N	each	14401-01
Starch Indicator Solution	100 mL MDB*	349-32
Sulfamic Acid Powder Pillows	25/pkg	20762-68

REQUIRED APPARATUS FOR 300-ML BOD BOTTLE

Bottle, with stopper, BOD, 300-mL	each	621-00
Clippers, for opening pillows	each	968-00
Cylinder, graduated, 250-mL	each	508-46
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46

REQUIRED REAGENTS FOR 60-ML BOD BOTTLE

Description	**Unit**	**Cat. No.**
Dissolved Oxygen 1 Reagent Powder Pillows	100/pkg	981-99
Dissolved Oxygen 2 Reagent Powder Pillows	100/pkg	982-99
Dissolved Oxygen 3 Reagent Powder Pillows	25/pkg	987-68
Sodium Thiosulfate Titration Cartridge, 0.2000 N	each	22675-01

REQUIRED APPARATUS FOR 60-ML BOD BOTTLE

Bottle, with stopper, BOD, 60-mL	each	1909-02
Clippers, for opening pillows	each	968-00
Cylinder, graduated, 50-mL	each	1081-41
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43

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* Contact Hach for larger sizes.

OPTIONAL REAGENTS

Iodate-Iodide Standard Solution, 10 mg/L as DO	500 mL*	401-49

OPTIONAL APPARATUS

Cap, BOD Bottle, plastic	6/pkg	2419-06
Clamp Holder	each	326-00
Clamp, 2-prong, extension, 38 mm	each	21145-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Sewage Sampler, Lab-Line	each	427-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

Procedures and kits for portable dissolved oxygen measurements using this method are available from Hach.

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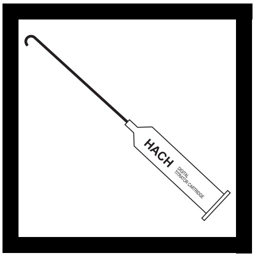
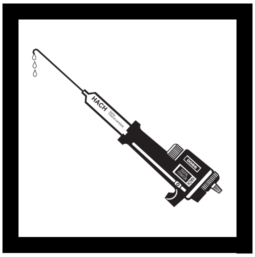
* Contact Hach for larger sizes.

SALINITY (0 to 100 ppt* as Salinity)

Using Mercuric Nitrate

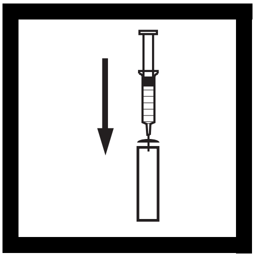


1. Insert a clean, straight-stem delivery tube to a Mercuric Nitrate Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.

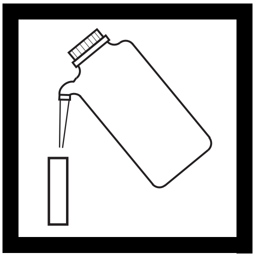


2. Flush out the delivery tube by turning the knob until titrant begins flowing from the end of the tube. Wipe the tip and reset the counter to zero.

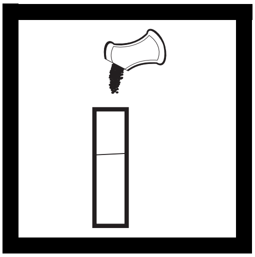
***Note:** For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

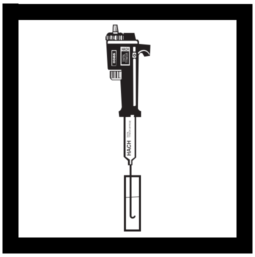


3. Using the 3-mL (3-cc) syringe, collect a 2.0-mL water sample. Add to the vial provided.



4. Fill the vial to the 10-mL mark with deionized water.





Digits Required x **0.1**

= ppt Salinity

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* ppt = parts per thousand

5. Add the contents of one Diphenylcarbazone Reagent Powder Pillow to the vial and mix.

***Note:** Results will not be affected if a small portion of the diphenylcarbazone reagent powder does not dissolve.*

6. Titrate the sample with mercuric nitrate until the color changes from yellow to light pink.

Record the number of digits.

7. Determine the salinity of the water sample in parts per thousand (ppt) by multiplying the reading by 0.1.

***Note:** Results may be expressed as mg/L Cl^- by multiplying the ppt salinity by 569. Results may be expressed as mg/L NaCl by multiplying the ppt salinity by 940.*

Summary of Method

The mercuric nitrate method of chloride analysis has become popular due to the sharp yellow to pinkish-purple end point of diphenylcarbazone. A single, stable powder has been developed, combining the color indicator with an appropriate buffer to establish the correct pH.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Diphenylcarbazone Reagent Powder Pillows	100/pkg	967-99
Mercuric Nitrate Titration Cartridge, 2.570 N	each	23937-01

REQUIRED APPARATUS

Vial, 2, 5, 10, 15, 20, 25-mL marks	each	2193-00
Syringe, 3 cc, Luer lock tip	each	43213-00
Demineralizer Assembly, 473 mL	each	21846-00

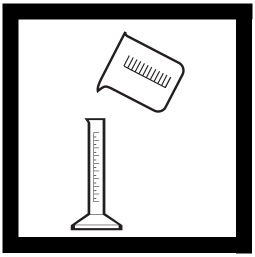
OPTIONAL APPARATUS

TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

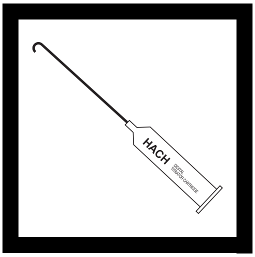
Method 8216

SULFITE (4 to greater than 400 mg/L as SO_3^{2-})

