Chapter 13
Chemical Oxygen Demand

The COD (Chemical Oxygen Demand) test represents the amount of chemically digestible organics (food). COD measures all organics that were biochemically digestible as well as all the organics that can be digested by heat and sulfuric acid. It is used in the same applications as BOD. COD has the advantage over BOD in that the analysis can be completed within a few hours whereas BOD requires 5 days. The major drawback of the COD test is the presence of hazardous chemicals and toxic waste disposal.

COD Theory

Like the BOD test, oxygen is used to oxidize the organics to carbon dioxide and water. However, instead of free dissolved oxygen, chemically bound oxygen in potassium dichromate $K_2Cr_2O_7$ is used to oxidize the organics.

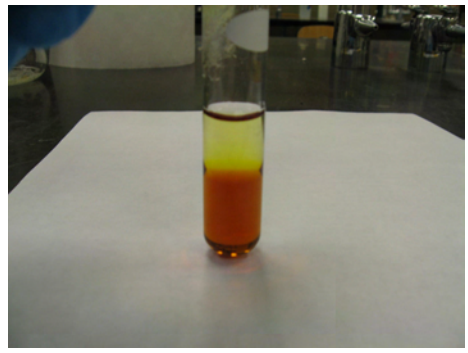
As the potassium dichromate is used up the Cr^{+3} ion is produced. The amount of dichromate used is proportional to the amount of organics present. Likewise, the amount of Cr^{+3} ion present is proportional to the amount of organics digested.

$$\text{Organics} + \underset{\text{(Orange)}}{K_2Cr_2O_7} \rightarrow \underset{\text{(Green)}}{Cr^{+3}}$$

Most labs use the Hach Method to measure COD. This method uses test tubes with pre-measured amounts of potassium dichromate, sulfuric acid, and catalyst. For the digestion to occur, the reaction needs acid, heat, and a catalyst.

The acid is sulfuric acid and is already in the tube. The sample will get very hot when the sample is added to the acid and mixed. Be sure the cap is on tight before mixing and mix just prior to placing in the digestion reactor.

SAFETY: Be very careful when adding water to acid. This is contrary to normal safety procedure. Be sure to wear goggles, gloves, apron, etc. and do not mix until the cap is tightened on the test tube.



The heat will be provided by the digestion reactor which is set at 150°C. The sample is refluxed (digested) for 2 hours. During the 2 hours, the organics are oxidized by the acid, potassium dichromate and catalyst.

The catalyst is silver. However, silver must be soluble and will precipitate if chlorides are present in the sample. To prevent silver precipitation, mercury has been added to the reagents in the tube. The mercury will remove the chloride interference.

Once the 2 hour refluxing period is finished, the remaining potassium dichromate is measured using the spectrophotometer.

Since this is a spectrophotometric test, a standard curve can be prepared as discussed earlier. However, this method is so reliable, that the Hach standard curve stored in the spectrophotometer software program is normally used to determine the sample concentration directly. As discussed earlier, a reagent blank and standard must be prepared to zero the spectrophotometer and validate the curve.

Sample Collection

The sample is usually collected the same as BOD, but is not generally used for NPDES purposes. Most NPDES permits specify BOD because it gives a better representation of the organics that are affecting the receiving stream. The COD sample may be a composite or a grab sample. Because there are no microorganisms involved in this procedure, preservation is usually acidification using sulfuric acid to a pH below 2. Refrigeration is acceptable if BODs are also to be run on the sample. The sample holding time is 7 days, much longer than the 24 hours allowed for the BOD test.

Sample Handling

The sample volume used for the COD test is 2.0 ml so measuring the sample volume is critical. Be sure to mix the sample well and homogenize if necessary. Pipet quickly to avoid settling errors. CODs can be run on industrial samples that may have high BODs. If the COD strength is greater than 1650 mg/L, the sample must be diluted. Make a 1:2 dilution by measuring 50 ml of sample and adding to 50 ml of deionized water, then add 2.0 ml of the well mixed dilution to the test tubes.

COD Procedure

KHP Standard Preparation

1. Place about 5 grams of Potassium Hydrogen Phthalate (KHP) in an aluminum weighing dish.
2. Place the aluminum dish in the drying oven at 110°C for 2 hours. Remove the dish from the oven and place in the desiccator until time of use.
3. Weigh 0.4251 gm of dried KHP on a calibrated analytical balance.
4. Transfer completely to a 1000 ml volumetric flask.
5. Fill to the mark with deionized water**.** This prepares a 500 mg/L standard. Store in the refrigerator.

