Cat. No. 45600-18

COD Reactor Model 45600
&
THM Reactor Model 49100
Instrument Manual

ap/dk 3/00 4ed

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SAFETY PRECAUTIONS

Please read this entire manual before unpacking, setting up, or operating this instrument. Pay particular attention to all danger and caution statements. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure the protection provided by this equipment is not impaired, do not use or install this equipment in any manner other than that which is specified in this manual.

Use of Hazard Information

If multiple hazards exist, this manual will use the signal word (Danger, Caution, Note) corresponding to the greatest hazard.

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

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

NOTE
Information that requires special emphasis.

Precautionary Labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.

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

⚠ ***1.2 Operation***

⚠ ***1.4 Line Voltage Selection***

⚠ ***1.5 Reactor Preparation, 150 ×C or 100 °C Mode***

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⚠ ***2.4 Block Removal and Installation (Cleaning the COD Reactor)***

⚠ COD Reactor Operation

This instrument is used to incubate glass vials containing small quantities of hazardous ingredients at high temperature. Read and comply with the precautionary labels on the instrument and read the Material Safety Data Sheets (MSDS) supplied with the reagent vials. Refer to *SECTION 1 OPERATION*.

⚠ THM Reactor Operation

This instrument is used to incubate glass vials at high temperature. Read and comply with the precautionary labels on the instrument and read the Material Safety Data Sheets (MSDS) supplied with the reagent vials. Refer to *SECTION 1 OPERATION*.

Handling Reagent Vials

Use care when handling the vials and wear protective clothing. Refer to *SECTION 1 OPERATION*. After completion of the testing, dispose of used vials in accordance with all federal, state and local regulations. Use only Hach prepared COD reagent vials in the Model 45600 COD Reactor.

Safety Equipment

Use protective clothing when operating the Reactor, including goggles or face mask, and gloves. Refer to *SECTION 1 OPERATION*. Use of the optional safety shield is strongly recommended for use with the COD or THM Reactor.

Reagent Spills

Clean up spilled reagents immediately. Refer to *Section 1.7* on page *17*. If reagent contacts skin, rinse the affected area thoroughly with water. Avoid breathing released vapors. Read the Material Safety Data Sheets (MSDS) supplied with each reagent for complete chemical information.

Fire Hazard

Avoid the presence of flammable liquids near the operating Reactor. A fire hazard could be created.

⚠ Power Cord

A power cord suitable for U.S. and Canadian 115 V ac line voltage is supplied with the Model 45600 COD Reactor and Model 49100 THM Reactor. If either model is to be configured for 230 V ac, an approved UL/CSA power cord with NEMA 6-15P type cord cap must be used in place of the 115 V ac power cord supplied.

The Model 45600-02 COD Reactor and Model 49100-02 THM Reactor are factory configured for European 230 V ac line voltage. The power cord supplied with this model has a Continental European type plug and is listed by VDE for 250 V ac line voltage.

Line Voltage Selection

Verify proper line voltage select switch position and appropriate fuse rating. Refer to *Section 1.4* on page *15*.

Fuse Replacement

Use fuses with the specified current and voltage ratings. Refer to *Section 2.3* on page *20*.

SPECIFICATIONS

Specifications subject to change without notice.

Ambient Operating Temperature: +10 to +45 °C

Storage Temperature: –40 to +60 °C

Temperature Stability: ±0.5 °C (100 to 150 °C)

Capacity (COD): 25 16 × 100-mm vials, one thermometer. Optional accessory block available with capacity for twenty-one 16-mm and four 22-mm tubes, and one thermometer.

Capacity (THM): 10 1-inch vials, one thermometer

COD Accuracy (150 °C mode): ±2 °C @ 25 °C ambient

THM Accuracy (100 °C mode): ±2 °C @ 25 °C ambient

Range Adjustment (COD):100 to 155 °C adjustment minimum

Range Adjustment (THM):50 to 105 °C adjustment minimum

Timer: 0 to 120 minutes with audible alarm and automatic shutoff mode

Block: Removable, black anodized aluminum, 11.4 cm square × 6.3 cm high

Thermometer: 1-inch dial type, 0 to 200 °C, 1% accuracy, can be recalibrated, 2 °C divisions

Power Requirements: Selectable 115 V ac/230 V ac, ±8.5%, 50/60 Hz, 2.4/1.2 Amp ac, 220 W

Dimensions: 20.3 cm wide × 12 cm high × 30.5 cm deep

Weight: Net: 3.5 kg; Shipping: 4 kg

Warm-up Time: 30 to 40 minutes from +25 °C to +150 °C

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.

SECTION 1 OPERATION

1.1 General Description

1.1.1 COD Reactor

The Model 45600 COD Reactor (*Figure 1*) is a 25-well, dry-bath incubator that provides the 150 °C temperature environment required in Hach's test system for chemical oxygen demand (COD) determinations. In addition to the COD requirements, this model provides features for timed operation as well as temperature adjustment. In the COD digestion mode, the temperature switch is set in the 150 °C position and the temperature is maintained within ± 2 °C constantly. Heater block temperature can be verified by placing the thermometer supplied with the instrument in the temperature well provided in the block.

In the adjustable temperature mode (100 to 155 °C), the instrument can be used for digestion of other samples that require different digestion temperatures. A 2-hour timer is incorporated for applications where timed digestion is desired. When this feature is used, the bell will sound and the unit will shut off at the end of the selected time period. The timer also can be used without the shut-off feature when operating in the infinity mode.

1.1.2 THM Reactor

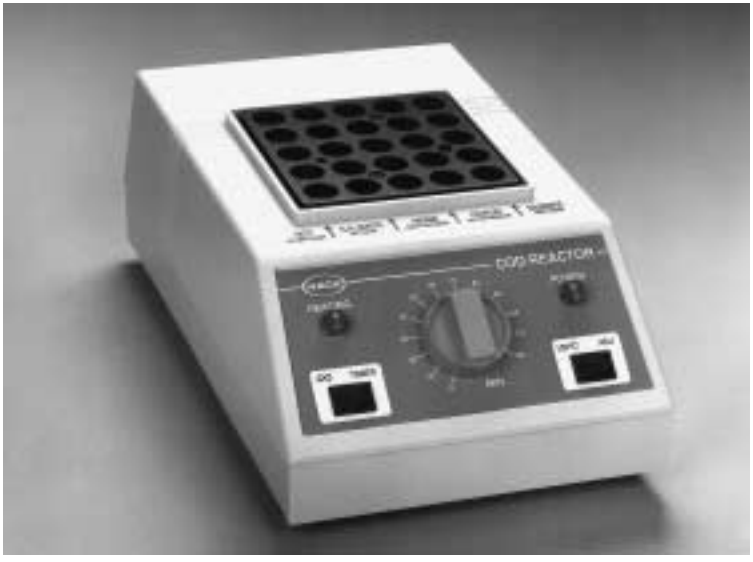
The Model 49100 THM Reactor is a 10-well, dry bath incubator that provides the 100 °C temperature environment required in Hach's test system for Trihalomethanes (THM) Plus™ determination. In addition to the THM requirements, this model provides features for timed operation and temperature adjustment. In the THM digestion mode, the temperature switch is set in the 100 ° position and the temperature is constantly maintained within ±2 °C. Verify the heater block temperature by placing the thermometer supplied with the instrument in the temperature well in the block.

1.1.3 Additional Features

The instrument can be switched to operate on either 115 or 230 V ac. Accessories supplied with the COD Reactor and THM Reactor include a dial gauge thermometer, power cord, the appropriate fuses, and instruction manual with quick reference card. Optional accessories offered are a safety shield and a special heater block with wells sized to hold twenty-one 16-mm tubes and four 22-mm tubes. Refer to *OPTIONAL ACCESSORIES* on page *27*.

The optional safety shield is 15-inch high, 3/16-inch thick polycarbonate attached to a heavy steel base. It is placed on the laboratory bench in front of the COD Reactor or THM Reactor to protect the operator from splattered reagent in the unlikely event that a reagent vial should break.

Figure 1 Model 45600 COD Reactor



1.2 ⚠ Operation

DANGER
This instrument is used to incubate test samples that may contain hazardous materials. Protective clothing, including gloves and goggles or face mask, should be worn. Any spills should be wiped up immediately and if skin is contacted, rinse the affected area thoroughly with water. Please read all Material Safety Data Sheets (MSDS) for complete chemical information.

GEFAHR
Dieses Gerät dient zur Inkubation von Testproben mit eventuell gefährlichen Stoffen. Sie sollten bei der Handhabung unbedingt Schutzkleidung, wie Handschuhe und Schutzbrille oder eine Gesichtmaske tragen. Verschüttetes Produkt ist unverzüglich aufzuwischen. Bei Kontakt mit der Haut muß die betroffene Stelle sofort gründlichst mit Wasser gespült werden. Bitte lesen Sie die kompletten chemischen Informationen und Daten aller Datenblätter mit den Material Sicherheitsanweisungen (IDDMS).

PELIGRO
Este instrumento se utiliza para incubar muestras de prueba que pueden contener materiales peligrosos. Por lo tanto, es necesario usar ropa de protección incluso guantes y antiparras o máscara facial. Los derrames deben limpiarse de inmediato y, en caso de contacto con la piel, lave la zona afectada con abundante agua. Para la información completa sobre los productos quimicos, lea todas las Hojas de Datos sobre Seguridad de Materiales (HDSM).

DANGER
Cet appareil sert à l'incubation d'échantillons contenant des matières dangereuses. Pour la manipulation, nous recommandons le port de vêtements de protection, de gants et de lunettes ou d'un masque. Si le produit est renversé, il doit être essuyé immédiatement. En cas de contact accidentel avec la peau, la zone concernée doit être abondamment rincée à l'eau. Priére de lire attentivement les fiches produits avec les données de sécurité (FPDS) contenant des informations chimiques complètes.

PERIGO
Este instrumento é usado para a incubação de espécimes de que podem conter. Roupa protetora, incluindo luvas e óculos de proteção ou protetor facial, deve ser usada. Qualquer material entornado deve ser imediatamente limpo e, no caso de contato com a pele, a área afetada dever ser bem lavada com água. Leia as Folhas de Informação de Segurança do Material (FISM) para obter os dados químicos completos.

1.3 Operating Controls and Indicators

(See Figure 2)

Power Indicator–lights when line power is turned on. If instrument is in the Timer Mode, there must be time showing on the Timer for the POWER indicator to be lit.

Temperature Mode Switch–selects constant 150 °C operation for the COD Reactor and 100 °C operation for the THM Reactor, **or** the adjustable temperature operating mode whereby an alternative temperature can be selected with the 100 to 155 °C ADJUST control on the back panel for the COD reactor or the 50 to 105 °C ADJUST control for the THM reactor.

Timer–used to select digestion time in minutes. Indicator knob shows digestion time remaining.

Timer Switch–used in conjunction with timer to operate the reactor in a timed digestion when set to TIMER position. The reactor will shut off at the end of the elapsed time. When the timer switch is in the Infinity position, the timer can be off or used as an audible alarm to track the digestion time. The heater block will remain at the selected temperature as long as the instrument power is on.

Heating Indicator–lights only when heater is operating. The heater cycles on and off while maintaining a stable temperature.

Power Entry Module–includes a power switch, power receptacle and line fuses.

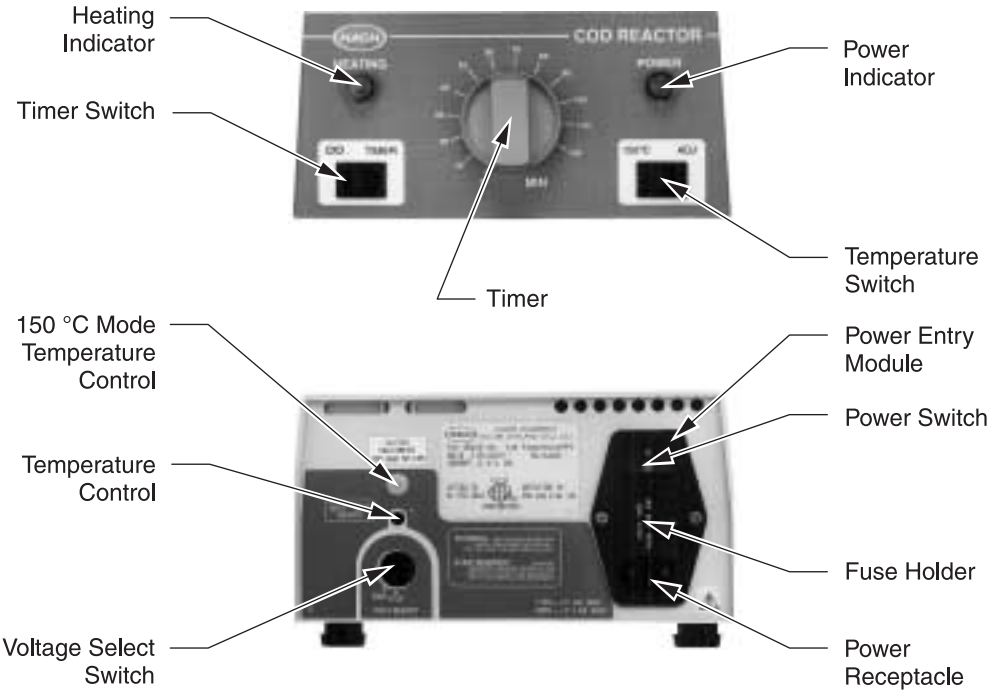
Voltage Select Switch–adapts instrument for 115-volt or 230-volt operation. Factory set for 115 V ac.