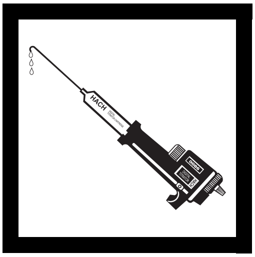
Using Iodate-Iodide



1. Select a sample volume corresponding to the expected sulfite (SO_3^{2-}) concentration from *Table 1*.

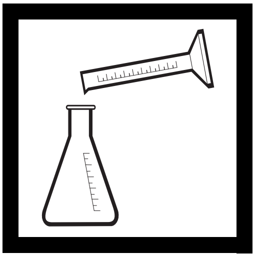


2. Insert a clean delivery tube into the Iodate-Iodide Titration Cartridge (KIO_3-KI). Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

***Note:** For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 125-mL Erlenmeyer flask. Dilute to about the 50-mL mark with deionized water.

***Note:** Avoid unnecessary agitation throughout the procedure.*

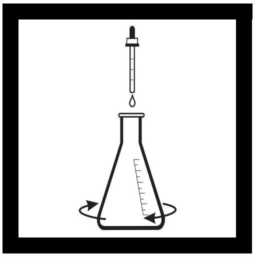
***Note:** See Sampling and Storage on page 178.*

Table 1

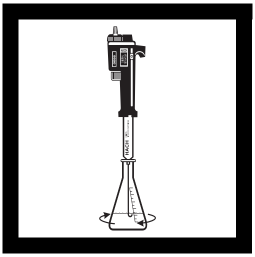
Range (mg/L as SO_3^{2-})	Sample Volume (mL)	Titration Cartridge (N KIO_3-KI)	Catalog Number	Digit Multiplier
Up to 160	50	0.3998	14961-01	0.4
100-400	20	0.3998	14961-01	1.0
200-800	10	0.3998	14961-01	2.0
>400	5	0.3998	14961-01	4.0

5. Add the contents of one Dissolved Oxygen 3 Reagent Powder Pillow and swirl gently to mix.

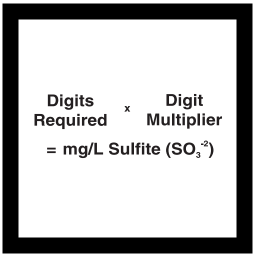
Note: *0.5 mL of 19.2 N Sulfuric Acid Standard Solution may be substituted for the powder pillow.*



6. Add one dropperful of Starch Indicator Solution and swirl to mix.



7. Place the delivery tube tip into the solution and swirl the flask while titrating with the iodate-iodide to a permanent blue end point. Record the number of digits required.



8. Calculate:

Digits Required x Digit Multiplier = mg/L Sulfite (SO_3^{2-})

Note: *To obtain the concentration of other sulfite forms, multiply the mg/L SO_3^{2-} determined in step 8 by the appropriate multiplier from Table 2.*

Table 2

Form	Multiplier
Bisulfite, Hydrogen Sulfite (HSO_3^-)	1.01
Sodium Bisulfite, Sodium Hydrogen Sulfite ($NaHSO_3$)	1.30
Sodium Metabisulfite, Sodium Pyrosulfite ($Na_2S_2O_5$)	1.19
Sodium Sulfite (Na_2SO_3)	1.58

Sampling and Storage

Samples must be analyzed immediately. Cool hot samples to 50 °C or lower.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Sulfite Standard Solution Voluette® Ampule, 5,000 mg/L SO_3^{2-}.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 and 0.3 mL, titrating to the end point after each.
4. Each 0.1 mL addition of standard should require 25 additional digits of titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

A standard solution equivalent to 40 mg/L sulfite can be prepared by diluting 10.0 mL of 0.025 N Sodium Thiosulfate Titrant to 250 mL in a volumetric flask. Titrate a 50 mL sample, using the above procedure.

Interferences

Sulfide, organic matter and other oxidizable substances will cause positive error in the titration. Nitrite will react with sulfite to cause low results. Some metals, especially copper, catalyze the oxidation of sulfite to sulfate. Addition of one Dissolved Oxygen 3 Powder Pillow per liter of sample immediately upon sampling will help eliminate the effects of nitrite and copper.

Summary of Method

Sulfite ion is titrated with potassium iodate-iodide standard solution under acidic conditions to a blue starch end point. The volume of titrant used is proportional to the sulfite concentration.

