CHEMetrics

Water Analysis Systems

COD

vials for the
determination of
chemical oxygen demand

Test Procedure

Range 0 - 40 mg/L (ULR)
Range 0 - 150 mg/L (LR)
Range 0 - 1,500 mg/L (HR)
Range 0 - 15,000 mg/L (HR+)

SAFETY INFORMATION

COD reagent vials contain sulfuric acid, which causes severe burns. Read MSDS before using. During any handling, wear laboratory grade safety glasses with top and side shields. Also wear gloves and protective clothing. Avoid contact with reagent. It is recommended that this test procedure be performed under a chemical fume hood.

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TEST METHOD

Chemical oxygen demand is a measure of the oxidizable organic matter content of a wastewater sample. The sample is reacted with an acidic solution of potassium dichromate in the presence of a catalyst (silver) and digested for 2 hours at a temperature of 150°C. Oxidizable organic compounds reduce the dichromate ion ($Cr_2O_7^{2-}$) to the chromic ion (Cr^{3+}). In the ULR and LR kits, the decrease in dichromate ion is measured colorimetrically. In the HR and HR+ kits, the amount of chromic ion produced is measured. The test results are expressed as the number of milligrams of oxygen consumed per liter of sample (mg/Liter COD).

REFERENCES

APHA Standard Methods, 21st ed., method 5220 D (2005).

ASTM D 1252-.00, Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water, Test Method B.

EPA Methods for Analysis of Waters and Wastes, method 410.4 (1983).

A. M. Jirka and M. J. Carter, "Micro Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand," Analytical Chemistry, Vol. 47, p. 1397 (1975).

J. A. Winter, "Method Research Study 3, Demand Analysis, An Evaluation of Analytical Methods for Water and Wastewater," USEPA, (1971).

MATERIAL SAFETY DATA SHEET

I. Chemical Identification

TRADE NAME: Chemical Oxygen Demand (COD) Vials Kit
DESCRIPTION: Reagent vials for determination of the oxidizable organic matter content of wastewater. Each K-7340S, K-7350S, K-7351S, K-7355, K-7356, K-7360S, K-7361S, K-7365, and K-7366 vial contains 3.3 mL of reagent. Each K-7370S, K-7371S, K-7375, and K-7376 vial contains 5.1 mL of reagent.
NFPA RATINGS: HEALTH: 3 FLAMMABILITY: 0 REACTIVITY: 2

II. Hazards Identification

Danger! Toxic. Corrosive. Causes severe burns.
ACUTE TOXICITY: Causes severe burns. May cause abdominal pain, circulation disturbances, nausea, vomiting, rapid pulse, and respiration.
ROUTES OF EXPOSURE: Ingestion, inhalation, skin absorption
TARGET ORGANS: Central nervous system, kidneys
CHRONIC TOXICITY: Teeth erosion, chronic irritation or inflammation
ROUTES OF EXPOSURE: Inhalation, skin absorption
TARGET ORGANS: Teeth, lungs, central nervous system, kidneys
OVEREXPOSURE: Any tissue contacted may become severely burned. If inhaled, the mist or vapor may cause teeth erosion, soreness of the mouth and/or difficulty in breathing.
MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE: Eye, skin and respiratory disorders.

III. Composition/Information on Ingredients

COMPONENT:	Sulfuric Acid	
CAS NO.:	7664-93-9	PERCENT: >64
COMPONENT:	Deionized Water	
CAS NO.:	7732-18-5	PERCENT: <34
COMPONENT:	Mercuric Sulfate[1]	
CAS NO.:	7783-35-9	PERCENT: < 1.0
COMPONENT:	Silver Sulfate	
CAS NO.:	10294-26-5	PERCENT: < 1.0
COMPONENT:	Potassium Dichromate	
CAS NO.:	7778-50-9	PERCENT: < 0.5

1. K-7351S, K-7356, K-7361S, K-7366, K-7371S, K-7376 do not contain Mercuric Sulfate

IV. First Aid Measures

EYE AND SKIN CONTACT: Immediately flush eyes and skin with water for 15 minutes. Remove contaminated clothing. Seek medical advice.

INGESTION: Do not induce vomiting. Give large quantities of water. Give at least 1 ounce milk of magnesia in an equal amount of water, or 3 egg whites. Never give anything by mouth to an unconscious person. Seek medical attention.
INHALATION: Remove to fresh air. Give artificial respiration if necessary. Seek medical advice.