Temperature Control–used to select alternative incubation temperature when temperature switch is in the ADJ position. Clockwise rotation of the control increases the temperature. Temperature is adjustable between 100 and 155 °C for the COD Reactor and between 50 and 105 °C for the THM Reactor.

150 °C Mode Temperature Control (COD Reactor)–used in the 150 °C temperature mode to adjust the temperature setting to a constant 150 °C. Refer to *Section 2.1* on page *19.*

100 °C Mode Temperature Control (THM Reactor)–used in the 100 °C temperature mode to adjust the temperature setting to a constant 100 °C. Refer to *Section 2.2* on page *20.*

Figure 2 COD Reactor Controls, Indicators and Connectors



1.4 ⚠ Line Voltage Selection

Note: Misapplication of AC line power to this instrument can cause serious damage to the instrument. Prior to connection, verify that the Voltage Select Switch is set for the proper AC line requirement.

This instrument is factory set and properly fused for 115 V ac line requirements. To convert the instrument for 230 V ac line requirements, proceed as follows:

1. Disconnect power cord from power entry module receptacle.
2. Rotate the indicator slot on the Voltage Select Switch to the 230 position.

3. Remove the two 3-amp fuses and replace them with two 1.6-amp fuses. Refer to *Section 2.3* on page *20*.

4. Restore the power cord connection.

1.5 ⚠ Reactor Preparation, 150 °C or 100 °C Mode

Set the Power switch to **I** (on) and the Temperature switch to either 150 °C for the COD Reactor or 100 °C for the THM Reactor. Verify that the Timer switch is set to infinity. Allow a warm-up period of approximately 30 minutes. When the Heating Indicator begins to cycle on and off, the block temperature is stable. The proper temperature can be verified by placing a thermometer into the small well provided in the heater block.

The instrument is now ready for digesting samples. If the timer is to be used to turn the reactor off at the end of the digestion, set the timer switch to the **TIMER** position and rotate the timer knob clockwise to the desired digestion time.

1.6 ⚠ Reactor Preparation, Temperature Adjust Mode

1. Set the Power switch to **I** (on) and set the Temperature switch to **ADJ**. Verify that the timer switch is set to infinity.

2. Place a thermometer in the heater block thermometer well and allow the temperature reading to stabilize.

Note: *Use care when adjusting the temperature control. This control is a single-turn potentiometer and can be permanently damaged if too much torque is applied at the end of adjustment travel. At the first sign of resistance to rotation, stop applying torque. If over-adjustment does occur and the potentiometer is damaged, contact a Hach Service Center. Refer to REPAIR SERVICE on page 30.*

3. Using a non-conducting screwdriver or trimmer pot adjustment tool, turn the temperature adjust control slightly counterclockwise if the temperature must be lowered or clockwise if the temperature must be raised. Allow the thermometer reading to stabilize to determine if further adjustment is needed. Repeat this step until the thermometer reading stabilizes at the desired temperature. If the optional glass thermometer is used, remove the thermometer.

1.7 Operational Notes

- Do not place the COD Reactor or THM Reactor in a draft, in direct sunlight or near equipment that emits heat or cold. Temperature stability could be affected.
- Use of the optional safety shield is strongly recommended.
- Use of an optional glass thermometer is recommended only for checking the heater block temperature during instrument preparation. Because the thermometer is breakable, it is advisable to remove the thermometer during normal operation of the reactor.
- Use vial and tube sizes that match the heater block wells for best results.
- During operation, the temperature of the empty block will differ slightly from the temperature of the block full of vials. Also, loading the block with cold tubes will lower the block temperature several degrees and require a few minutes to recover as the tubes warm. If the temperature does not recover completely, the appropriate temperature control can be adjusted to compensate. See *Section 2.1 150 ℃ Temperature Adjustment* on page *19* or *Section 2.2 100 °C Temperature Adjustment* on page *20.*
- The dial thermometer supplied with the COD Reactor can be recalibrated by placing the stem into an ice-water bath, allowing it to come to equilibrium and adjusting the nut beneath the dial to obtain a reading of zero °C.

Note: *In the event of an accidental spill into the heater block, disconnect power to the instrument and allow it to cool. After the instrument has cooled, remove all reagent tubes and remove the heater block for cleaning. Refer to Section 2.4 Block Removal and Installation (Cleaning the COD Reactor) on page 22. If the spill was severe and not contained on or in the heater block, damage may have occurred to the instrument's electrical components. Contact the appropriate service center. Refer to REPAIR SERVICE on page 30.*

SECTION 2 MAINTENANCE

There are no scheduled maintenance requirements for this instrument. It should be kept clean, and reagent spills should be wiped up promptly. The temperature setting for the 150 °C mode or the 100 °C mode can be adjusted as described below if necessary. If your reactor does not perform properly, please contact a Hach Service Center for instructions. Refer to *REPAIR SERVICE* on page *30.*

2.1 150 °C Temperature Adjustment

The 150 °C temperature setting may need readjustment in time due to component aging. Best accuracy will be obtained if the setting is made while the block is full of vials. Proceed as follows:

1. Place COD Digestion Reagent Vials in all the tube wells and insert the thermometer into the temperature well.

2. Set the timer switch to infinity, the temperature mode switch to 150 °C and the power switch to **I** (on). Allow the block temperature to stabilize.

3. Observe the thermometer reading when the temperature has stabilized.

Note: *Use care when adjusting the temperature control. This control is a single-turn potentiometer and can be permanently damaged if too much torque is applied at the end of adjustment travel. At the first sign of resistance to rotation, stop applying torque. If over-adjustment does occur and the potentiometer is damaged, contact a Hach Service Center. Refer to REPAIR SERVICE on page 30.*

4. Remove the plug from the 150 °C Temperature Control opening. See *Figure 2* on page *15*. Using a non-conducting screwdriver or trimmer pot adjustment tool, slightly adjust the 150 °C control clockwise to increase the block temperature or counterclockwise to decrease it, allowing time for the temperature to stabilize between adjustments. Repeat as necessary until the thermometer reading stabilizes at the proper temperature. Replace the plug in the back panel opening.

2.2 100 °C Temperature Adjustment

The 100 °C temperature setting may need readjustment in time due to component aging. Best accuracy will be obtained if the setting is made while the block is full of vials. Proceed as follows:

1. Place THM Plus™ Reagent Vials in all the tube wells and insert the thermometer into the temperature well.

2. Set the Timer switch to infinity, the Temperature Mode switch to 100 °C and the Power switch to **I** (on). Allow the block temperature to stabilize.

3. Observe the thermometer reading when the temperature has stabilized.

Note: *Use care when adjusting the temperature control. This control is a single-turn potentiometer and can be permanently damaged if too much torque is applied at the end of adjustment travel. At the first sign of resistance to rotation, stop applying torque. If over-adjustment does occur and the potentiometer is damaged, contact a Hach Service Center. Refer to REPAIR SERVICE on page 30.*

4. Remove the plug from the 100 °C Temperature Control opening. See *Figure 2* on page *15*. Using a non-conducting screwdriver or trimmer pot adjustment tool, slightly adjust the 100 °C control clockwise to increase the block temperature or counterclockwise to decrease it, allowing time for the temperature to stabilize between adjustments. Repeat as necessary until the thermometer reading stabilizes at the proper temperature. Replace the plug in the back panel opening.

2.3 ⚠ Fuse Replacement

DANGER
For continued protection against fire, replace fuses only with fuses of specified type and current rating.

GEFAHR
Zur Wahrung des kontinuierlichen Brandschutzes dürfen die Sicherungen nur mit Sicherungen des gleichen Typs und mit gleichen Stromkennwerten verwendet werden.

PELIGRO
Para una continua protección contra incendios, reemplace los fusibles únicamente por los del tipo y capacidad recomendados.

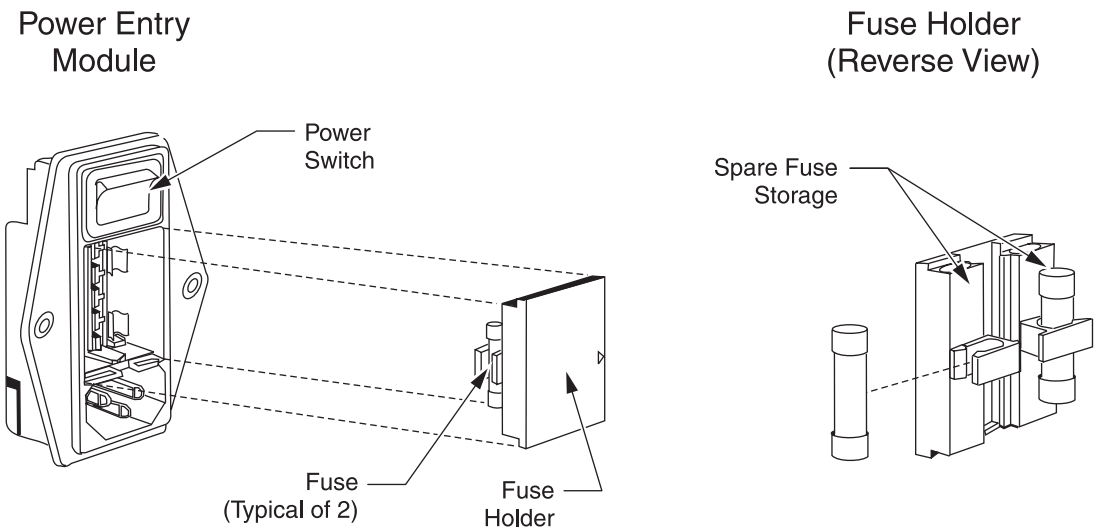
DANGER
Pour assurer la protection contre les incendies, remplacez les fusibles uniquement avec des fusibles du même type et pour la mème tension.

PERIGO
Para proteção continiua contra fogo, troque os fusíveis somente por fusíveis do tipo especificado para a força da corrente.

The fuse holder is located on the back panel within the power entry module. See *Figure 3*.

1. Disconnect the power cord from the instrument before removing the fuse holder.
2. Remove the fuse holder by inserting a small screwdriver or other pointed tool in the small opening and prying out the holder. Both sides of the power line are fused.
3. Replace the fuses with two 3A fuses for 115-volt operation or two 1.6A fuses for 230-volt operation. Refer to *REPLACEMENT PARTS* on page *27* for the proper fuse description and catalog number. Spare fuses can be stored in the two slide-out clips in the fuse holder.
4. Replace the holder and reconnect the power cord.

Figure 3 Fuse Replacement



2.4 ⚠ Block Removal and Installation (Cleaning the COD Reactor)

DANGER
Do not touch the heater block without hand protection unless you are certain it has cooled. A severe burn could result.

GEFAHR
Heitzeinheit nicht mit bloßen Händen berühren, wenn sie nicht mit Sicherheit ausgekühlt ist. Vorsicht: Sie riskieren schwere Verbrennungen.

PELIGRO
No toque el bloque calefactor con la mano desprotegida, a menos que esté seguro de que se haya enfriado. En caso contrario, pueden ocurrir quemaduras graves.

DANGER
Pour éviter les brûlures graves, ne jamais toucher le bloc chauffant sans protection aux mains à moins d'être sûr qu'il s'est refroidi.

PERIGRO
Não toque no bloco do aquecedor sem proteger a mão, a menos que esteja certo que ele já esfriou.

Place the removable heater block in the instrument with the same orientation each time to avoid confusion in test documentation. When viewed from the front of the instrument, readability of the well designations is best with the numbers running from left to right and the letters from front to back.

