
Chemical Oxygen Demand

Method SB1500/150

Finalized Method Approved for
NPDES Compliance Testing

COD Method SB1500/150

Method for the Analysis of Chemical Oxygen Demand in Water and Wastewater¹.

Method SB1500

This method is designed for the analysis of water and wastewater at 2 ranges, 0-150 ppm and 0-1500 ppm. The method determines the amount of oxygen required by the components of a sample when they are subjected to oxidation by potassium dichromate. Under the test conditions, oxidizable organic compounds reduce the yellowish dichromate ion to greenish chromic ion. The reagent contains silver ion to act as a catalyst, and mercury ion is used to complex possible chloride interferences.

The specified vials have been prepared using ACS reagent grade reagents and a proprietary chemical formula reviewed by USEPA. This method is accepted by the USEPA for NPDES compliance monitoring.¹¹

Sample Collection and Storage

Collect samples in plastic or glass containers. If analysis is not determined within 24 hours of collection, preserve sample by adding sulfuric acid until the sample pH is <2 (Approx. 2 ml per liter of sample.). Sample should be stored at 4°C. Preserved, refrigerated samples have a holding time of 28 days.

Sample Analysis

Step 1.0

Homogenize 50-100 ml sample in a clean blender for 15-30 seconds.

Step 2.0

Turn on the COD reactor. Allow approximately 30minute for a room-temperature block to reach 150°C.

Step 3.0

Determine which range test is desired, and obtain proper Test Vials.

Note: The vials contain materials which may be hazardous to the health and safety of the analyst if improperly used or accidentally mishandled. Proper safety precautions, including use of protective eyewear and clothing, should be established and observed when conducting this test. It is recommended that, prior to re-capping the vial after sample addition, the vial be wrapped in a soft cloth to protect against breakage. Tighten cap firmly, but take care not to cap too tightly, or the vial, cap, or both may break. Always use a safety shield during the digestion process.

Remove the cap from a COD Reagent Vial. Inspect the vial for any signs of breakage or cracking. Replace with a new vial if any damage to the vial is noted.

Pipette 2.00 ml of a well mixed sample, blank, or calibration standard into the vial by holding the vial at an angle. Prepare a minimum of 3 standards and one blank from 0-1500ppm or 0-150ppm. Calibration should be designed to cover the expected range of the samples. Report data only from results within the calibration range, diluting off scale samples until within the range.

Take care not to spill and reagent. If this occurs discard vial and repeat the above steps with a new vial. Rinse spilled area thoroughly with running water if this occurs.

Note: Contents of vial contain hazardous materials. Dispose properly according to applicable federal and state guidelines.

Replace cap on vial firmly. Holding vial by the cap, invert several times to mix the reagent with the sample.

CAUTION: The vial will become very hot during this mixing process.

Step 4.0

Carefully place up to 100 vials into the preheated COD reactor or other digestion block. Allow to digest for 2 hours at 150°C. Place safety shield in front of the COD reactor.

Some samples may be digested in less than 2 hours. If it is necessary to utilize this option, remove the vial from the digester and measure the concentration at 15 min intervals. If two or more readings remain stable, digestion can be considered complete.

Step 5.0

After the 2 hour digestion process, remove the vials from the COD reactor and carefully place into a rack. Allow to cool a few minutes. When safe to handle invert the vials 3 times each. Replace in rack and cool to room temperature. Allow any precipitate to settle completely before performing Spectrophotometric measurement.

Step 6.0

Measure samples, standards and blanks in a spectrophotometer, following manufacturers recommendations regarding operation. Wipe the blank sample vial with a damp cloth holding the vial by its cap. Be sure vial is clean and dry, then insert into spectrophotometer.

For samples in the 0-1500 ppm range, set the wavelength to 620 nm. Set the instrument to 100% Transmittance using the blank vial.

For the 0-150 ppm range, set the spectrophotometer wavelength to 420 nm. Using the blank vial, set the transmittance value to 35% T. The 150 ppm standard should be 100%T.

Measure the percent transmittance of standards. Convert to absorbance and plot concentration of standards versus sample absorbance using a calculator, graph paper or other appropriate means.

Note: The 0-150 ppm range method has a negative slope.

Once the calibration curve is determined, repeat measurement procedure with samples and QC standards.

Standard Preparation

Step 1.0

Prepare standards from ACS Reagent grade Potassium Acid Phthalate. Dry at 120°C overnight and store in a dessicator. Stock solutions are prepared by weighing 425 mg of potassium acid phthalate and adding it to 500 ml of reagent grade water in a 1000 ml volumetric flask. Dissolve then bring to volume. The solution will contain 1000 mg/L COD.

Reagent Grade water should be checked to ensure high quality. Dilution and blank water must be free of COD. Observation of blank readings against 5 ml of deionized water can help indicate degraded water quality.

To prepare 1500 mg/L COD Standard, prepare as above, but weigh 637.5 mg of the potassium acid phthalate.

Step 2.0

Prepare a series of standards to cover the desired calibration range by serial dilution of stock standards.

Blanks for Spectrophotometric or Colorimetric Analysis

Blanks should be prepared with each Lot of COD Reagent vials at a minimum. Vials are subject to UV degradation, and should be stored protected from light. To determine quality of blank, compare a newly prepared blank against 5 mls of deionized water. Record the absorbance readings at 620 and 420 nm. Prepare a new blank if the reading changes by 0.010 absorbance units or more.

Precision for Spectrophotometric Analysis

In a single laboratory by a single analyst using two different Lot Numbers of COD tubes the following precision was observed:

COD Tube Range	Lot #	Standard Value (ppm)	Standard Deviation
0-1500 ppm	31001A	500	8.1
0-1500 ppm	40204A	500	10.27
0-150	40425A	100	0.44
0-150	40314A	100	2.77

Estimated Detection Level

The EDL for the 0-1500 ppm range tubes is 20 ppm and for the 0-150 ppm range tubes is 4 ppm.

Interferences

The primary interference experienced in this determination is from chloride. Enough mercuric sulfate is added to the tubes to complex up to 2000 ppm of chloride. Higher levels can be tolerated by diluting the sample. If dilution will result in COD measurements lower than required, 0.5 g of mercuric sulfate may be added to each vial to compensate for the increased chloride interference. This will complex up to 4000 ppm chloride.

¹ Jirka, A.M., Carter, M.J., *Analytical Chemistry*, 1975, 47(8), 1397.

² 40CFR Ch. 1 (7-1—02 Edition)