V. Fire Fighting Measures

FLASH POINT: N/A AUTOIGNITION POINT: N/A
FLAMMABILITY LIMITS: UPPER: N/A LOWER: N/A
SUSCEPTIBILITY TO SPONTANEOUS HEATING: None
SHOCK SENSITIVITY: None EXTINGUISHING MEDIA: N/A

FIRE/EXPLOSION HAZARDS: May emit toxic fumes in fire.
EXTINGUISHING MEDIA: Use media appropriate to surrounding fire conditions.

VI. Accidental Release Measures

Mercury and its compounds are extremely toxic! Be extremely careful not to contact the spill or breathe any vapors. Absorb spilled liquid with non-reactive sorbent material. Dispose of all mercury contaminated material at an E.P.A. hazardous waste facility. Decontaminate area with commercially available mercury absorbing compounds.
Product is regulated as RCRA hazardous waste. Product is regulated as a hazardous air pollutant. Product is regulated as a hazardous water pollutant.

VII. Handling and Storage

Caution. Avoid contact with eyes, skin, and clothing.
Wash thoroughly after handling.
Use adequate ventilation. Do not breathe mist or vapor.
Store unused vials in a cool, dark place. Segregate from caustics.

VIII. Exposure Controls/Personal Protection

OSHA PEL: 0.1 mg/m^3 C Mercury, 5 µg/m^3 TWA Chromate, 1 mg/m^3 TWA Sulfuric Acid, 0.01 mg/m^3 TWA Silver

ACGIH TLV: 0.025 mg/m^3 TWA (skin) Mercury, 0.05 mg/m^3 TWA Chromium, 0.2 mg /m^3 TWA Sulfuric Acid, 0.01 mg/m^3 TWA Silver

PROTECTIVE EQUIPMENT: Fume hood, Lab coat; Impact: and splash-resistant eyewear; Protective gloves compatible with the hazardous reagent constituents identified on this MSDS.

OTHER CONTROL MEASURES: See OSHA Standard 29 CFR 1910.1026 for control measures related to chromate (chromium VI) exposure.

IX. Physical and Chemical Properties

STATE: Liquid APPEARANCE: Turbid (only products containing mercuric sulfate), amber
ODOR: Not determined
SOLUBILITY IN WATER: Miscible pH: <0.5
BOILING POINT: >100° C MELTING POINT: N/A
VAPOR PRESSURE: Not determined
VAPOR DENSITY (air = 1): Not determined SPECIFIC GRAVITY: >1

X. Stability and Reactivity

INCOMPATIBILITIES: Reacts violently with caustics.
HAZARDOUS DECOMPOSITION PRODUCTS: May emit toxic fumes of sulfur oxides in fire.
OXIDIZER: Mild
CONDITIONS TO AVOID: Contact with strong caustics; exposure to light or organic contamination (will affect product stability)
Stable under normal conditions.

XI. Toxicological Information

CARCINOGENIC STATUS: Inorganic mercury compounds: ACGIH - Group A4, not classifiable as a human carcinogen; IARC - Group 3, not classifiable as to its carcinogenicity to humans
Chromium VI (hexavalent) compounds: IARC - Group 1, carcinogenic to humans; ACGIH - Group A1, confirmed human carcinogen; NTP - known to be a human carcinogen; California Proposition 65 - carcinogen

TOXICOLOGICAL STATUS: Mercury compounds: California Proposition 65: reproductive toxicant (developmental)

XII. Ecological Information

Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
No other data available at this time.

XIII. Disposal Considerations

Dispose of in accordance with all Federal, State and Local Regulations.