Before attempting to remove the block, turn the instrument off and allow the block to cool. Remove all the vials. Remove the block as follows:

1. The heater block is secured in place with two socket-head machine screws that are accessible from the top of the block. Using the hexagonal wrench supplied with the COD Block Replacement Kit, loosen and remove the two socket-head screws. The block will adhere to the heater plate beneath it because of the thermal compound applied on the bottom surface. Use side-to-side and/or front-to-back rocking motions to free the block and lift it from the instrument.

2. If there has been a reagent spill in one of the wells, rinse under a water tap to remove any residue. Remove the thermal compound from the bottom of the block and the heater plate. Use the applicator supplied with the COD Block Installation Kit to scrape the block and plate to remove the old

compound. Dampen a cloth with isopropyl alcohol and wipe the block and plate clean.

Note: *If the old thermal compound is not removed, poor thermal conductance can occur, resulting in slower block warm-up and response times.*

3. Prepare the block to be installed by applying a coat of thermal compound to the bottom surface. Use the compound and applicator supplied in the COD Block Replacement Kit. Use the saw-toothed edge of the applicator to apply a layer of uniform thickness that covers the bottom of the block completely.

4. Place the block into the instrument with the well numbers from left to right across the back and the well letters along the left side. Install the two socket-head screws and tighten with the hexagonal wrench.

5. Restore power to the instrument and install the thermometer in the small well. Check the temperature of the block when it becomes stable. If necessary, adjust the temperature setting as described in *Sections 2.1* and *2.2*. If the optional glass thermometer is used, remove the thermometer before use.

2.5 Cleaning the THM Reactor

Turn the instrument off, unplug the instrument, and allow the block to cool. Remove all the vials. Use a damp cloth to wipe the block clean.

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

REQUIRED APPARATUS

Description	Cat. No.
COD Block Replacement Kit	45649-00
Includes:	
Screw, 8x32 socket-head (2)	
Thermal Compound, 2-oz jar	
Thermal Compound Applicator	
Wrench, hexagonal, 9/64 inch	
Instruction Sheet	
COD Reactor Replacement Block Kit, 25 16-mm wells (includes COD Block Replacement Kit)	45609-01
Fuse, 3A, 250 V, Slow-Blo (T), for 115 Vac operation (UL, CSA approved) (2 needed) (supplied with 45600-00 instruments)	45640-00
Fuse, 1.6A, 250 V, Slow-Blo (T), for 230 Vac operation (UL, CSA approved) (2 needed) (supplied with 45600-02 instruments)	30307-00
Fuse, 1.6A, 250 V, Slow-Blo (T), for 230 Vac operation (IEC type, VDE approved) (2 needed) (supplied with 45600-02 instruments)	30306-00
Manual, Instruction	45600-18
Power Cord, UL, CSA approved for 115 Vac operation	18010-00
Power Cord, VDE approved for European 230 Vac operation	46836-00
Quick Reference Card	45600-44
Thermometer, dial gauge, 0 to 200 °C	45655-00

OPTIONAL ACCESSORIES

COD Accessory Block Kit, 21 16-mm wells and 4 22-mm wells, (includes COD Block Replacement Kit)	45717-01
Isopropyl Alcohol, tech. grade, 100 mL	12276-42
Gloves, Heat Resistant	21788-00
Safety Goggles	20972-00
Safety Shield	23810-00
Trimmer Pot Adjustment Tool	18933-00

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**.

International Customers

Hach maintains a worldwide network of dealers and distributors. To locate the representative nearest you, send E-mail to **intl@hach. com** or contact:

In Canada, Latin America, Africa, Asia, Pacific Rim:
HACH Company
P.O. Box 389, Loveland CO 80539-0389 U.S.A.
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:
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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
FAX: (204) 694-5134
E-mail: canada@hach.com

In Latin America, the Caribbean, the Far East, the Indian Subcontinent, Africa, Europe, or the Middle East:
Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, 80539-0389
U.S.A.
Telephone: (970) 669-3050
FAX: (970) 669-2932
E-mail: intl@hach.com

WARRANTY

Hach warrants most products against defective materials or workmanship for at least one year from the date of shipment; longer warranties may apply to some items.

HACH WARRANTS TO THE ORIGINAL BUYER THAT HACH PRODUCTS WILL CONFORM TO ANY EXPRESS WRITTEN WARRANTY GIVEN BY HACH TO THE BUYER. EXCEPT AS EXPRESSLY SET FORTH IN THE PRECEDING SENTENCE, HACH MAKES NO WARRANTY OF ANY KIND WHATSOEVER WITH RESPECT TO ANY PRODUCTS. HACH EXPRESSLY DISCLAIMS ANY WARRANTIES IMPLIED BY LAW, INCLUDING BUT NOT BINDING TO ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

LIMITATION OF REMEDIES: Hach shall, at its option, replace or repair nonconforming products or refund all amounts paid by the buyer. **THIS IS THE EXCLUSIVE REMEDY FOR ANY BREACH OF WARRANTY.**

LIMITATION OF DAMAGES: IN NO EVENT SHALL HACH BE LIABLE FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES OF ANY KIND FOR BREACH OF ANY WARRANTY, NEGLIGENCE, ON THE BASIS OF STRICT LIABILITY, OR OTHERWISE.

This warranty applies to Hach products purchased and delivered in the United States.

Catalog descriptions, pictures and specification, although accurate to the best of our knowledge, are not guarantee or warranty.

For a complete description of Hach Company’s warranty policy, request a copy of our Terms and Conditions of Sale for U.S. Sales from our Customer Service Department.

CERTIFICATION

Hach Company certifies this instrument was tested thoroughly, inspected and found to meet its published specifications when it was shipped from the factory.

The COD and THM Reactors have been tested and are certified as indicated to the following instrumentation standards:

Product Safety

UL 1262 (ETL Listing # H0492805390), 115V model, 45900-00

CSA C22.2 No. 1010.1 (ETLc Certification # H0492805390), 115V model, 45900-00

Certified by Hach to EN 61010-1 (IEC1010-1) per 73/23/EEC, supporting test records by Dash, Straus & Goodhue (now Intertek Testing Services), 230V model, 45900-02.

Immunity

EN 61326:1998 (EMC Requirements for Electrical Equipment for Measurement, Control and Laboratory Use) **per 89/336/EEC EMC**: Supporting test records by Hach Company, certified compliance by Hach Company.

Standards include:
IEC 1000-4-2:1995 (EN 61000-4-2:1995) Electrostatic Discharge Immunity (Criteria B)

IEC 1000-4-3:1995 (EN 61000-4-3:1996) Radiated RF Electromagnetic Field Immunity (Criteria A)

IEC 1000-4-4:1995 (EN 61000-4-4:1995) Electrical Fast Transients/Burst (Criteria B)

IEC 1000-4-5:1995 (EN 61000-4-5:1995) Surge (Criteria B)

IEC 1000-4-6:1996 (EN 61000-4-6:1996) Conducted Disturbances Induced by RF Fields (Criteria A)

IEC 1000-4-11:1994 (EN 61000-4-11:1994) Voltage Dip/Short Interruptions (Criteria B)

Additional immunity Standard/s include:
ENV 50204:1996 Radiated Electromagnetic Field from Digital Telephones (Criteria A)

Emissions

Per **89/336/EEC EMC: EN 61326:1998** (Electrical Equipment for measurement, control and laboratory use-EMC requirements): Supporting test records by Hach Co.

Required Standard/s include:
EN 55014 (CISPR 14) Emissions, Testing by ETL/Dash, Straus & Goodhue (now Intertek Testing Services) NVLAP # 0270,

EN 55022 (CISPR 22) Emissions, Class B Limits Testing by Hach Company

Additional Standard/s include:
EN 61000-3-2 (IEC 1000-3-2) Harmonic Disturbances Caused by Electrical Equipment

EN 61000-3-3 (IEC 1000-3-3) Voltage Fluctuation (Flicker) Disturbances Caused by Electrical Equipment

CANADIAN RADIO INTERFERENCE- REGULATION, 1374, Class A: Supporting test records by Hach Company and ETL/Dash, Straus & Goodhue (now Intertek Testing Services) NVLAP # 0270, certified compliance by Hach Company.

This Class A digital apparatus meets all requirements of the Canadian Interference- Causing Equipment Regulations.

Cet appareil numérique de la classe A respecte toutes les exigences du Règlement sur le matériel brouilleur du Canada.

FCC PART 15, Class "A" Limits: Supporting test records by Hach Company and Dash, Straus & Goodhue (now Intertek Testing Services) NVLAP # 0270, certified compliance by Hach Company.

This device complies with Part 15 of the FCC Rules. Operation is subject to the following two conditions:

(1) this device may not cause harmful interference, and (2) this device must accept any interference received, including interference that may cause undesired operation.

Changes or modifications to this unit not expressly approved by the party responsible for compliance could void the user's authority to operate the equipment.

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to Part 15 of the FCC Rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radiate radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference, in which case the user will be required to correct the interference at his own expense. The following techniques of reducing the interference problems are applied easily.

1. Disconnect the COD or THM Reactor from it's power source to verify that it is or is not the source of the interference.

2. If the COD or THM Reactor is connected into the same outlet as the device with which it is interfering, try another outlet.

3. Move the COD or THM Reactor away from the device receiving the interference.

4. Reposition the receiving antenna for the device receiving the interference.

5. Try combinations of the above.

APPENDIX A: Hach COD Methods

Dichromate Reactor Digestion Method
USEPA Approved

Digestion
Colorimetric Measurement
Titrimetric Measurement

OXYGEN DEMAND, CHEMICAL For water, wastewater and seawater

Dichromate Reactor Digestion Method*
USEPA approved for reporting wastewater analysis**

Introduction

The Chemical Oxygen Demand (COD) test is used widely to estimate the amount of organic matter in wastewater. It is a measurement of the oxygen equivalent of the materials present in the wastewater that are subject to oxidation by a strong chemical oxidant, in this case dichromate. When wastewater contains only readily available organic bacterial food and no toxic matter, the COD test results provide a good estimate of Biochemical Oxygen Demand (BOD) values.

In the Dichromate Reactor Digestion Method test, the COD procedure is simpler than Dichromate Reflux Method. Small volumes of the water sample are pipetted into vials containing the premeasured reagents, including catalysts and chloride compensator. The vials are incubated until digestion is complete and then cooled. The COD measurement is made either with the spectrophotometer (accepted for reporting by the U.S. Environmental Protection Agency) or by titration.

Material Safety Data Sheets and Labels

Material Safety Data Sheets (MSDS) are supplied with all reagents. It is good laboratory practice to read the MSDS and the reagent container labels to familiarize yourself with the reagents used in this procedure.

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* Jirka, A.M.; Carter, M.J. *Analytical Chemistry*, 1975, 47(8): 1397.
** *Federal Register*, April 21, 1980, 45(78): 26811-26812. The Ultra Low Range (0 to 40 mg/L) COD Vials are **not** USEPA approved. High Range Plus (0 to 15,000 mg/L) COD Vials are **not** USEPA approved. Titrimetric measurement is **not** USEPA approved.

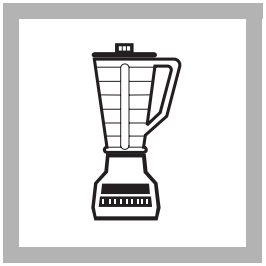
Analysis Procedure

Both the titrimetric measurement and the colorimetric measurement for determining Dichromate Chemical Oxygen Demand (COD) are detailed in this procedure. Sample digestion is required for both methods, with the choice of the final measurement method left to the analyst. Colorimetric measurement is the simpler and quicker of the two and is USEPA approved. Hach's titrimetric measurement should be used if turbidity or colored species remain after digestion; it is not USEPA approved.

Waste Management

Final samples will contain mercury, silver, and chromium at concentration levels regulated as hazardous waste by the Federal RCRA. Contact your governing local, state, or federal agency for further information on proper disposal of these materials.