REQUIRED REAGENTS

Sulfite Reagent Set (about 100 tests)..22723-00
Includes: (1) 349-32, (1) 987-99, (1) 14961-01

Description	Unit	Cat. No.
Dissolved Oxygen 3 Reagent Powder Pillows	100/pkg	987-99
Iodate-Iodide Titration Cartridge, 0.3998 N	each	14961-01
Starch Indicator Solution	100 mL MDB*	349-32

Water, deionized	4 L	272-56

REQUIRED APPARATUS

Description	Unit	Cat. No.
Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Select one or more based on sample concentration:		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41

OPTIONAL REAGENTS

Sodium Thiosulfate Standard Solution, 0.025 N	1000 mL	24093-53
Sulfite Standard Solution, Voluette® Ampules, 5,000 mg/L SO_3 10 mL	16/pkg	14267-10
Sulfuric Acid Standard Solution, 19.2 N	100 mL MDB	2038-32

OPTIONAL APPARATUS

Bottle, wash poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Flask, volumetric, Class B, 250 mL	each	547-46
Pipet, TenSette® 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5 mL	each	14515-37
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 20 mL	each	14515-20
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pipet Filler, safety bulb	each	14651-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

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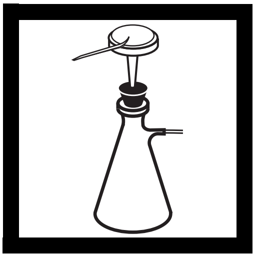
* Contact Hach for larger sizes.

TURBIDITY STANDARDS

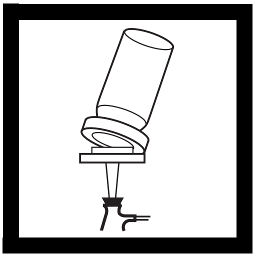
Preparing Turbidity-Free Water

Phase 1: Filtration Assembly

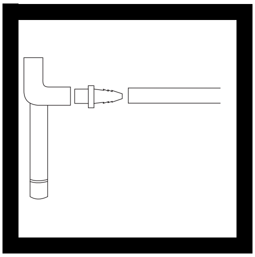
1. Attach the filter funnel stem to a 1000-mL filtering flask.



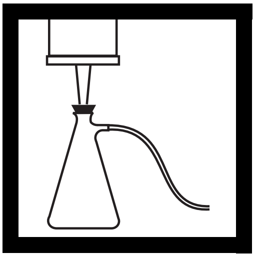
2. Using plastic tweezers, position a 0.45 micron membrane filter on top of the funnel stem.



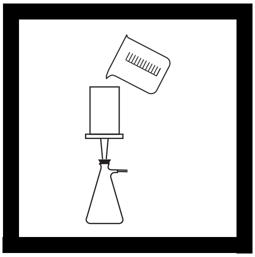
3. Cover the stem with the filter housing.



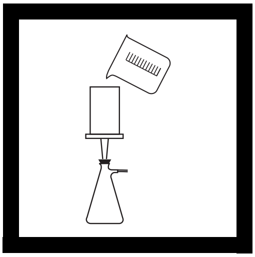
4. Attach a vacuum hose to the water aspirator and turn on water.



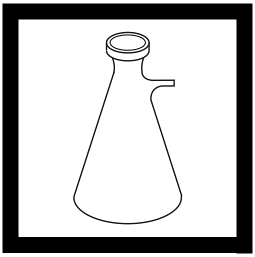
5. Attach the vacuum hose to the sidearm.



6. Pour a total of about 800 mL, in three portions, of deionized water through the filter funnel and wait until it passes through the filter. Discard this rinse water.



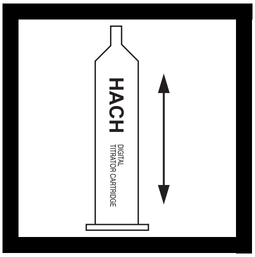
7. Again add 800 mL of deionized water through the filter funnel and collect in a filter flask. Remove vacuum hose from sidearm and turn off water.



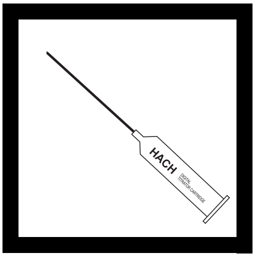
8. Use this filtered deionized water for all formazin dilutions.

TURBIDITY STANDARDS, continued

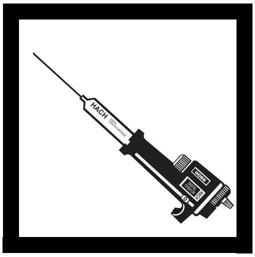
Phase 2: Preparing Standards using a Formazin Cartridge



1. Shake the Formazin Cartridge vigorously for one minute to mix the formazin suspension.



2. Attach a clean delivery tube to the 4000 NTU Formazin Cartridge. Cut the hooked end off the delivery tube with clippers. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



3. Flush the delivery tube by turning the delivery knob until a few drops of formazin are ejected from the tube. Zero the counter and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

See Table 1

4. Select the standard concentration from the list below. Dispense the formazin into a clean Class A volumetric flask. Dilute with turbidity-free water to the mark and mix well. Refer to the table below for the standard(s) you require.

Table 1

Formazin Standard Concentration (NTU)	Number of Digits Required	Flask Size
100	1000	50-mL
40	400	50-mL
10	100	50-mL
4	80	100-mL

Prepararation of a 1 NTU Formazin Standard

There will be a residual amount of turbidity in even the purest water used to make formazin dilutions. At the 1 NTU level this can affect the value of the formazin standard significantly, causing a positive error. The following procedure corrects for the turbidity of the dilution water when making a 1 NTU formazin standard in a 500-mL, Class A, volumetric flask.

1. Standardize the turbidimeter with a secondary standard on a range appropriate for the measurement of the dilution water, usually the 0-1 NTU range.