Select the Method

Hach Chemical Co. uses two methods for COD, a high range 0-1500 mg/L and a low range, 0-150. Use the low range for effluent samples and the high range for all other samples. The procedure for both methods is essentially the same until measuring with the spectrophotometer. The concentration of dichromate in the low level method is 10x lower than in the high level method.

Blank Preparation

1. Obtain a Hach COD high level tube (Dark orange)
2. Using a 2.0 ml volumetric pipet, add 2 ml of deionized water to the COD tube.
3. Replace the cap and tighten.

SAFETY: When liquid is added to the tubes, the tubes will become very hot when mixed.

4. Carefully mix by inverting several times to suspend the powder in the bottom of the tube.
5. Place the tube in the Hach Reactor at 150°C.

KHP Standard Preparation

1. Obtain a second Hach COD high level tube (dark orange)
2. Using a 2.0 ml volumetric pipet, add 2 ml of the 500 mg/L KHP standard to the COD tube.
3. Replace the cap and tighten.
4. Carefully mix by inverting several times to suspend the powder in the bottom of the tube.
5. Place the tube in the Hach Reactor at 150°C.

High Level Sample

1. Obtain a third Hach COD high level tube (dark orange)
2. Using a 2 ml serological pipet, add 2 ml of the sample to the COD tube. If necessary, homogenize the sample for 1 minute. If the sample is expected to be >1500 mg/L, the sample can be diluted. Add 2 ml of each dilution to a separate COD tube. For instance, a 1:2 dilution could be made by adding 50 ml of the homogenized sample to 50 ml of DI water. Mix and quickly pipet into the COD tube to avoid settling errors.

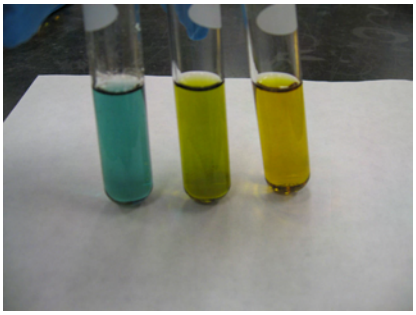


Figure: Sample dilutions. Left sample is >1500 mg/L. All dichromate is gone.

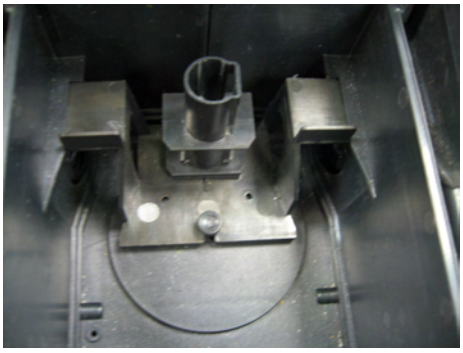
3. Replace the cap and tighten.
4. Carefully mix by inverting several times to suspend the powder in the bottom of the tube.
5. Place the tube in the Hach Reactor at 150°C.

Sample Digestion

1. Turn on the power switch located in the back of the digestion apparatus. Allow the digestion apparatus to warm up by pressing the infinity switch (∞).
2. After the blanks, standards, and samples have been placed in the digester, turn the timer to 120 minutes.
   Press the timer button to begin the timed digestion. The digestion apparatus will turn off automatically.

Sample Measurement

1. Turn on the Spectrophotometer and allow to warm up for 10 minutes.
2. Insert the Hach COD tube adapter.



3. Set up the spectrophotometer to the correct Hach program (2720). The wavelength should be displayed. Record the wavelength used.

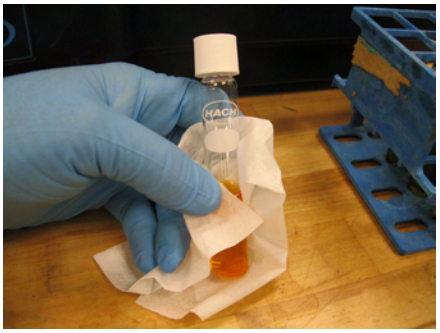


Figure: Wipe with kimwipe® to remove fingerprints, dirt.

4. Using a kimwipe®, wipe off the outside of the COD Blank. Insert the blank into

the sample holder with the Hach name facing forward.