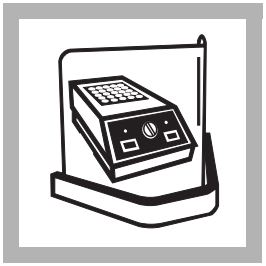
Digestion **Method 8000**



1. Homogenize 100 mL of sample for 30 seconds in a blender.

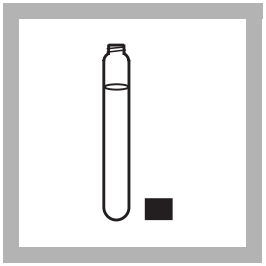
Note: *Mix the sample prior to homogenization. To improve accuracy and reproducibility, pour the homogenized sample into a 250 mL beaker and gently stir with a magnetic stir plate. For samples containing large amounts of solids, increase the homogenization time.*

Note: *Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and clothing for adequate user protection. If contact occurs, flush the affected area with running water. Follow instructions carefully.*



2. Turn on the COD Reactor. Preheat to 150 °C. Place the plastic shield in front of the reactor.

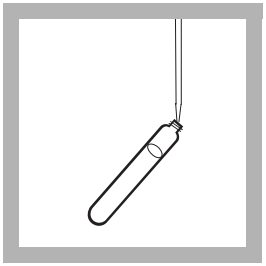
Note: *Ensure safety devices are in place to protect analyst from splattering should reagent leaking occur.*



3. Remove the cap of a COD Digestion Reagent Vial for the appropriate range:

Sample Conc. Range (mg/L)	COD Digestion Reagent Vial Type
0 to 40	Ultra Low Range
0 to 150	Low Range
0 to 1500	High Range
0 to 15,000	High Range Plus

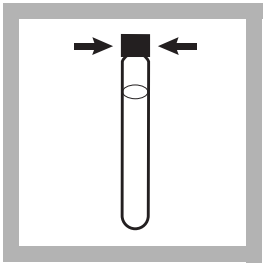
Note: *The reagent mixture is light-sensitive. Keep unused vials in the opaque shipping container, in a refrigerator if possible. The light striking the vials during the test will not affect results.*



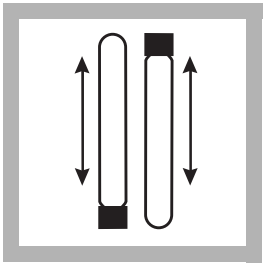
4. Hold the vial at a 45-degree angle. Pipet 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) of sample into the vial.

Note: For the 0–15,000 mg/L range, *pipet only 0.20 mL of sample, not 2.00 mL of sample, using a TenSette® Pipet. For greater accuracy a minimum of three replicates should be analyzed and the results averaged.*

Note: *Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Do not run tests with vials that have been spilled. If vials spill, wash them with running water.*

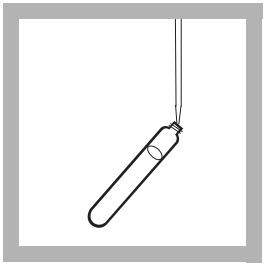


5. Replace the vial cap tightly. Rinse the outside of the COD vial with deionized water and wipe the vial clean with a paper towel.



6. Hold the vial by the cap and over a sink. Invert gently several times to mix the contents. Place the vial in the preheated COD Reactor.

Note: *The vial will become very hot during mixing.*



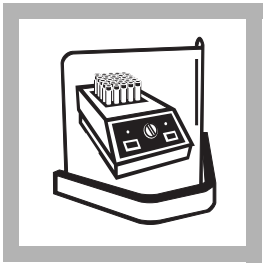
7. Prepare a blank by repeating *steps 3 to 6*, substituting 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) deionized water for the sample.

Note: *Be sure the pipet is clean.*

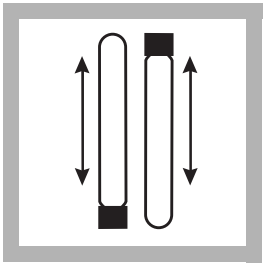
Note: *One blank must be run with each set of samples. Run samples and blanks with the same lot of vials.*

8. Heat the vials for 2 hours.

Note: *Many samples are digested completely in less than 2 hours. If desired, measure the concentration (while still hot) at 15 minute intervals until the reading remains unchanged. Cool the vials to room temperature for final measurement.*



9. Turn the reactor off. Wait about 20 minutes for the vials to cool to 120 °C or less.



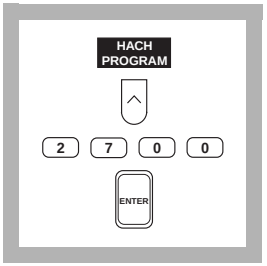
10. Invert each vial several times while still warm. Place the vials into a rack. Wait until the vials have cooled to room temperature.

Note: *If a pure green color appears in the reacted sample, measure the COD and, if necessary, repeat the test with a diluted sample.*

11. Use one of the following techniques to measure the COD:

- Colorimetric method, 0–40 mg/L COD
- Colorimetric method, 0–150 mg/L COD
- Colorimetric method, 0–1500 mg/L COD
- Colorimetric method, 0–15,000 mg/L COD
- Titrimetric method, 0–150, 0–1500, 0–15,000 mg/L COD

Colorimetric Measurement, 0 to 40 mg/L COD* Method 8328



1. If using the DR/4000 Spectrophotometer, press the soft key under **HACH PROGRAM**.

Select the stored program number for ultra low range COD by pressing **2700** with the numeric keys.

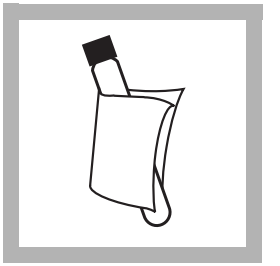
Press: **ENTER**

2. The display will show:
HACH PROGRAM:
2700 COD, ULR

The wavelength (λ), **350 nm**, is automatically selected.

3. Insert the Test Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

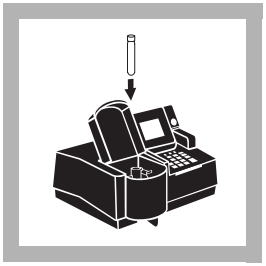
Note: *The DR/4000 Test Tube Adapter is NOT designed to allow readings on hot vials (150 °C).*



4. Clean the outside of the blank with a towel.

Note: *Wiping with a damp towel, followed by a dry one will remove fingerprints or other marks.*

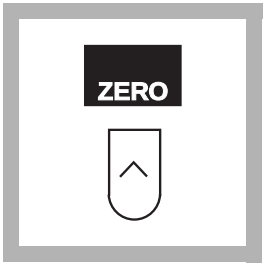
* Ultra Low Range Reagent Vials are not USEPA approved and may be used only with spectrophotometers with 350-nm capability.



5. Place the blank into the adapter with the Hach logo facing the front of the instrument. Close the light shield.

Note: *Preparation of the blank is described in the digestion procedure.*

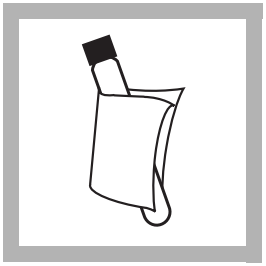
Note: *The blank is stable when stored in the dark; see Blanks for Colorimetric Measurement on page 51.*



6. Press the soft key under ***ZERO.***

The display will show:
0.0 mg/L COD

Note: *For alternate concentration units press the* ***OPTIONS*** *soft key. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*



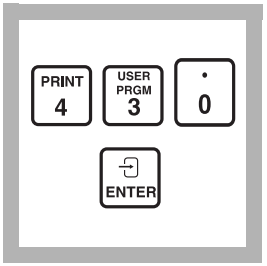
7. Clean the outside of the sample vial with a towel.

8. Place the sample vial into the adapter with the Hach logo facing the front of the instrument. Close the light shield. Results in mg/L COD (or chosen units) will be displayed.

Note: *Results may be expressed as mg/L COD or mg/L O_2. Press the soft key under* ***OPTIONS*** *and then press* ***FORM:*** *to scroll through the available choices.*

Note: *If the display shows* **45 mg/L COD** *and/or* **OVER!***, the upper limit of the range has been exceeded. Repeat the test with a dilute sample or use a Low Range or High Range COD Reagent Vial.*

Colorimetric Measurement, 0 to 150 mg/L COD — Method 8000

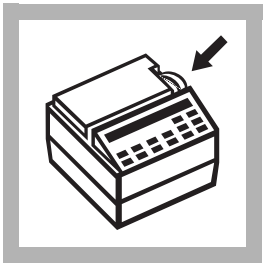


1. Enter the stored program number for chemical oxygen demand (COD), low range.

Press: **4 3 0 ENTER**

The display will show:

Dial nm to 420



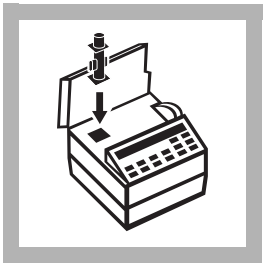
2. Rotate the wavelength dial until the small display shows:

420 nm

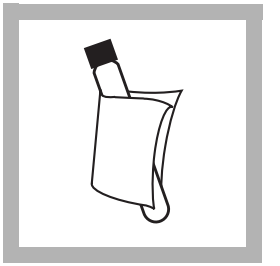
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L COD LR**

Note: *Approach the wavelength setting from the higher to lower values.*

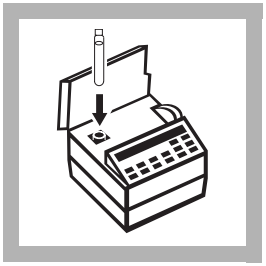


3. Place the COD Vial Adapter into the cell holder with the marker to the right.



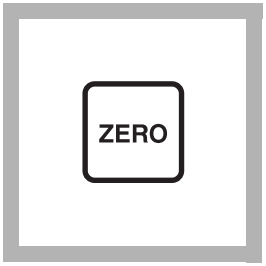
4. Clean the outside of the blank with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



5. Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *The blank is stable when stored in the dark; see Blanks for Colorimetric Determination following these procedures.*

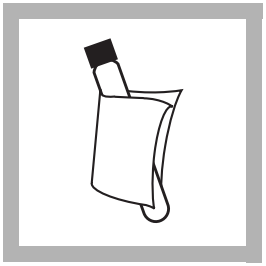


6. Press: **ZERO**

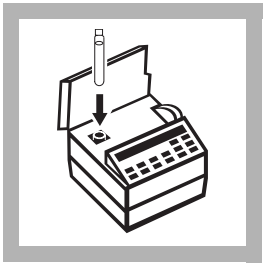
The display will show:

Zeroing. . . .

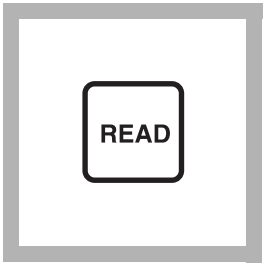
then: **0. mg/L COD LR**



7. Clean the outside of the sample vial with a towel.



8. Place the sample vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



9. Press: **READ**

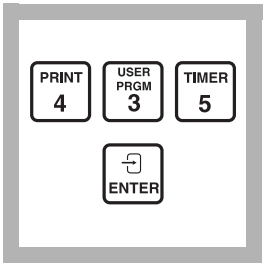
The display will show:

Reading. . . .

then the result in mg/L COD will be displayed.

Note: *For most accurate results with samples near 150 mg/L COD, repeat the analysis with a diluted sample.*

Colorimetric Measurement, 0 to 1500 and 0 to 15,000 mg/L COD* **Method 8000**

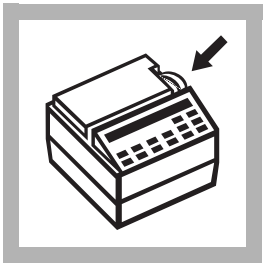


1. Enter the stored program number for chemical oxygen demand, high range.

Press: **4 3 5 ENTER**

The display will show:

Dial nm to 620



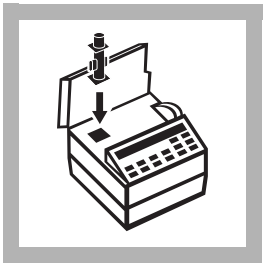
2. Rotate the wavelength dial until the small display shows:

620 nm

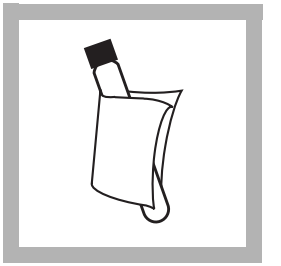
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L COD HR**



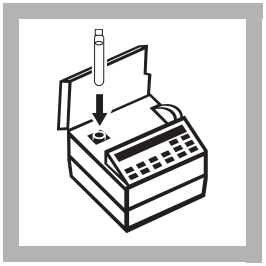
3. Place the COD Vial Adapter into the cell holder with the marker to the right.