2. Measure and record the turbidity of the dilution water to be used in making the 1 NTU formazin standard.

3. Calculate the number of digits necessary to dispense the proper amount of formazin into a 500-mL, Class A, volumetric flask for a 1 NTU formazin standard:

   $$\text{DIGITS} = 100(1 - T_W)$$

   Where:

   T_W is the turbidity of the dilution water

4. Carefully dispense the calculated number of digits into a 500-mL volumetric flask. Dilute with dilution water to the 500-mL mark and mix well.

Preparation of any Formazin Standard

The following formula may be used to determine the correct number of digits necessary to dispense formazin for a standard of any value.

$$\text{DIGITS} = (0.2)(V)(T_D - T_W)$$

Where:

T_D = desired turbidity of the formazin standard

T_W = turbidity of the dilution water (this term may be dropped if it is 1% or less of the TD value)

V = volume of the flask in mL

Example 1:
One liter of a 0.5 NTU formazin standard is required. It is found that the dilution water has a turbidity of 0.05 NTU. Because the dilution water turbidity is 10% of the desired standard, the dilution water correction must be made.

The number of digits of formazin is equal to:

DIGITS = (0.2) (1000.0) (0.5-0.05) = 90

Thus, 90 digits of formazin dispensed in a 1000 mL, Class A, volumetric flask and diluted to volume with 0.05 NTU water will give a 0.5 NTU formazin standard. The size of the volumetric flask should be chosen so that the number of digits calculated is approximately 100 or more.

Example 2:
50 mL of a 50 NTU formazin standard is required. It is found that the dilution water is 0.1 NTU. Because the dilution water is only 0.2% of the desired standard, the dilution water correction can be ignored.

The number of digits necessary to dispense the formazin is:

DIGITS = (0.2) (50.0) (50) = 500

500 digits of formazin diluted with 50.0 mL of dilution water will give a 50 NTU formazin standard.

Interferences

Because dirty or scratched glassware, air bubbles and color in a sample will interfere with turbidity measurements, sample cells must be scratch-free and samples should be colorless without air bubbles.

Summary of Method

The measurement of turbidity is based on the scattering of light by the suspended particles (clay, sand, bacteria) in solution. The amount of light scattered at 90° to the incident light is directly proportional to the turbidity.

Turbidity is measured in nephelometric turbidity units (NTUs). These units of measurement are based on the amount of light scattered by particles of a polymer reference standard called formazin. Formazin, a mixture of hydrazine sulfate and hexamethylenetetramine, produces particles which scatter light in a reproducible manner.

The Hach 4000 NTU Formazin Cartridge, when used with the Hach Digital Titrator, offers a quick, yet accurate method for the preparation of formazin standards used in turbidimeter calibration.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Formazin Titration Cartridge, 4000 NTU	each	2461-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Filter Holder, 47 mm, magnetic base	each	13529-00
Aspirator, vacuum pump, poly	each	2131-00
Filters, membrane, 0.45 microns	100/pkg	13530-00
Flask, filtering, 1000 mL	each	546-53
Flask, volumetric, Class A, 50 mL	each	14574-41
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 500 mL	each	14574-49
Stopper, rubber, No. 7, one hole	6/pkg	2119-07
Tubing, rubber, 2.4 mm ID	12 ft	560-19
Tweezers, plastic	each	14282-00

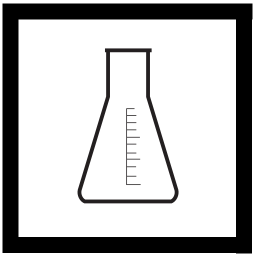
OPTIONAL APPARATUS

Bottle, wash poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

Method 8218

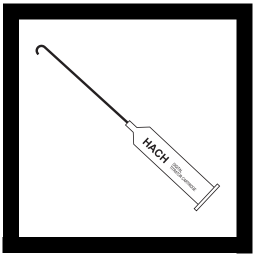
VOLATILE ACIDS

Using Sodium Hydroxide

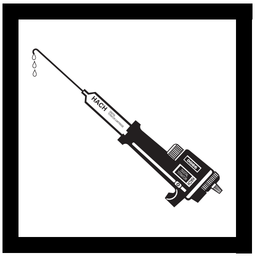


1. Distill the sample and collect 150 mL of distillate.

Note: *Use the Volatile Acids Procedure, Sample Distillation, accompanying the General Purpose Distillation Apparatus Set or the distillation procedure described in Standard Methods for the Examination of Water and Wastewater.*

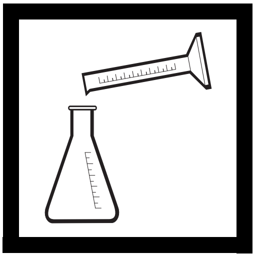


2. Attach a clean delivery tube to a 0.9274 N Sodium Hydroxide titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



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

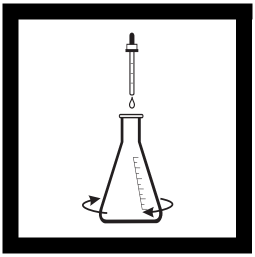
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



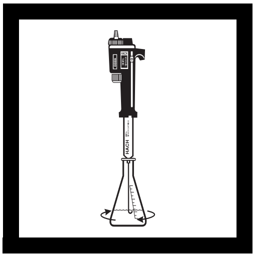
4. Select the distillate volume corresponding to the expected volatile acids concentration as acetic acid from *Table 1*. Using a graduated cylinder, transfer the distillate volume into a clean 250-mL Erlenmeyer flask and dilute to about the 150-mL mark with deionized water.