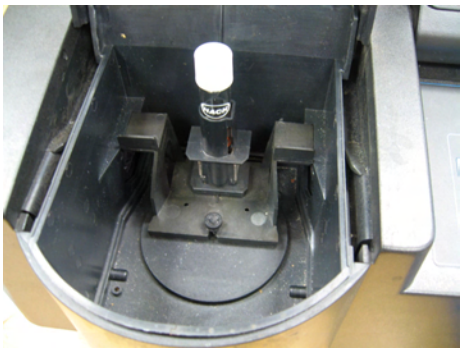


Figure: Insert tube into cell holder

Close the cover and press the ZERO button. The display should now show "0". Record the display value on the data sheet

Figure: Zero the spectrophotometer using a reagent blank.

5. Using a kimwipe®, wipe off the outside of the COD 500 mg/L KHP Standard. Insert the standard into the sample holder with the Hach name facing forward. Close the cover and press the READ button. Record the display value on the data sheet.

6. Using a kimwipe®, wipe off the outside of the sample. Insert the sample into the sample holder with the Hach name facing forward. Close the cover and press the READ button. Record the display value on the data sheet.

Troubleshooting

Very little goes wrong in this test. Most errors come back to lab technician techniques. The most critical errors occur with the blank and KHP standard.

The spectrophotometer must be warmed up and zeroed using the reagent blank. If the volume of DI water added to the reagent blank is not 2.0, the color of the reagent blank will be either lighter or darker than expected. This error will be most noticeable when using the low range method.

Likewise, if the KHP standard does not fall at 500 $\pm$ 50, the samples should be invalidated. The lab technician should critique the standard preparation procedure.
1. Was the balance calibrated prior to weighting the KHP?
2. Was the standard weighed correctly?
3. Was the powder spilled during standard preparation?
4. Was the KHP volume pipetted correctly?
5. Were the caps on the standard loose during digestion?
6. Were the sample cells wiped clean?
7. Is the correct wavelength being used?
8. Has the KHP standard deteriorated? cloudy?

If the KHP standard and the digestion reactor temperature are incorrect, the data must be invalidated.

Quality Control

The lab technician should document the following information to support the COD data. Use the following checklist to determine if sufficient information has been recorded to support the data in court.

Sample

 Sample holding time cannot exceed 7 days. Corrective Action: Reject samples and request a resample.
 Samples must be preserved with sulfuric acid or refrigeration until time of analysis. Corrective Action: Adjust refrigerator to below 4°C. Service the refrigerator if the temperature does not adjust properly.
 pH meters must be calibrated daily, prior to use. A minimum of 2 buffers should be used, with a 3rd buffer typically used. Corrective Action: If the pH meter cannot be calibrated, replace the electrode. Document the electrode replacement.
 Samples must be warmed to room temperature prior to COD analysis.
 Samples with large chunks of non-homogeneous materials should be homogenized for 1-2 minutes for better precision and accuracy. Avoid excessive homogenization which might cause volatilization of some solids.
 Samples must be mixed well and measured quickly to avoid settling errors.

Equipment

 Hach Digester must be 150°C $\pm$ 2.0^{o}C and should be checked. Corrective Action: Digester outside the control limits must be adjusted.
 Immerse the thermometer in the heating block for duration of digestion.
 Calibrate the digester thermometer at least annually against a NIST certified thermometer.
 Use an analytical balance capable of weighing 0.0001 gm to weigh the KHP
Calibrate the analytical balance annually using a certified balance technician.
 Calibrate the analytical balance monthly using Class 1 weights. Select a series of weights which covers the range of balance operation. Usually 1, 2, 5, 20, 50, and 150 gm weights are used
Corrective Action: If the weights deviate more than 0.0002 grams, the balance needs service.
 Calibrate the spectrophotometer using a reagent blank for each run.

COD Test

 Prepare fresh KHP standard at least quarterly. Discard if growth or precipitation present.
 KHP is dried and stored in desiccator
 Zero the analytical balance prior to each weighing series
 Use volumetric pipets for standards and blanks. Use large bore serological pipets for samples.
 Performance evaluation samples should be run at least annually
 KHP standard run with each set of samples.
 KHP standard value 100 mg/L $\pm$ 10 for low level, 500 $\pm$ 50 for high level.
Corrective action: If the KHP standards are outside the acceptable levels, new KHP should be prepared and the analysis repeated. Samples should be invalidated.

 Document dates/times
 Document heating block temp
 Document reagents: lot number, expiration date, purchase date.
 Reagent blank used to zero the spectrophotometer
 Document KHP standard-preparation/purchase date, concentration
 Document wavelength used
 Document method used
 Thermometer calibration
 Balance calibration

- PE samples annually
- Make/Model spectrophotometer
- Document time digestion begins and ends on the data sheet.
- Run duplicates 10% of time