4. Clean the outside of the blank with a towel.

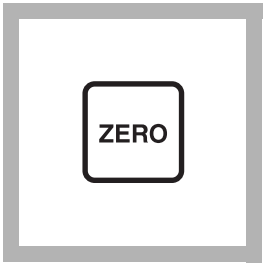
Note: *Wiping with a damp towel followed by a dry one will remove fingerprints or other marks.*

* The High Range Plus (0 to 15,000 mg/L) COD Vials are not USEPA approved.



5. Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *The blank is stable when stored in the dark. See Blanks for Colorimetric Measurement following these procedures.*

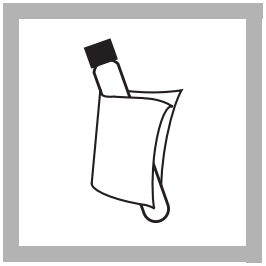


6. Press: **ZERO**

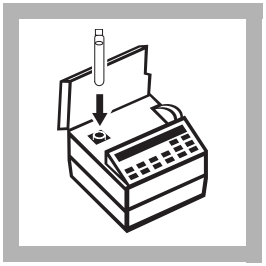
The display will show:

Zeroing. . . .

then: **0. mg/L COD HR**



7. Clean the outside of the sample vial with a towel.



8. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

9. Press: **READ**

The display will show:

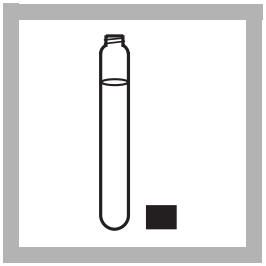
Reading. . . .

then the result in mg/L COD will be displayed.

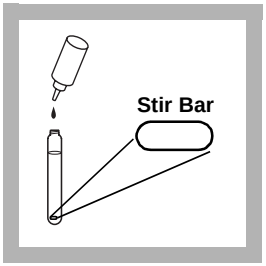
Note: *When using High Range Plus COD Digestion Reagent Vials multiply the reading by 10.*

Note: *For most accurate results with samples near 1500 or 15,000 mg/L COD, repeat the analysis with a diluted sample.*

Titrimetric Measurement, 0 to 150, 0 to 1500, and 0 to 15,000 mg/L COD* Method 8231

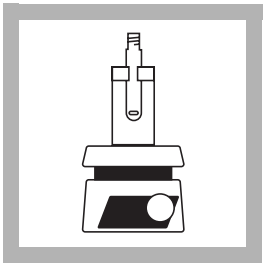


1. Carefully remove the cap of a digested vial. Rinse the inside walls with less than 1 mL of deionized water.

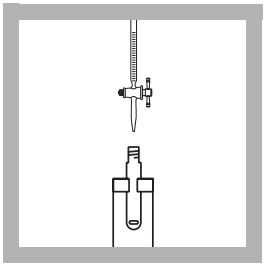


2. Add a small Teflon-coated stirring bar and one drop of the appropriate Ferroin Indicator Solution. When using the Low Range COD Digestion Vials, use Low Range Ferroin Indicator Solution. When using the High Range or High Range Plus COD Digestion Reagent Vials, use High Range Ferroin Indicator Solution.

Note: *If the color of the prepared sample changes from blue-green to orange-brown, the COD value is out of range. Dilute the sample and repeat the digestion.*



3. Place the vial on the titration stand. Turn on the magnetic stirrer.

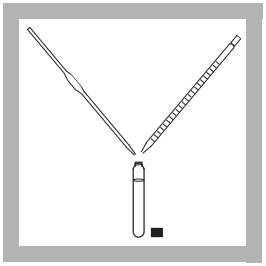


4. Titrate with the appropriate Ferrous Ammonium Sulfate Standard Solution (FAS) until the sample color changes sharply from greenish-blue to orange-brown. When using the Low Range COD Digestion Reagent Vials, use 0.0125 N FAS. When using the High Range or High Range Plus COD Digestion Reagent Vials, use 0.125 N FAS. Record the mL of titrant required. The mL required for the prepared sample is value B. The mL required for the blank is value A.

Note: *Mix the FAS bottle well before using.*

Note: *Values A and B are used in step 8.*

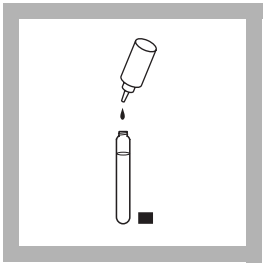
* Titrimetric measurement of reactor-digested samples is not USEPA approved.



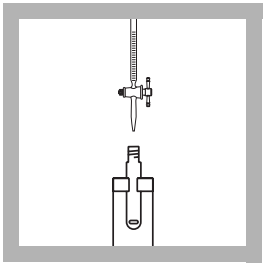
5. Pipet 2.00 mL of Potassium Dichromate Standard Solution into an empty vial. When using the Low Range COD Digestion Reagent Vials, use a 0.025 N solution. When using High Range or High Range Plus COD Digestion Reagent Vials, use a 0.25 N solution.

Add 3 ml of sulfuric acid to the vial. Swirl to mix. Wait for the solution to cool until the vial is comfortable to touch.

Note: *Steps 5 through 7 need only be done daily because the FAS deteriorates over time.*



6. Add one drop of the Ferroin Indicator Solution selected in *step 2*.



7. Add a stir bar and titrate with the Ferrous Ammonium Sulfate Standard Solution selected in *step 4* until the color changes from greenish-blue to orange-brown. Record the number of mL required. This is value C in the following equation.

Note: *Mix the FAS bottle well before using.*

Note: *To remove the stir bar from the vial, tip the vial at an angle in one hand and hold the stir bar retriever in the other. Place the retriever near the bottom of the vial on the OUTSIDE. Move the retriever up the wall to the top of the vial.*

$$(A - B) \times \frac{2000}{C} \times M = \text{mg/L COD}$$

8. Determine the mg/L COD according to the equation above.

Where:

A = mL used in titration of reagent blank

B = mL used in titration of prepared sample

C = mL used in titration of standard solution in Step 7 above

M = 0.1 when using Low Range COD Digestion Reagent Vials

M = 1 when using High Range COD Digestion Reagent Vials

M = 10 when using High Range Plus COD Digestion Reagent Vials

For example, when using Low Range COD Reagent Vials:

A= 3.95 mL
B = 2.00 mL
C = 4.00 mL
M = 0.1

mg/L COD

$$= (3.95 - 2.00) \times \frac{2000}{4.00} \times 0.1$$

$$= 97.5$$

Sampling and Storage

Collect samples in glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days. When significant amounts of preservatives are used, a volume correction should be made for the extra acid by dividing the total volume (sample + acid) by the sample volume and multiplying this value by the final test reading.

Accuracy Check

Standard Solution Method

Check the accuracy of the 0 to 40 mg/L range with a 30 mg/L COD standard solution. Using Class A glassware, prepare a 1000-mg/L solution by diluting 850 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1000 mL of organic-free deionized water. Prepare a 30 mg/L dilution by diluting 3.00 mL of this solution into a 100.0 mL volumetric flask. Dilute to volume with deionized water, stopper, and invert 10 times to mix.

Check the accuracy of the 0 to 150 mg/L range with a 100 mg/L standard. Prepare by dissolving 85 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1 liter of deionized water. Use 2 mL as the sample volume. The expected result will be 100 mg/L COD. Or, dilute 10 mL of 1000-mg/L COD Standard Solution to 100 mL to produce a 100-mg/L standard.

Check the accuracy of the 0 to 1500 mg/L range by using either a 300 mg/L or 1000 mg/L COD Standard Solution. Use 2 mL of one of these solutions as the sample volume; the expected result will be 300 or 1000 mg/L COD respectively.

Or, prepare a 500 mg/L standard by dissolving 425 mg of dried (120 °C, overnight) KHP. Dilute to 1 liter with deionized water.

Check the accuracy of the 0 to 15,000 mg/L range by using a 10,000 mg/L COD standard solution. Prepare the 10,000 mg/L solution by dissolving 8.500 g of dried (120 °C, overnight) KHP

in 1 liter of deionized water. Use 0.2 mL of this solution as the sample volume; the expected result will be 10,000 mg/L COD.

Preparing Organic-Free Water

To prepare organic-free water with no measurable COD:

1. Pour 1.0 liter of deionized water with low COD in a 2-liter Erlenmeyer flask.
2. Add the contents of one Potassium Persulfate Powder Pillow to the flask. Swirl to dissolve.
3. Suspend a UV lamp in the flask so the glass portion of the bulb is immersed and the black bakelite portion is above the solution. Follow the safety and operation instructions recommended in the UV lamp kit. Safety UV goggles should be worn for eye protection.
4. Irradiate the solution with UV light for at least 2 hours (overnight is fine).
5. Remove the lamp from the solution. Add one level 0.05-gram scoop of Nickel Sulfate to the solution.
6. Heat the water to a boil. Remove the flask from the hot plate and cover it with a watch glass.
7. Let the flask cool to room temperature. The water will have zero oxygen demand. Seal the flask top with aluminum foil to prevent organic contamination. The water should stay free of oxygen demand for one week if properly sealed.

Blanks for Colorimetric Measurement

The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark. Monitor decomposition by measuring the absorbance at the appropriate wavelength (350, 420, or 620 nm.) Zero the instrument in the absorbance mode, using a culture tube (see *OPTIONAL APPARATUS* on page *56*) containing 5 mL of deionized water. Measure the absorbance of the blank and record the value. Prepare a blank when the absorbance has changed by approximately 0.010 absorbance units.

Precision For Colorimetric Measurement

In a single laboratory using standard solutions of 100 mg/L COD and 500 mg/L COD and two lots of reagent with the DR/2010 Spectrophotometer, a single operator obtained a standard deviation of ± 2.7 mg/L COD, ± 18 mg/L COD and ± 100 mg/L COD for 0 to 150, 0 to 1500 and 0 to 15,000 mg/L ranges, respectively.

Estimated Detection Limit (EDL)

The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. The EDL for program 2700 is 0.2 mg/L COD, and for program 430 is 2 mg/L COD.

The EDL for program 435 is 5 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see your Hach spectrophotometer instrument manual.

Interferences

Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate, which will eliminate chloride interference up to the level specified in column 1 in the table below. Samples with higher chloride concentrations should be diluted. Dilute the sample enough to reduce the chloride concentration to the level given in column 2.

If sample dilution will cause the COD concentration to be too low for accurate determination, add 0.50 g of mercuric sulfate ($HgSO_4$) to each COD vial before the sample is added. The additional mercuric sulfate will raise the maximum chloride concentration allowable to the level given in column 3.

Bromide interference will not be controlled by mercuric sulfate.

Vial Type Used	Maximum Cl^- concentration in sample (mg/L)	Suggested Cl^- concentration of diluted sample (mg/L)	Maximum Cl^- concentration in sample with 0.5 g $HgSO_4$ Added (mg/L)
Ultra Low Range	2000	1000	NA
Low Range	2000	1000	8000
High Range	2000	1000	4000
Ultra High Range	20,000	10,000	40,000

Summary of Method

The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). When the 0–40 mg/L or 0–150 mg/L colorimetric measurement is used, the amount of Cr^{6+} remaining is determined. When the 0–1500 mg/L or 0–15,000 mg/L colorimetric measurement is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.

REQUIRED REAGENTS (for colorimetric measurement)

Description	Quantity Required Per Test	Unit	Cat. No.
Select the appropriate COD Digestion Reagent Vial:			
Ultra Low Range, 0 to 40 mg/L COD	1–2	25/pkg	24158-25
Low Range, 0 to 150 mg/L COD	1–2	25/pkg	21258-25
High Range, 0 to 1500 mg/L COD	1–2	25/pkg	21259-25
High Range Plus, 0 to 15,000 mg/L COD	1–2	25/pkg	24159-25
Water, deionized	varies	4 L	272-56

REQUIRED REAGENTS (for titrimetric measurement)*

Description	Quantity Required Per Test	Unit	Cat. No.
Select One or Both Potassium Dichromate Standard Solutions			
0.025 N	2 mL	500 mL	164-49
0.25 N	2 mL	1000 mL	1809-53
Sulfuric Acid, ACS	3 mL	500 mL**	979-49
Water, deionized	varies	4 L	272-56
Select the appropriate COD Digestion Reagent Vial			
Low Range	1–2	25/pkg***	21258-25
High Range	1– 2	25/pkg***	21259-25
High Range Plus	1–2	25/pkg	24159-25
Select one or both Ferroin Indicator Solutions			
Low Range	1– 2 drops	29 mL DB	20551-33
High Range	1–2 drops	29 mL DB***	1812-33
Select one or both Ferrous Ammonium Sulfate Standard Solutions***			
0.0125 N	varies	1000 mL	14237-53
0.125 N	varies	500 mL	20548-49

* Does not include reagent or apparatus for reagent blanks or standardization.