Table 1

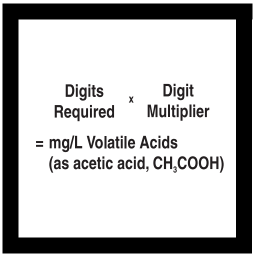
Range (mg/L as CH_3COOH)	Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
100-400	150	0.9274	14842-01	1
200-800	75	0.9274	14842-01	2
600-2400	25	0.9274	14842-01	6



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.



6. Place the delivery tube tip into the solution and swirl while titrating with sodium hydroxide until a light pink color appears. Record the number of digits required.



Digits Required x Digit Multiplier

= mg/L Volatile Acids (as acetic acid, CH_3COOH)

7. Calculate:

Digits Required x Digits Multiplier = mg/L Volatile Acids (as acetic acid, CH_3COOH)

***Note:** Approximately 70% of the volatile acids in the sample will be found in the distillate. This has been accounted for in the calculation.*

Summary of Method

A sample acidified with sulfuric acid is distilled and the distillate titrated to the phenolphthalein end point with sodium hydroxide standard.

REQUIRED REAGENTS

Volatile Acids Reagent Set (about 100 tests) 24602-00
Includes: (1) 942-99, (1) 14842-01

Description	Unit	Cat. No.
Phenolphthalein Indicator Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.9274 N	each	14842-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 250 mL	each	508-46
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46

OPTIONAL APPARATUS

Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Distillation Heater and Support Apparatus, 115 Vac	each	22744-00
Distillation Heater and Support Apparatus, 230 Vac	each	22744-02
Distillation Apparatus Set	each	22653-00
Standard Methods for the Examination of Water and Wastewater, 19th ed.	each	22708-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

APPENDIX A
ACCURACY CHECK AND STANDARD ADDITIONS

Most of the procedures in this manual have an accuracy check based on the standard additions method. Standard additions is a widely accepted technique for checking the validity of test results. Also known as “spiking” and “known additions,” the technique adds a small amount of the component (parameter) being measured to an analyzed sample and the analysis is repeated. The increase in the test results should equal the amount of the standard added. The results can be used to check the performance of the reagents, the apparatus, and the procedure.

First Step - The Accuracy Check

Perform the procedure and accuracy check as described in this manual. In each accuracy check the number of digits expected for each increment is given. If the actual number of digits required is within 1% of the expected number of digits, the analyst can conclude the answer for the sample is accurate and the reagents, apparatus, and method used are working properly.

Second Step - The Decision Tree

If the actual number of digits varies noticeably, then it must be concluded the problem was caused by either the reagents, the apparatus, the procedure or an interfering substance. By following a logical troubleshooting approach, the source of the problem can be systematically determined. Using the step-by-step decision tree in *Figure 1* will greatly ease identifying the problem. An explanation of each step in the decision tree follows.

