SOP-C-102

Determination of Chemical Oxygen Demand

Revision 8

Approval:

Laboratory Manager — Date: 2-19-20

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Initials: JM
JM

Texas Institute for Applied Environmental Research

i. Identification of the method

a. Hach 8000, Chemical Oxygen Demand, with additions to meet project requirements

ii. Applicable matrix or matrices

a. Nonpotable water and aqueous solutions

iii. Limits of detection and quantitation

a. 10 to 150 mg/L without dilution

iv. Scope and application, including parameters to be analyzed

a. This procedure applies to the chemical oxygen demand (COD) analysis of all water samples received by the laboratory at the Texas Institute for Applied Environmental Research (TIAER) for TNI accredited data production.

v. Summary of the method

a. Organic materials are oxidized in strong acid and mercury catalyst and measured spectrophotometrically compared to a standard curve.

vi. Definitions

a. COD (chemical oxygen demand)-A quantitative amount of oxygen utilized or depleted by chemical species present in water per unit volume and time.
b. Hach COD Reactor-The brand name of an apparatus which is designed specifically for digesting water samples in the HACH COD pre-mix reaction solution vials.
c. Hach COD pre-mix digestion reaction solution vials-Disposable vials which contain a commercially prepared reagent and are used as the digestion reaction container in the Hach digester and as the sample cuvette in the Hach DR/2000™ Spectrophotometer Hach Company-P.O. Box 608, Loveland, CO 80539-0608, Phone number 1-800-227-4224.
d. Standard QA/QC definitions are found in QAM-Q-101, “Laboratory Quality Control”.

vii. Interferences

a. High turbidity can be minimized by dilution.

b. Chloride can cause additive interference in saline waters where chloride concentrations exceed 2000 mg/L. If a water sample is suspected of having high chloride levels, the sample may be analyzed for chloride concentration prior to COD analysis. Standards and blanks are then made from high chloride concentration solutions.
c. The introduction of any extraneous organic materials into the reaction mixture, such as leaves and insects, must be prevented. The analyst is trained in handling samples, reagents, and preparatory equipment used in COD analysis.

viii. Safety

a. The pre-mix digestion solution contains sulfuric acid, chromic acid, mercuric sulfate, silver sulfate, and is toxic. The hazardous waste generated by this procedure is handled and disposed of in accordance with QAM-W-101, "Disposal of Laboratory Waste".
b. Impact resistant safety glasses, latex or rubber gloves, and a laboratory jacket are worn as needed during all phases of this procedure.
c. A protective shield may be in place around the reactors during digestion.
d. Reaction vials may be emptied and triple rinsed with DI, but the preferred method is to leave intact and have the waste disposal company lab pack the vials together.
e. Caution: Heat is immediately generated when mixing after addition of water sample to the acid vial.
f. All aspects of this procedure comply with QAM-S-101, "Laboratory Safety".

ix. Equipment and supplies

a. Equipment
   i. Hach DR/2800™ Spectrophotometer, or equivalent, which is pre-programmed to measure COD in mg/L
   ii. Hach COD Reactor block digester, or equivalent
   iii. Plastic safety shield placed around the COD Reactor
   iv. Kimwipes® or soft wiping cloth for cleaning the sample vial/cuvette

v. 1mL Eppendorf/Micropipetter 200 – 1000 µL range, and a 0.01 – 0.10 mL pipetter and pipet tips; other pipetters or pipettes may be used.
vi. Hach COD pre-mix digestion reaction solution vial/cuvettes
vii. Class "A" volumetric and other labware

x. Reagents and standards

a. Reagents
   i. The Hach COD low range digestion solution contained in the pre-mixed vial/cuvettes, (catalog # 21258-15 or equivalent). This solution contains mercuric sulfate, silver sulfate, sulfuric acid, and chromic acid and is **extremely toxic**.
   ii. Deionized water (DI), ASTM Type II or better

b. Standards
   i. 1000 mg/L KHP Stock Standard (calibration)
      1. Dry about 1 gram of primary standard grade potassium hydrogen phthalate (KHP) for at least overnight at 120° centigrade.
      2. Cool the KHP to room temperature in a dessicator.
      3. Weigh and quantitatively transfer 0.850 g of the dried KHP to a 1000 mL volumetric flask. Dissolve in about 800 mL DI and dilute to volume. Store at >0-≤6°C, discard after 3 months.
   ii. Calibration Standards: from the stock standard above, prepare a series of standards in 200 mL Class "A" volumetric flasks to levels of 10, 25, 50, 75, 100 and 150 mg/L KHP in DI. Add 4 drops of concentrated H_2SO_4 to acidify the calibration standard. Store at >0-≤6°C, discard after 28 days.
   iii. 1000 mg/L KHP Second Source Stock Standard (verification)
      1. Prepare the Second Source Stock Standard (verification) as above, but from a separate source.
      2. The ICV, CCV, LCS & LCSD standards of potassium hydrogen phthalate are from a different lot number or manufacturer than the reagent used to make the calibration standards. Commercially prepared stock standards are acceptable, even preferable, if they meet traceability requirements.
      3. From the second source stock, prepare a standard to serve as the ICV, CCV, LCS and LCSD at 75 mg/L.