** Contact Hach for larger sizes.

*** Ferrous Ammonium Sulfate Standard Solutions, as prepared by Hach, have a length of cadmium wire in each bottle. The cadmium wire will help preserve the standard solution. Before filling the buret, the bottle should be swirled to bring the upper layer of solution in contact with the wire. When titrating these solutions, do not return unused portions from the buret to the bottle or allow solution to stand in the buret for long periods of time. Do NOT use an automatic buret with a reservoir that holds more solution than can be used in one day.

REQUIRED APPARATUS (for colorimetric measurement)

Description	Quantity Required Per Test	Unit	Cat.
COD Reactor, 115/230 Vac, 50/60 Hz, North American fuses and plug	1	each	45600-00
COD Reactor, 230 Vac, 50 Hz, European fuses and plug	1	each	45600-02
COD Test Tube Adapter, DR/4000	1	each	48189-00
COD Vial Adapter, DR/2010	1	each	44799-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet, volumetric, Class A, 2.00 mL	1	each	14515-36
Pipet Filler, safety bulb	1	each	14651-00
Test Tube Rack	1–2	each	18641-00

REQUIRED APPARATUS (for titrimetric measurement)

Description	Quantity Required Per Test	Unit	Cat.
Bottle, wash, 500 mL	1	each	620-11
Buret Clamp, double	1	each	328-00
Buret, automatic, Class A, 5.00 mL	1	each	20550-37
COD Reactor, 115/230 Vac, 50/60 Hz, North American fuses and plug	1	each	45600-00
COD Reactor, 230 Vac, 50 Hz, European fuses and plug	1	each	45600-02
Pipet, volumetric, Class A, 2.00 mL	1	each	14515-36
Pipet, Mohr, 5.00 mL	1	each	20934-37
Pipet Filler, safety bulb	1	each	14651-00
Safety Shield, laboratory bench	1	each	23810-00
Stir Bar	1	each	20549-59
Stir Bar Retriever	1	each	15232-00
Stirrer, magnetic, 120 Vac, 50/60 Hz	1	each	23444-00
Stirrer, magnetic, 240 Vac, 50/60 Hz	1	each	23444-02
Support Stand	1	each	563-00
Test Tube Rack, steel, 8 place	1 or 2	each	18641-00
Titration Stand, test tube	1	each	18642-00

OPTIONAL REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
COD Digestion Reagent Vials, 0 to 40 mg/L COD		150/pkg	24158-15
COD Digestion Reagent Vials, 0 to 150 mg/L COD		150/pkg	21258-15
COD Digestion Reagent Vials, 0 to 1500 mg/L COD		150/pkg	21259-15
COD Standard Solution, 300 mg/L		200 mL	12186-29
COD Standard Solution, 1000 mg/L		200 mL	22539-29
Mercuric Sulfate, ACS		28.3 grams	1915-20
Nickel Sulfate, ACS		25 grams	11264-24
Potassium Acid Phthalate, ACS		500 g	315-34
Sulfuric Acid, ACS		500 mL*	979-49
Potassium Persulfate Powder Pillows		100/pkg	20847-69

OPTIONAL APPARATUS

Balance, analytical, 115 Vac		each	26103-00
Balance, analytical, 220 Vac		each	26103-02
Beaker, 250 mL		each	500-46
Blender, 120 Vac, 1.2-L, 2-speed		each	26161-00
Blender, 220 Vac, 1.2-L, 2-speed		each	26161-02
Culture Tube, 16 x 100		6/pkg	22758-06
Culture Tube Cap		6/pkg	22411-06
Cylinder, graduated, 5 mL		each	508-37
Electromagnetic Stirrer, 120 V ac, with electrode stand		each	45300-01
Electromagnetic Stirrer, 230 V ac, with electrode stand		each	45300-02
Flask, volumetric, Class A, 1000 mL		each	14574-53
Flask, volumetric, Class A, 100 mL		each	14574-42
pH Indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
Pipet, serological, 5 mL		each	532-37
Pipet Tips, for 19700-01 TenSette® Pipet		50/pkg	21856-96
Pipet, volumetric, Class A, 10 mL		each	14515-38
Safety Shield for COD Reactor		each	23810-00
Spoon, measuring, 0.5 g		each	907-00
Stir Bar, 22.2 x 4.76 mm		each	45315-00
Stir Bar Retriever		each	15232-00
UV Lamp Kit, 115 Vac		each	20828-00
UV Lamp Kit, 230 Vac		each	20828-02

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

* Contact Hach for larger sizes.

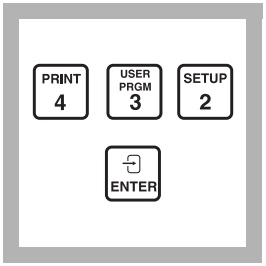
APPENDIX B: Hach COD Methods

Manganese III COD Method

Digestion
Colorimetric Measurement

OXYGEN DEMAND, CHEMICAL (20 to 1000 mg/L) For water and wastewater

Manganese III Reactor Digestion Method * (with optional chloride removal)



1. Enter the stored user program number for Manganese III COD.

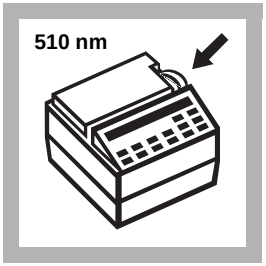
Press: **4 3 2 ENTER**

The display will show:

Dial nm to 510

Note: *If samples cannot be analyzed immediately, see Sampling and Storage on page 64.*

Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



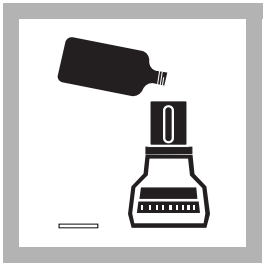
2. Rotate the wavelength dial until the small display shows:

510 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then:
mg/L COD Mn III

Note: *Approach wavelength settings from higher to lower values.*



3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*

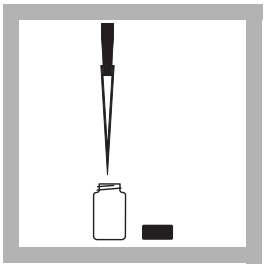
4. If the sample contains chloride†, go to *step 6* and follow the chloride removal procedure.

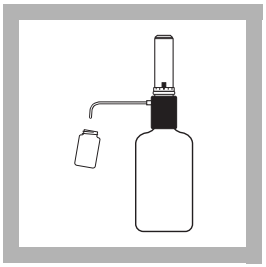
If chloride is not present in significant amounts, pipet 0.50 mL of homogenized sample into a Mn III COD vial. Cap and invert several times to mix.

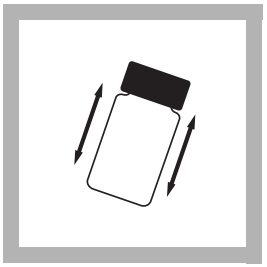
Note: *If the sample COD value is not between 20 to 1000 mg/L and the chloride removal procedure is not necessary, dilute the sample with deionized water to obtain a range of 20 to 1000 mg/L COD. Multiply the final result by the dilution factor.*

†To determine if chloride will interfere, run the sample with and without the chloride removal procedure and compare the results.

* U.S. patent 5,556,787.







5. Prepare a blank (see note) by substituting 0.50 mL of deionized water for the sample. Continue with *step 19* of this procedure.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range should be about 1.45–1.51.*

Chloride Removal Procedure (*Steps 6–18*)

6. Using a TenSette® Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell. If the sample COD exceeds 1000 mg/L, dilute the sample as described in *Table 1*.

Note: *If suspended solids are present, continue mixing the sample while pipetting.*

7. Using an automatic dispenser or TenSette Pipet, add 1.0 mL of concentrated sulfuric acid to the mixing cell.

Note: *Mixing concentrated sulfuric acid and water is not additive. Adding 1.0 mL of concentrated sulfuric acid to 9.0 mL of sample does not result in a final volume of 10.0 mL. This factor is built into the calibration curve.*

8. Cap the cell tightly and invert it several times. The solution will become hot. Cool to room temperature before proceeding.

Note: *Acidified samples are stable for several months when refrigerated at 4 °C.*

Table 1 Dilution Table (for use with Chloride Removal Procedure only)

Sample (mL)	Deionized Water (mL)	Range (mg/L COD)	Multiplication Factor
6.0	3.0	30–1500	1.5
3.0	6.0	60–3000	3
1.0	8.0	180–9000	9
0.5	8.5	360–18,000	18

All dilutions require that the ratio of sample to sulfuric acid remain at 9:1. For other dilutions that are not listed in Table 1, simply add the sample volume + deionized water and divide by the sample volume to obtain the multiplication factor.

Example:

Dilute the sample to a range of 90–4500 mg/L COD
Sample Volume (2.0 mL) + Deionized water (7.0 mL) = Total Volume (9.0 mL)

$$\text{Multiplication Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}} = \frac{9.0\ \text{mL}}{2.0\ \text{mL}} = 4.5$$

Standard test range is 20–1000 mg/L COD.

Example Test Range = 4.5 (20) to 4.5 (1000) = 90-4500 mg/L COD

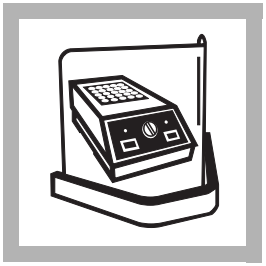
It is best to use 0.5 mL or more of sample for diluting. If sample values exceed 18,000 mg/L COD, use a separate sample dilution before the sample chloride removal procedure.

9. Prepare a blank (see note) by repeating *steps 6–8*, substituting 9.0 mL of deionized water for the sample.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range, when using chloride removal, should be about 1.42–1.47.*

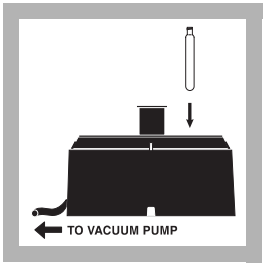
Note: *Use a clean pipet or rinse it thoroughly.*

Note: *One blank must be run with each lot of reagents. Run all samples and blanks with the same lot of vials (lot number is on the container label).*



10. If not already on, turn on the COD Reactor and heat to 150 °C. Place the shield in front of the reactor.

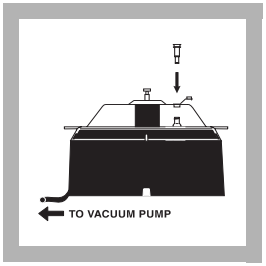
Note: *Ensure safety devices are in place to protect the analyst from splattering if leaks occur. Spilled reagent will affect test accuracy and is hazardous. Do not run tests with vials which have been spilled.*



11. Label each Mn III COD vial and remove the cap. Place the vial in one of the numbered holes in the Vacuum Pretreatment Device (VPD)* base.

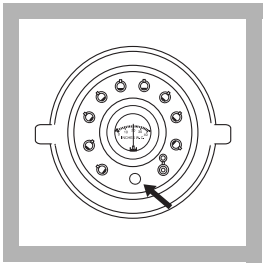
Note: *The VPD must be attached to a vacuum pump (not an aspirator-type vacuum) that can create a vacuum of 20 to 25 inches of mercury.*

*Patent pending.



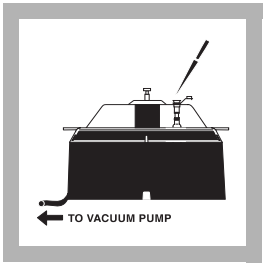
12. Place the VPD top on the base. Insert a fresh Chloride Removal Cartridge (CRC)** directly above each Mn III COD Reagent Vial. Plug any open holes in the VPD top using the stoppers provided.

** U.S. patents 5,667,754 and 5,663,914.



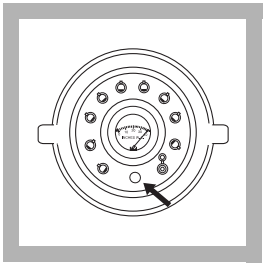
13. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the VPD until the internal gauge reads 20 inches of water.