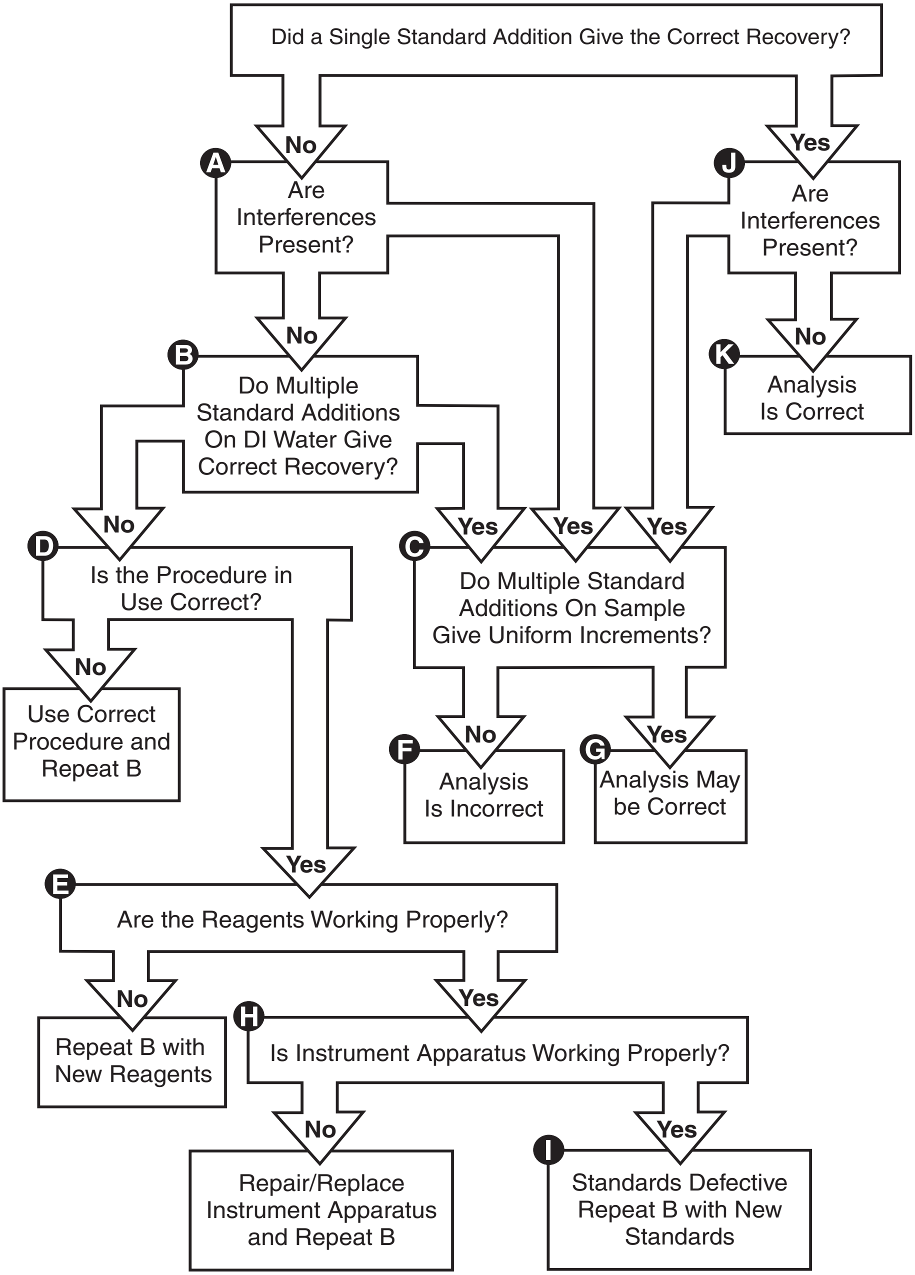
Third Step - The Branches

Branch A

Suppose the first, or all three standard additions to the sample did not give the correct incremental digit increase. A possible cause for this could be the presence of interferences. Other causes could be defective reagents, an incorrect procedure, defective apparatus or a defective standard used for standard addition. If interferences are

APPENDIX A, continued

Figure 1
Decision Tree



either absent or assumed to be absent, proceed to Branch B. If interferences are present, proceed to Branch C. The Chloride Procedure, Silver Nitrate Method, is used as an example throughout these steps.

Branch B

Repeat the Accuracy Check given in the procedure substituting the same volume of deionized water for the sample. For example, using the Chloride Procedure, Silver Nitrate Method:

1. Take a 50.0-mL sample of deionized water and follow the Chloride Procedure, Silver Nitrate Method. Record the number of digits required for the titration.
2. Add 0.10 mL of Chloride Standard Solution, 12,500 mg/L, and titrate to the end point. Record the number of digits required for the titration.
3. Repeat, using two more additions of 0.1 mL of 12,500 chloride standard, titrating to the end point after each addition. Record the number of digits required.
4. Tabulate the date as shown below:

Table 1

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	______	0	______
0.1	______	______	______
0.2	______	______	______
0.3	______	______	______

The **Total Standard Added (mL)** will vary depending on the procedure used.

The **Total Number of Digits Used** are the total digits recorded after each titration.

The **Total Standard Added (mg/L)** is determined for each addition by the following equation:

$$\frac{\text{Total Standard Added (mL)}}{\text{Sample Volume (mL)}} \times \text{Standard Concentration (mg/L)}$$

$$= \text{Total Standard Added (mg/L)}$$

The **Total Parameter Found (mg/L)** is determined by following the calculation step of the procedure used. Use the same volume of deionized water as used for the sample. The addition of standard will not change the digit multiplier.

Performing the above procedure, the completed table would look like this:

Table 2

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	0	0	0
0.1	25	25	25
0.2	50	50	50
0.3	75	75	75

To complete the table the following calculations were made based on the above formula:

First Addition

$$\frac{0.1}{50} \times 12{,}500 = \text{Total Standard Added (mg/L)} = 25 \text{ mg/L}$$

Second Addition

$$0.1 + 0.1 = 0.2 \text{ mL} = \text{Total Standard Added (mL)}$$

0.2 mL in the above formula gives 50 mg/L total standard added.

Third Addition

$$0.1 + 0.1 + 0.1 = 0.3 \text{ mL} = \text{Total Standard Added (mL)}$$

0.3 mL in the above formula gives 75 mg/L total standard added.

The data shown above reveals several points:

- The chemicals, apparatus, procedures and standards are in good working condition. This conclusion is made because chloride added to the deionized water sample was recovered entirely in the same uniform steps of addition.

- Because chloride added to deionized water was recovered, but was not recovered during the Accuracy Check, one may conclude the sample contains interferences which prevent the test reagents from operating properly.
- The first analysis of the water sample gave an incorrect result.

If the above results gave the expected increments between additions, proceed to Branch C. If the results did not give the expected increments, proceed to Branch D.

Branch C

If interfering ions are present, it may be concluded the analysis is incorrect. However, with the completed accuracy check it may be possible to arrive at an approximation of the correct result. Tabulate the results as follows:

Table 3

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	______	0	______
______	______	______	______
______	______	______	______
______	______	______	______

The **Total Standard Added (mL)** will vary depending on the procedure used.

The **Total Number of Digits Used** are the total digits recorded after each addition of standard as specified in the accuracy check.

The **Total Standard Added (mg/L)** is determined for each addition by the following equation:

$$\frac{\text{Total Standard Added (mL)}}{\text{Sample Volume (mL)}} \times \text{Standard Concentration (mg/L)} = \text{Total Standard Added (mg/L)}$$

The **Total Parameter Found (mg/L)** is determined by following the calculation step of the procedure used. Use the same volume of deionized water as used for the sample. The addition of standard will not change the digit multiplier.

If steps between each addition are roughly uniform (i.e., 25 digits or 25 mg/L difference between each addition), proceed to Branch G. If the results are not uniform (i.e., 13, 10, and 6 mg/L), proceed to Branch F.