Add 4 drops of concentrated H_2SO_4 to acidify the calibration standard. Store at >0-≤6°C, discard after 28 days.

iv. Limit of Quantitation (LOQ) standard: Prepare one working standard from the stock standard above to a level of 10 mg/L. Add 4 drops of concentrated H_2SO_4 to acidify. Prepare fresh daily.

v. Spiking Solution, 10,000 mg/L COD

1. Repeat steps above for the stock standard, but substitute a 100 mL flask for the 1000 mL flask.

xi. Sample collection, preservation, shipment and storage

a. Holding Time: 28 days
b. Preservation: Refrigerate sample to >0-≤6° C, pH < 2 with H_2SO_4
c. Sample collection and shipment are project dependent and outside the purvue of the laboratory.

xii. Quality control

a. All aspects of this procedure comply with QAM-Q-101, "Laboratory Quality Control".
b. Special care is taken when cleaning the sample cells prior to reading the concentration. This will ensure removal of any light path interference.
c. Pipette tips are changed after each sample.
d. The reactor temperature is monitored throughout the digestion period to ensure complete digestion of the samples and recorded in the Equipment Temperature Log (Q-103-2) at least once.

xiii. Calibration and standardization

a. Calibration and standardization may be stored internally, not to exceed 150 mg/L undiluted. Calibration data is readily available.
b. Normally, standards are only used to check the efficacy of the internally stored curve. If used to calibrate, standard rules from QAM-Q-101 apply, including 0.995 or better r^2, 25% agreement of standards within the curve to expected values, and recovery of the LOQ standard.

xiv. Procedure

a. Sample Digestion

i. Turn on the Hach COD Reactor and preheat to 150° C. Document equipment temperature and thermometer/correction factor used.
ii. Highly turbid or inhomogeneous samples are well agitated or blended prior to being pipetted into the vials.
iii. Label one reaction vial/cuvette for each calibration blank, standard, sample, and all associated QC to be analyzed.
iv. Pipette 2 mL of each solution into the appropriate labeled vial.
v. For spikes, mix 10 mL of the sample and 0.05 mL of the 10,000 mg/L KHP working standard, then pipette 2 mL of the mixture into the designated vial/cuvette. This is a spike of 50 mg/L. Adjust sample dilutions for spikes as necessary in reruns that are over the 150 mg/L range.
vi. Secure the cap and invert each sample vial several times until the settled particulates are displaced from the bottom of the vial and are dispersed evenly throughout the reaction mixture. Caution: Heat is immediately generated when mixing.
vii. Place the reaction vials into the preheated Hach COD reactor block.
viii. Set the reactor timer for 2 hours and place the protective shield or other protection around the reactor.
ix. After the samples have digested for about 15 minutes, remove and invert each vial to ensure complete mixing has been accomplished.
x. Allow the digestion reaction to proceed until the two hour digestion reaction time has been reached.
xi. After the samples have digested for two hours, allow them to cool to about 120° C in the reactor.
xii. Remove the vials from the reactor and invert each one several times to ensure the mixture is homogeneous.
xiii. Place the sample vials into a holding rack and allow them to cool and settle for at least 15 to 20 minutes.

b. Spectrophotometric Determination of COD
i. Turn on the Hach DR/2800™ Spectrophotometer or equivalent and allow about a 15 minute warmup period.
ii. Wipe the vial/cuvettes with a soft cloth or Kimwipe® until no smudge or liquid remains on the glass surface.

iii. Calibrate the DR/2800™ according to the method outlined in QAM-I-104, "Operation and Calibration of the Hach COD Meter", and set the wavelength to 420 nm. Other spectrophotometers may be used.

iv. Place reaction vial/cuvette into holding slot of the meter. Ensure that the painted vial label faces the same direction for each reading. Read the COD value for each blank, standard, sample, duplicate and spike according to the method outlined in QAM-I-104. Other meters may require calibration prior to operation, but the DR/2000™ stores calibration and only needs to be verified with the QC standards above.

v. Record the sample number or label and mg/L COD value measured for each vial/cuvette in a personal logbook.

vi. Enter QC and sample data into the ESDMS QC module. Report the blanks, percent recoveries and percent deviations as quality control acceptance criteria in accordance with QAM-Q-101.

xv. Data analysis and calculations;

a. Calculate the mg/L COD for the spike using the following formula.

C spike=Spiked Result - Unspiked Result

b. Calculate the percent recovery for the standards and spikes using the following formulas.

percent recovery = (M /C) x 100

M= mg/L COD measured

C= mg/L COD calculated

c. Calculate the relative percent deviation for each duplicate using the following equation.

RPD= (mg/L COD) sample - (mg/L COD) duplicate X 100

[(mg/L COD) sample + (mg/L COD) duplicate]/2

xvi. Method performance

a. refer to QAM-Q-101, "Laboratory Quality Control"

xvii. Pollution prevention

a. Pollution prevention: refer to QAM-W-101, "Disposal of Laboratory Waste"

xviii. Data assessment and acceptance criteria for quality control measures

a. For data assessment and acceptance, refer to QAM-Q-101, "Laboratory Quality Control"

xix. Corrective actions for out-of-control data

a. refer to QAM-Q-105, "Corrective Actions".

xx. Contingencies for handling out-of-control or unacceptable data

a. refer to QAM-Q-105, "Corrective Actions".

xxi. Waste management

a. Waste management: refer to QAM-W-101, "Disposal of Laboratory Waste"

xxii. References

a. DR/2800™ Spectrophotometer Procedures Manual, Hach Company, 2007, Edition 2. Method 8000.
b. The National Environmental Laboratory Accreditation Conference Institute (TNI) standard, 2016.
c. Personal Logbook 09-008, pp. 21-23. DOP for curve linearity and spiking solution, LOD study and LOQ compliance.

xxiii. Any tables, diagrams, flowcharts and validation data

none