Note: *The optimum setting allows the sample to flow through the CRC in about 30 to 45 seconds.*



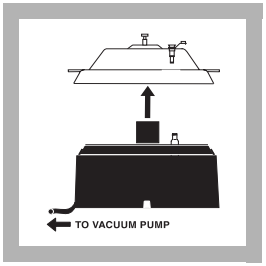
14. Pipet 0.60 mL of acidified sample (made in *steps 6–8*) into the CRC. Pipet 0.60 mL of acidified blank into another CRC. It should take about 30–45 seconds to draw the liquid through the CRC into each vial.

Note: *If the sample does not flow through the CRC, increase the vacuum until flow starts, then reduce the vacuum to 20 inches of water. Proceed as usual.*

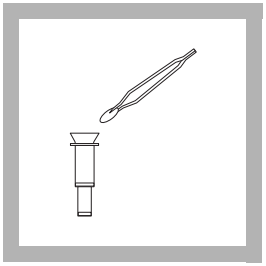


15. Close the vacuum regulator valve completely to achieve full vacuum. After 1 minute under full vacuum, open the VPD vacuum regulator valve to release the vacuum.

Note: *The maximum range of the VPD vacuum gauge is 40 inches of water. It will not indicate the full vacuum level obtained. Full vacuum is 20–25 inches of mercury, measured at the vacuum pump with a gauge calibrated for inches of mercury.*



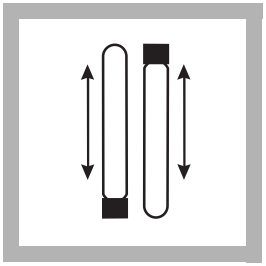
16. Turn the pump off. Remove the VPD top and set it beside the base.



17. Use forceps to remove the filter from the top of each CRC. Place each filter in the corresponding Mn III COD Vial (use the numbers on the VPD as a guide).

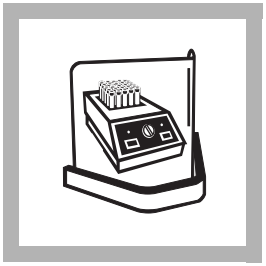
Note: *To avoid cross contamination, clean forcep tips between samples by wiping with a clean towel or rinsing with deionized water.*

Note: *If the sample does not contain suspended solids, it is not necessary to transfer the filter to the digestion vial.*



18. Remove the Mn III COD vial from the vacuum chamber and replace the original cap. Screw the cap on tightly. Invert several times to mix.

Note: *Dispose of the used Chloride Removal Cartridge. Do not reuse it.*



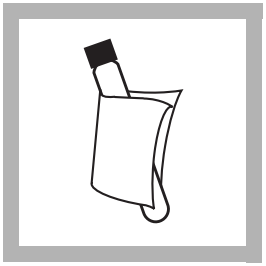
19. Place the vials in the COD Reactor that is preheated to 150 °C. Digest for 1 hour.

Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*

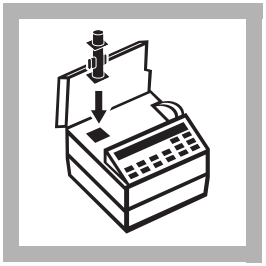
20. Remove the vials and place them in a cooling rack for 2 minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about 3 minutes.

Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.*

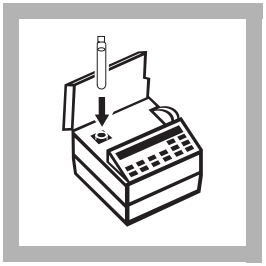


21. Remove the vials from the water and wipe with a clean, dry paper towel.

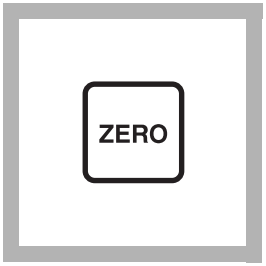
Invert the vials several times to mix.



22. Place the COD Vial Adapter into the cell holder.



23. Place the blank into the sample cell adapter. Place the cover on the adapter.



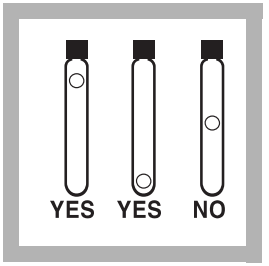
24. Press: **ZERO**

The display will show:

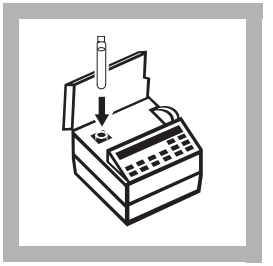
Zeroing. . .

then:

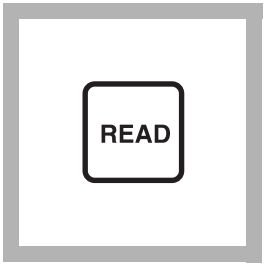
0 mg/L COD Mn III



25. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



26. Place the sample in the sample cell adapter. Place the cover on the adapter.



27. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L COD will be displayed.

Note: *Adjust the result for any sample dilution in steps 4 or 6.*

Sampling and Storage

Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see your Hach spectrophotometer manual for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be 800 ± 26 mg/L COD. An 800 mg/L COD solution can also be purchased directly from Hach (see *OPTIONAL REAGENTS AND APPARATUS* on page *67*).

Method Performance

(for Manganic III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the DR/2010 Spectrophotometer, a single operator obtained a standard deviation of ± 20 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 432 is 4 mg/L COD. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see your Hach spectrophotometer manual.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run routine samples with and without the chloride removal, then compare results.

Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. To correct for these interferences, determine their concentrations separately. Then perform the COD test on a standard solution made up to match those concentrations, and subtract that COD value from the sample COD test result.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant"

(APHA *Standard Methods*, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Chloride Removal Cartridges (CRC)	1	25/pkg	26618-25
Chloride Removal Cartridges (CRC)	1	150/pkg	26618-15
Manganese III COD Reagent Vials, 20 to 1000 mg/L COD	1	25/pkg	26234-25
Manganese III COD Reagent Vials, 20 to 1000 mg/L COD	1	150/pkg	26234-15
Sulfuric Acid, concentrated, ACS	1 mL	4 kg	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, COD, DR/2010	1	each	44799-00
Blender, Osterizer, 120 Vac, 14-speed	1	each	26747-00
Blender Container, 50–250 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	1	12/pkg	24018-12
COD Reactor, 115/230 Vac, 50/60 Hz, North American fuses and plug	1	each	45600-00
or			
COD Reactor, 230 Vac, 50 Hz, European fuses and plug	1	each	45600-02
Forceps, extra fine point	1	each	26696-00
Mixing Bottle, glass, for sample + acid	1	each	24347-06
Pipet, TenSette®, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette®	2	50/pkg	21997-96
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette®	2	50/pkg	21856-96
Safety Shield	1	each	23810-00
Test Tube Rack, steel, 8 place	1	each	18641-00
Vacuum Pretreatment Device (VPD)	1	each	49000-00
Vacuum Pump, 115 Vac	1	each	14697-00
or			
Vacuum Pump, 220 Vac	1	each	14697-02

OPTIONAL REAGENTS AND APPARATUS

COD Standard Solution, 800 mg/L COD	200 mL		26726-29
Dispenser, Digital, for sulfuric acid	each		25631-37
Pipet Tips, for 19700-10 TenSette®	1000/pkg		21997-28
Pipet Tips, for 19700-10 TenSette®	250/pkg		21997-25
Potassium Acid Phthalate, ACS	500 g		315-34

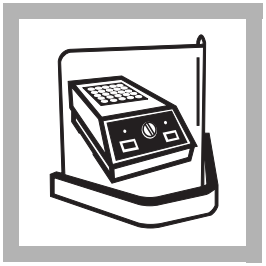
For Technical Assistance, Price and Ordering see GENERAL INFORMATION.
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

APPENDIX C: THM Plus™ Method

Digestion and Colorimetric Measurement

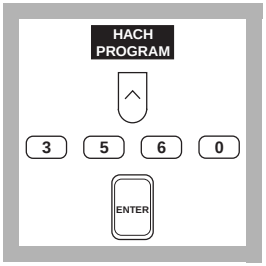
THM Plus™ Trihalomethanes* 0–200 ppb as Chloroform For drinking water

THM Reactor Method



1. Place the reactor in a fume hood and place a plastic shield in front of the reactor.

Turn on the COD Reactor. Preheat to 100 °C.



2. Press the soft key under ***HACH PROGRAM***. Select the stored program number for Trihalomethane (THM) Plus by pressing **3560** on the numeric keys.

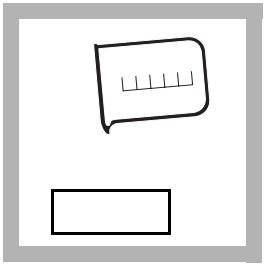
Press **ENTER**.

Note: *For the most precise results, use matched cells. See Sample Cell Matching on page 77.*

3. The display will show:

HACH PROGRAM: 3560 THM Plus

The wavelength (λ), 515 nm, is automatically selected.

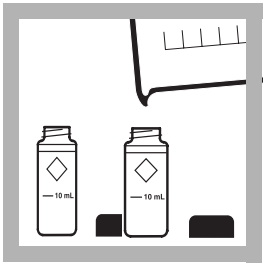


4. Prepare a cooling bath by adding 500 mL of cold (18–25 °C) tap water to an evaporating dish.

Note: *Maintain the water temperature between 18 and 25 °C.*

Note: *If analyzing more than four samples, use 450 mL of water.*

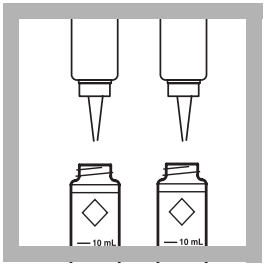
* Patent Pending



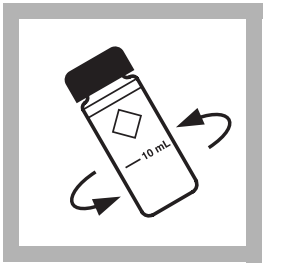
5. Fill two sample cells to the 10 mL mark with sample. Label one **sample** and the other **blank**.

Note: *Perform steps 5 through 9* ***rapidly*** *so as not to lose volatile THMs from the sample. If you are testing more than one sample, complete steps 5 through 9 for one sample before going on to the next.*

Note: *If dispensing sample with a pipette, the pipette must dispense quickly without causing aeration or back pressure.*

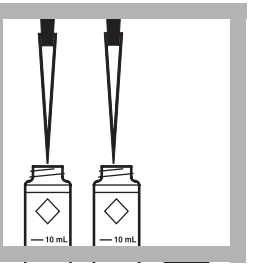


6. Add three drops of THM Plus Reagent 1 to each cell.



7. Cap tightly and mix gently by swirling each cell three times.

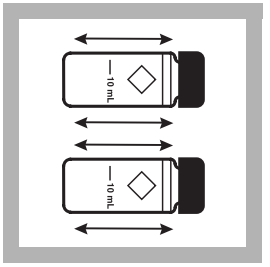
Note: *Vigorous shaking can cause loss of THMs.*



8. Use a TenSette® pipette to add 3 mL of THM Plus Reagent 2 to each cell.

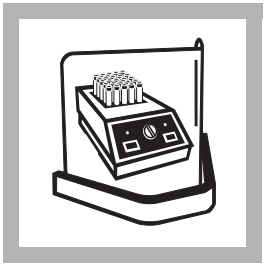
Note: *The liquid is viscous and a small amount may remain in the tip after dispensing. This will not affect the results.*

Note: *The THM Plus Reagent 2 must be at room temperature before use.*

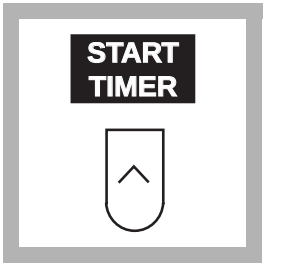


9. Cap tightly and mix by shaking ten times.

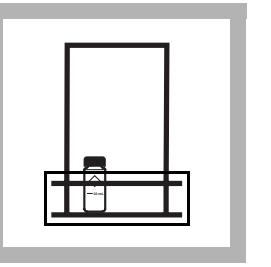
Note: *Thorough mixing ensures that all of the THM goes into the liquid and does not accumulate in the head space.*



10. Place the sample cell in the THM reactor at 100 °C. Set the blank aside.



11. Press ***800 START TIMER*** to begin an eight-minute reaction period.

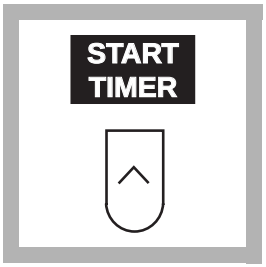


12. At the end of the reaction period, remove the cell from the reactor and place in the cell holder assembly.

Place the assembly in a cooling bath.