For example, a sample of water was analyzed for chloride with the result being 100 mg/L. The analyst, suspecting interferences, made one standard addition of 0.10 mL of 12,500-mg/L chloride standard to 50.0 mL of sample. Rather than an increase of 25 mg/L as expected, the analyst found an increase of 13 mg/L.

The analyst added a second and third addition of 0.1 mL of standard. The titrations were made and the results tabulated. The increments were 10 (123 minus 113) and 6 (129 minus 123) mg/L, respectively. The analyst proceeded to Branch F.

Table 4

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L
0	100	0	100
0.1	113	25	113
0.2	123	50	123
0.3	129	75	129

To complete the table the following calculations were made based on the above formula:

First Addition

$$\frac{0.1}{50} \times 12{,}500 = \text{Total Standard Added (mg/L)} = 25 \text{ mg/L}$$

Second Addition

$$0.1 + 0.1 = 0.2 \text{ mL} = \text{Total Standard Added (mL)}$$

0.2 mL in the above formula gives 50 mg/L Total Standard Added.

Third Addition

0.1 + 0.1 + 0.1 = 0.3 mL = Total Standard Added (mL)

0.3 mL in the above formula gives 75 mg/L Total Standard Added.

Branch D

Carefully check the instructions or directions for use of the procedure, making sure the proper techniques, reagents, titrant, sample volume, and digit multiplier were used. Verify there is no air or liquid, other than the titrant being used, in the delivery tube by ejecting several drops of solution. If the procedure in use is found to be in error, repeat Branch B using the correct procedure. If the procedure is found to be correct, proceed to Branch E.

Branch E

Check the performance of the reagents. This may be done easily by using a known standard solution to run the test or by obtaining a new fresh lot of the reagent. A list of known standard solutions is given in *Table 1* on page *21*. If it is determined reagents are defective, repeat Branch B with new reagents. If the reagents are proven in good condition, proceed with Branch H.

Branch F

Examples of non-uniform increments between standard additions on a sample are shown below in *Table 5*, *Table 6* and *Figure 2* on page 201. These plots illustrate the effect of interferences upon the standard addition and upon substances in the sample. The plots were made by graphing the Total Standard Added (mg/L) on the X axis and the Total Parameter Found (mg/L) on the Y axis as shown in *Figure 2* on page 201.

Table 5 Plot A

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	100	0	100
0.1	113	25	113
0.2	123	50	123
0.3	129	75	129

Table 6 Plot B

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	0	0	0
0.1	25	25	0
0.2	50	50	25
0.3	75	75	50

Both of these plots show that the four data points do not lie on a straight line. Plot A illustrates an interference which becomes progressively worse as the concentration of the standard increases. This type of interference is not common and may be caused by an error or malfunction of the procedure, reagents or apparatus. Perform Branch B to ensure that the supposed interference is present.

Plot B illustrates a common chemical interference which becomes less or even zero as the concentration of the standard increases. The plot shows the first standard addition was consumed by the interference and the remaining additions gave the correct increase of 25 mg/L for each additional 0.1 mL of standard added. The apparent interference in Plot B could be the result of an error made in the standard addition, and the analysis should be repeated with a fresh portion of sample.

The two examples illustrate chemical interferences which most certainly mean the result of the first analysis of the water sample was incorrect. When this type of interference is encountered, review the Interference section for the procedure for corrective steps. If this fails, the analyst should attempt to analyze the sample with an alternate method which, if possible, uses a different type of chemistry.

Branch G

Examples of uniform increments between standard additions on a sample are shown below in *Table 7* and *Table 8* on page 200. These plots illustrate the effect of interferences upon the standard addition and upon substances in the sample. The plots were made by graphing the Total Standard Added (mg/L) on the X axis and the Total Parameter Found (mg/L) on the Y axis as shown in *Figure 2* on page 201.

Table 7 Plot C

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	50	0	50
0.1	63	25	63
0.2	75	50	75
0.3	88	75	88

Plot C illustrates a common interference with a uniform effect upon the standard and the substances in the sample. The four data points form a straight line, but the titration increments between the additions is not correct. The straight line between the additions may be extrapolated back through the horizontal axis. The point of intersect of the line with the horizontal axis gives a more accurate estimate of the concentration of the substance in question for the sample. In the example, the first analysis of the sample gave 50 mg/L. The result located graphically (100 mg/L) using the accuracy check should be much closer to the correct result. Other interference effects may also be present, or interferences may not be consistent in all samples. Use of another method not subject to the interference, or elimination of the interference is preferred over extrapolation or use of the percent recovery calculation.