XIV. Transport Information

US DOT, IATA, and IMDG: Dangerous Goods in Excepted Quantities
Hazard Class: 8 UN No.: UN1830 Packing GROUP: II

XV. Regulatory Information

EUROPEAN INFORMATION:
EU Symbols: T - TOXIC, C - CORROSIVE
Risk Phrases: May cause cancer. May cause heritable genetic damage. Toxic by inhalation, in contact with skin, and if swallowed. Danger of cumulative effects. Causes severe burns. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
Safety Phrases: Avoid contact with skin and eyes. Wear suitable protective clothing, gloves, and eye/face protection. In case of contact with skin or eyes, rinse immediately with plenty of water and seek medical advice. If swallowed, seek medical advice immediately and show container or label. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible). This material and/or its container must be disposed of as hazardous waste.
CANADIAN INFORMATION:
WHMIS Classification: D1A, D2A, D2B, E
All chemical components of this product are listed on Canada's DSL.
U.S. INFORMATION:
RCRA: Contains RCRA regulated substances. EPA Waste ID Nos.: D002 (corrosive), D007 (chromium), D009 (mercury), D011 (silver)
OSHA: This product meets the criteria for a hazardous substance as defined in the Hazard Communication Standard (29 CFR 1910.1200).
SARA Section 313: This product contains a mercury compound, a silver compound, and potassium dichromate which are subject to the reporting requirements of Section 313 of SARA Title III.
CALIFORNIA PROPOSITION 65: This product contains a chemical known to the State of California as a carcinogen and a chemical known as a reproductive toxicant.
All chemical components of this product are listed on the TSCA Inventory.

XVI. Other Information - Revision Date: 05/27/11

THE ABOVE INFORMATION IS BELIEVED TO BE ACCURATE AND REPRESENTS THE BEST INFORMATION CURRENTLY AVAILABLE TO US. ALL PRODUCTS ARE OFFERED IN ACCORDANCE WITH THE MANUFACTURER'S CURRENT PRODUCTION SPECIFICATIONS AND ARE INTENDED SOLELY FOR USE IN ANALYTICAL TESTING. THE MANUFACTURER SHALL IN NO EVENT BE LIABLE FOR ANY INJURY, LOSS OR DAMAGE RESULTING FROM THE HANDLING, USE OR MISUSE OF THESE PRODUCTS.

SAMPLE COLLECTION

Collect samples in glass bottles. When it is necessary to preserve samples for storage, acidify to pH $\leq$ 2 with concentrated sulfuric acid. Store preserved samples at 4°C for no longer than 28 days after collection.

SOURCES OF ERROR

The ULR, LR and HR mercury containing COD reagents are formulated to withstand interferences from up to 2000 ppm chloride. The HR+ mercury containing COD reagent can be used on samples containing up to 20,000 ppm chloride without interference. Samples with higher chloride concentrations require dilution. Also, samples that contain high levels of chloride (>1000 ppm) and low levels of COD (<30% of the product range) will give false positive test results. In this case, sample dilution is recommended. Mercury free reagents (LR and HR) are also available for samples containing less than 100 ppm chloride (less than 1000 ppm for the mercury free HR+ kit).

Good technique and elimination of contamination are necessary for accurate results. Wash all glassware with 20% Sulfuric Acid.

For COD testing, LED based photometers do not produce accuracy, precision and sensitivity equivalent to that attainable with spectrophotometers. For NPDES reporting purposes for COD, a spectrophotometer is the preferred method of measurement.

The COD reagent is light sensitive. Store vials in the dark when not in use.

CALIBRATION & ACCURACY CHECK

1. To obtain test results in mg/Liter COD:
   - Use preprogrammed CHEMetrics or Hach[1] instrumentation for direct readout.
   - Use the supplied calibration equation (Step 12 of Test Procedure) for other brand spectrophotometers.
   - Generate a standard curve specific to the instrument being used by preparing a series of five standard solutions (one of which is a blank) which covers the expected range of the test.
2. COD standard solutions (see Reorder Information) are used to check the accuracy of the test or to generate an instrument-specific calibration curve.

1. Hach Company does not warrant the accuracy of the calibrations it supplies when they are applied to reagents other than its own.

USE OF THE CHEMetrics V-2000 PHOTOMETER

1. Install the 16 mm adapter into the V-2000 photometer. Turn the photometer on by pressing the **power** key.
2. Insert the 16 mm ZEROING VIAL (supplied with the instrument) into the V-2000, cover the vial with the light shield, and press the **zero** key. "Wait" is displayed, then the result is displayed as "0.000".
3. Press the **prgm** key, enter the appropriate program number (see below), then press the **yes** key. The instrument will display the appropriate method name and program number.