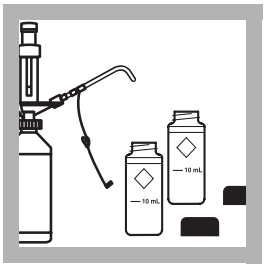
13. Press: ***NEXT TIMER*** twice.

Note: *Pressing* ***NEXT TIMER*** *twice skips Timer 1, which is used for a water bath digestion.*



14. Press: ***START TIMER 2***. Cool for three minutes.

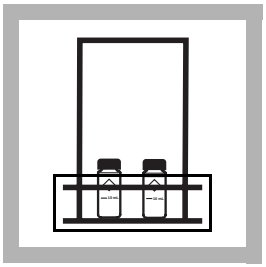
At the end of the cooling period, remove the cell from the cooling bath.



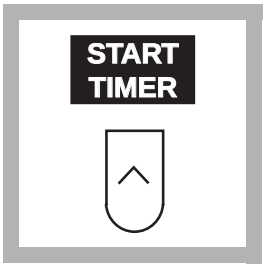
15. Use the Repipet Jr. to add 1 mL of THM Plus Reagent 3 to the sample cell and to the blank. Swirl to mix.

Note: *The sample will become warm*

Note: *The liquid is viscous and may not be entirely dispensed if measured using any other pipetting method.*



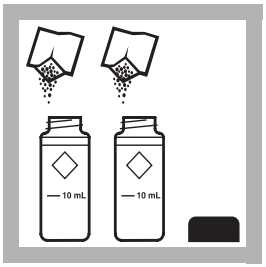
16. Replace the cooling water with fresh, cold tap water. Place the assembly containing the sample and blank cells into the cooling bath.



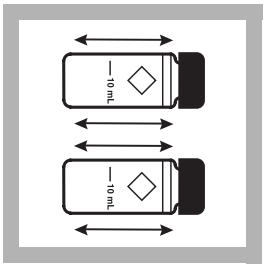
17. Press: ***START TIMER 3*** to begin a three-minute cooling time.

At the end of the cooling period, remove the cells from the cooling bath.

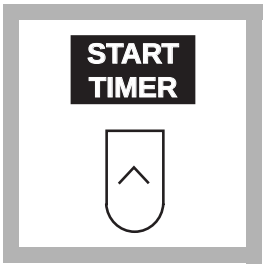
Note: *At the end of the cooling time, the sample temperature should be between 15 and 25 °C.*



18. Add one THM Plus Reagent 4 Powder Pillow each to the sample cell and to the blank.

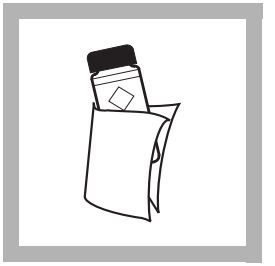


19. Cap each cell tightly and shake to dissolve.



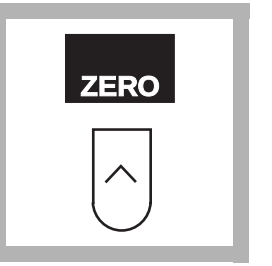
20. Press ***START TIMER 4*** to begin a 15-minute color development time.

21. While the color is developing, insert the AccuVac® Ampul Adapter into instrument.



22. Wipe the reagent blank with a damp towel, followed by a dry one, to remove fingerprints or other marks.

23. At the end of the 15 minutes, place the blank into the cell holder and close the light shield.



24. Press the soft key under ***ZERO***.

The display will show:

0 ppb $CHCl_3$

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****, and then the soft key under* ***UNITS****. Scroll through the available options. Press* **ENTER** *to return to the Read screen.*

25. Wipe the sample cell with a damp towel, followed by a dry one, to remove fingerprints or other marks.

26. Place the prepared sample into the cell holder. Close the lid. Results will be displayed in ppb chloroform.

Sampling and Storage

Collect samples in 40-mL glass bottles sealed with Teflon®-lined septa caps. Use Cat. No. 27940-05 or equivalent for best results. Fill the bottles slowly to overflowing so that no air is included with the sample. Seal the bottles tightly and invert to check that no air has been trapped.

Because trihalomethane compounds (THMs) are extremely volatile, immediate analysis yields the greatest accuracy. If the samples cannot be analyzed immediately, cool samples to 4 °C. This will slow the formation of any additional THM compounds in chlorinated samples. Store the preserved samples at 4 °C in an atmosphere free of organic vapors. Samples should not be held more than 48 hours. Allow the samples to equilibrate to room temperature before analyzing.

Ascorbic acid cannot be used as a preservative with the THM Plus method. Sodium Thiosulfate may be used as a preservative in samples containing hardness of 100 mg/L or less as $CaCO_3$.

Accuracy Check

Standard Additions Method

Prepare the standard additions sample at the same time as the unspiked water sample. Snap the neck off a THM Standard Ampule, 10 ppm as chloroform. Using a Wiretrol™ Pipet (Cat. No. 25689-05), add 0.050 mL of the standard to 10 mL of water sample. Immerse the tip of the pipet below the surface of the water sample and dispense the aliquot of chloroform standard. Cap the sample cell immediately and swirl three times to mix. Prepare the sample and the spiked sample according to the procedure steps 6–26.

a. Leave the unspiked sample in the sample compartment after completing step 26. Verify that the units displayed are in ppb. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and the ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 10.0.

c. Use the keypad to enter **10000**. Press **ENTER**.

d. Press the soft key under ***ENTRY DONE***.

e. Read the standard additions sample prepared above. Accept the standard additions reading by pressing the soft key under ***READ***. The addition should reflect 80–120% recovery. To view % Recovery, press the soft key under ***EDIT TABLE***.

See the *Procedures Manual* for more information.

Standard Solutions Method

⚠
Chloroform is extremely volatile! Do not shake it when mixing.

Prepare a 99 ppb chloroform standard by pipetting 10.0 mL of organic-free water into a sample cell. Snap the neck off a THM Standard Ampule, 10 ppm as chloroform. Using a Wiretrol Pipette (Cat. No. 25689-05), transfer 0.100 mL of the chloroform standard into the organic-free water. Immerse the end of the pipet tip under the water to dispense the chloroform. Cap the sample cell immediately and swirl three times to mix. Immediately perform steps 6–25 of the procedure. Do not make up the standard in advance. Use the standard immediately upon preparation.

Method Performance

Precision
Standard: 60 ppb $CHCl_3$

Program	95% Confidence Limits
3560	56–64 ppm $CHCl_3$

For more information on determining precision data and method detection limits, refer to the *Procedures Manual*.

Estimated Detection Limit

Program	EDL
3560	6 ppb $CHCl_3$

For more information on the derivation and use of Hach's estimated detection limit, see the *Procedures Manual*. To

determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see the *Procedures Manual*.

Sensitivity

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	21 ppb as $CHCl_3$

See the *Procedures Manual* for more information.

Sample Cell Matching

The THM Plus method requires that the 1" sample cells be optically matched for best performance. Although sample cells supplied by Hach Company are distortion-free, nicks and scratches from handling, fingerprints, and other foreign material on the glass surfaces may cause an optical mismatch between two sample cells and introduce error into the test results. This type of error may be avoided by optically matching the sample cells and following the cell precaution statements listed in the procedure.

Procedure:

1. Turn on your instrument and select the THM Plus method. Select the wavelength indicated in the procedure if your instrument has not automatically done so.
2. Change the instrument to the absorbance mode.
3. Pour at least 10 mL of deionized water into each of the samples cells to be matched.
4. Place one of the sample cells into the cell holder. Note and mark the orientation of the cell in the cell holder. Close the light shield. (Sample cells should be carefully wiped with a lint free cloth to remove any fingerprints or other foreign matter on the outside of the cell.)
5. Press: **ZERO**. The display will show: **0.000 Abs**
6. Place the next sample cell into the cell holder. Close the light shield.
7. Wait for the absorbance value to stabilize. Record the value.

8. Turn the cell 180 degrees and repeat *steps 6–7*. Try to achieve an absorbance value within ±0.001 Abs of the first cell. Note the orientation of the sample cell in the cell holder. This will allow the cells to be oriented consistently in the cell holder.

Reagent Storage

Refrigerate THM Plus Reagent 2 for maximum stability. Long-term exposure to temperatures above 35 °C may cause reagent degradation.

Interferences

The substances in the following table have been tested and found not to interfere up to the indicated levels (in ppm):

Interferences that have no effect up to the maximum level tested

Interference	Maximum Level tested
Chlorine	<10 ppm
Copper	<1000 ppm
Hardness, Ca	<1000 ppm as $CaCO_3$ May have some turbidity until Reagent 3 is added
Hardness, Mg	<4000 ppm as $CaCO_3$ May have some turbidity until Reagent 3 is added
Iron	<10 ppm
Lead	<2 ppm
Mercury	<10 ppm
Monochloramine	<20 ppm
Nickel	<10ppm
Sodium Bisulfite	<100 ppm
EDTA	Interferes negatively at all levels

Additional disinfection by-products that react

Compound	Effect
1,1,1-trichloro-2-propanone	Interferes positively
1,1,1-tricholoacetonitrile	Interferes positively
Chloral hydrate	Interferes positively
Dibromochloroacetic acid	Interferes positively
Dichlorobromoacetic acid	Interferes positively
Tribromoacetic acid	Interferes positively
Trichloroacetic acid	Interferes positively

Summary of Method

The THM Plus method reacts with the trihalogenated disinfection by-products formed as the result of the disinfection of drinking water with chlorine in the presence of naturally occurring organic materials. These disinfection by-products (DBPs) may be produced in the treatment plant or the distribution system as long as the water is in contact with free chlorine residual. The formation of the DBPs is influenced by chlorine contact time, chlorine dose and residual, temperature, pH, precursor concentration, and bromide concentration.

The predominant DBPs formed by the chlorination of drinking water are the trihalomethanes or THMs. The four trihalogenated compounds that form are chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. These four compounds comprise the Total Trihalomethanes (TTHMs) group which is regulated under the Safe Drinking Water Act. The combined concentration of the TTHMs, reported as chloroform, is regulated to be 100 ppb or less in drinking water samples. Other DBPs that may be present and react under the conditions of the THM Plus method are listed in Interferences.

In the THM Plus method, THM compounds present in the sample react with N, N,-diethylnicotinamide under heated alkaline conditions to form a dialdehyde intermediate. The sample is then cooled and acidified to pH 2.5. The dialdehyde intermediate formed is then reacted with 7-napthylamine-1,3 disulfonic acid to form a colored Schiff base which absorbs at 515 nm. The color formed is directly proportional to the total amount of THM compounds present in the sample. The results are reported as ppb chloroform.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

REQUIRED REAGENTS

Reagent Set (50 tests) 27908-00
Includes: (1) 27539-29, (1) 27540-48, (1) 27541-42, (1) 27566-99

Description	Quantity Required Per Test	Unit	Cat. No.
THM Plus Reagent 1	6 drops	30 mL/bottle	27539-29
THM Plus Reagent 2	6 mL	330 mL/bottle	27540-48
THM Plus Reagent 3	2 mL	100 mL/bottle	27541-42
THM Plus Reagent 4	2 pillows	100 pillows	27566-99

REQUIRED APPARATUS

Beaker, 600-mL		each	500-52
Cell Holder Assembly, TTHM	1	each	47880-00
Evaporating Dish, 125 mm x 65 mm	1	each	27647-00
Repipet Jr., 1 mL	1	each	21113-02
Pipet, Tensette, 1–10 mL	1	each	19700-10
Pipet tips, 1–10 mL (for 19700-10)		50/pkg	25589-96
Sample cells, 10 mL, w/caps.	2	6/box	24276-06
THM Reactor, Model 49100, 115 V ac		each	49100-00
THM Reactor, Model 49100, 230 V ac		each	49100-02
Wipers, Disposable, KimWipes		280/pkg	20970-00

OPTIONAL REAGENTS

THM Standard Ampules, 10 ppm as Chloroform		7/pkg	27567-07
Water, Reagent, Organic-free		500 mL	26415-49

OPTIONAL APPARATUS

Flask, volumetric, 100 mL, class A		each	14574-42
Pipet, filler, safety bulb		each	14651-00
Pipet, volumetric, class A, 10 mL		each	14515-38
Pipettes, Wiretrol™, 50–100 µL		250/pkg	25689-05
Vials, glass, 40-mL, with Septa cap		5/pkg	27940-05

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