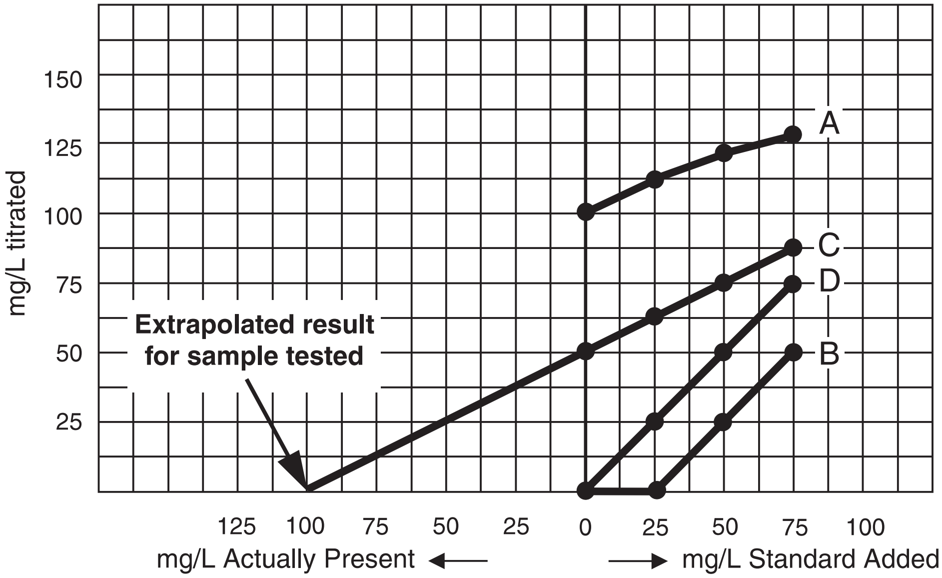
Apparent interferences also may be caused by errors in the method, a defect in the apparatus or standards. Before assuming the interference is chemical in nature, perform Branch B.

Table 8 Plot D

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	0	0	0
0.1	25	25	25
0.2	50	50	50
0.3	75	75	75

Plot D illustrates correct results but may hide a problem for the analyst. The increments found are uniform and the recovery of the standard was complete. The result of the first analysis was 0 mg/L and the plot graphs back through 0 mg/L. If interfering species are present, the interference may be sufficient to change the sample result but not sufficient to prevent the analyst from finding uniform increments and complete recovery of the additions. This would be an uncommon situation and results are probably correct unless unusual interferences are possible. Refer to the Interferences section in the specific procedure.

Figure 2
Multiple Standard Additions Graph



Branch H

Check operation of the apparatus used in the performance of the test. Verify the correct volumes of sample and standard were used. Check glassware used in the procedure, making sure that it is scrupulously cleaned. Dirty pipets and graduated cylinders are a source of contamination and will not deliver the correct volume. If a defect is found in the apparatus, repeat Branch B after repair or replacement of apparatus. If the apparatus is found to be in good working order, proceed with Branch I.

Branch I
After demonstrating that the procedure, reagents, and apparatus are correct and operating properly, the only possible cause for standard additions not functioning properly in deionized water is the standard used in performing the standard additions. Prepare or obtain a new set of standards and repeat Branch B.

Branch J

If the standard addition gave the correct result, the analyst must then determine if interfering substances are present. If interfering substances are not present, the result of the analysis prior to the standard addition is correct. If interfering substances are present, proceed to Branch C.

One of the greatest aids to the analyst is knowledge of the water sample's composition. An analyst need not know the exact composition of each sample but should be aware of potential interferences in the method of analysis to be used. When performing a particular method, the analyst should know if those interferences are present or not in order to have confidence in the accuracy of the results. Once the interferences are known, the Interference section of each procedure describes how to correct for many common interferences.

If the correct result is obtained with one standard addition when no interfering species are present, the chance of an error in sample results is very small. Possible sources of error not revealed include: sample quality, sample quantity (unless the sample and standard volume used is equal), and inconsistent end point determinations.

Call Hach Technical and Customer Support (1-800-227-4224) for additional help.

GENERAL INFORMATION

At Hach Company, customer service is an important part of every product we make.

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

REPLACEMENT PARTS AND ACCESSORIES

REPLACEMENT PARTS FOR MODEL 16900 DIGITAL TITRATOR

Description	Unit	Cat. No.
Digital Titrator including delivery tubes, manual, and case	each	16900-01
Delivery Tubes, 180° hook	5/pkg	17205-00
Case	each	46602-00
Digital Titrator Manual	each	16900-08

HOW TO ORDER

By Telephone:

6:30 a.m. to 5:00 p.m. MST
Monday through Friday
(800) 227-HACH
(800-227-4224)
By FAX: (970) 669-2932

By Mail:

Hach Company
P.O. Box 389
Loveland, CO 80539-0389
U.S.A.

Ordering information by E-mail: orders@hach.com

Information Required

- Hach account number (if available)
- Your name and phone number
- Purchase order number
- Brief description or model number
- Billing address
- Shipping address
- Catalog number
- Quantity

Technical and Customer Service (U.S.A. only)

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use. Specialists in analytical methods, they are happy to put their talents to work for you.
Call **1-800-227-4224** or E-mail **techhelp@hach.com**.

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In Canada, Latin America, Africa, Asia, Pacific Rim:
Telephone: (970) 669-3050; FAX: (970) 669-2932

In Europe, the Middle East, or Mediterranean Africa:
HACH Company, c/o
Dr. Bruno Lange GmbH
Willstätterstr. 11
D-40549 Düsseldorf

Germany
Telephone: +49/[0]211.52.88.0
Fax: +49/[0]211.52.88.231

REPAIR SERVICE

Authorization must be obtained from Hach Company before sending any items for repair. Please contact the HACH Service Center serving your location.

In the United States:
Hach Company
100 Dayton Avenue
Ames, Iowa 50010
(800) 227-4224 (U.S.A. only)
Telephone: (515) 232-2533
FAX: (515) 232-1276

In Canada:
Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
(800) 665-7635 (Canada only)
Telephone: (204) 632-5598
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