Range/Method Name	Program Number
0 -150 ppm (COD LR)	48
0-1500 ppm (COD HR)	49
0-15000 ppm (COD HR+)	49

4. Follow Steps 1 through 11 of the **COD Test Procedure** on pages 7 and 8 of this booklet.
5. Press the **setup** key and use the ▲ or ▼ keys until "BLANK" is displayed, then press the **yes** key.
6. "SET BLNK?" will be displayed, press the **yes** key.
7. "SAMPLE?" will be displayed. Insert a clean, dry, newly generated reagent blank vial into the V-2000, cover the vial with the light shield, then press the **yes** key. The instrument will read the blank, display an absorbance value momentarily, and then display the next setup function.
8. Press **meas** key. The instrument display will return to the appropriate method name and program number. Insert a clean, dry, newly generated COD test vial into the V-2000, cover the vial with the light shield, then press the **meas** key again. The instrument will read the vial and display the test result.

   NOTE: When running the COD HR+ method, the instrument readout must be multiplied by 10.

TEST PROCEDURE

1. Homogenize 500 mL of sample for 2 minutes in a blender.

   Note: Blending ensures an even distribution of any solids that may be present in the sample, thus improving the accuracy and reproducibility of the test.

2. Preheat the digester block to 150°C.
3. Remove the cap from a COD vial.
4. Pipet 2.00 mL (0.20 mL for HR+) of sample into the vial.

   Caution: The contents of the vial will become hot.

5. Replace the cap onto the COD vial, securing it tightly.
6. Carefully invert the vial several times to mix the contents.

   Note: For samples that may contain chloride, the vial must immediately be mixed thoroughly (by inverting it 10 times).

   Caution: When mixing, hold the vial by the cap only. The contents of the vial will become very hot.

7. Wipe the vial with a damp towel and place it in the preheated digester block.
8. Prepare the reagent blank by repeating Steps 3 through 7, using deionized water rather than sample in Step 4.

   Note: At least one reagent blank must be run with each set of samples and with each new lot number of COD vials. Use a blank vial from the same lot as the test COD vials.

9. Allow the vials to heat in the digester block at 150°C for 2 hours.

10. Turn the digester block off and allow the vials to remain in the unit to cool for 15 to 20 minutes.

11. **Use caution,** the glass vials are still **very** hot. Carefully remove each vial from the digester block, making certain that the cap is secured tightly. Invert each vial several times, and then place it in a rack to cool to room temperature. Allow at least 30 minutes for the vials to cool. Store the vials in the dark during this cool down time.

12. If applicable, follow instrument specific procedures for selecting wavelength and zeroing the spectrophotometer.

Range, mg/L	Wavelength	Calibration Equation
0 - 40	350	ppm (mg/L) = -52.2 (abs) +0.3
0 - 150	420	ppm (mg/L) = -337.1 (abs)
0 - 1,500	620	ppm (mg/L) = 2301 (abs) -3
0 - 15,000	620	ppm (mg/L) = 23010 (abs) -3

13. Wipe the exterior of the reagent blank vial until it is clean and dry. Place the reagent blank vial into the instrument sample compartment. This reagent blank is used to zero the instrument.

14. Wipe the exterior of a test COD vial until it is clean and dry. Place the vial into the instrument sample compartment to obtain test results.

15. If applicable, use the range specific calibration equation in Step 12 to convert absorbance values to test results in mg/L COD.

REORDER INFORMATION

(May 11, Rev. 23)

Mercury Containing Reagent COD Kits:

0 - 40 mg/L, contains 25 vials K-7340S

0 - 150 mg/L, contains 25 vials K-7350S

0 - 150 mg/L, contains 150 vials K-7355

0 - 1,500 mg/L, contains 25 vials K-7360S

0 - 1,500 mg/L, contains 150 vials K-7365

0 - 15,000 mg/L, contains 25 vials K-7370S

0 - 15,000 mg/L, contains 98 vials K-7375

Mercury Free Reagent COD Kits:

0 - 150 mg/L, contains 25 vials K-7351S

0 - 150 mg/L, contains 150 vials K-7356

0 - 1,500 mg/L, contains 25 vials K-7361S

0 - 1,500 mg/L, contains 150 vials K-7366

0 - 15,000 mg/L, contains 25 vials K-7371S

0 - 15,000 mg/L, contains 98 vials K-7376

COD Standards:

1,000 mg/L A-7301

10,000 mg/L A-7310

Digester Block, 120 V/240 V, holds 12 vials A-0111

COD Vial Rack, stainless steel, holds 40 vials . . . A-0107

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