



Method 9.12 – Effluent: chemical oxygen demand (COD)

1. Rationale

The method is used to estimate the amount of organic matter in effluent. It is a measurement of the oxygen equivalent of the oxidisable materials present in the effluent.

2. Principle

Small volumes of effluent are pipetted into vials containing a strong chemical oxidant (in this case dichromate) catalysts and a chloride compensator. The vials are incubated until the digestion is complete and cooled. The COD is measured using a colorimeter.

3. Apparatus

- 3.1 **Dedicated COD colorimeter** for use at 610 and 420 nm
- 3.2 **Graduated pipettes:** 2 and 10 cm³
- 3.3 **pH meter**
- 3.4 **COD reactor** with a plastic safety shield
- 3.5 **Test tube rack**
- 3.6 **Volumetric flask:** 100 cm³

4. Reagents

4.1 **Pre-measured reagents in screw cap vials**

Low range: 0 - 150 ppm COD
High range: 0 - 1 500 ppm COD

The contents of the vials (mainly sulphuric acid and potassium dichromate) are corrosive and toxic and gloves and safety glasses must be worn during handling. Vials should also only be opened inside a fume cupboard.

The vials fit snugly into the COD reactor and into the dedicated COD colorimeter.

The mixture of potassium dichromate and sulphuric acid is sensitive to ultraviolet light. To avoid reagent deterioration during storage, keep reagent vials protected from all light sources and in a refrigerator if available.

4.2 **Distilled water**

4.3 **COD standard solution:** 1 000 mg/litre

5. Procedure

5.1 Sample handling

Collect samples in glass bottles if possible. Biologically active samples should be tested as soon as possible. Samples containing solids should be well mixed to permit the removal of a representative aliquot. If samples cannot be analysed the same day that they are collected, add 2 cm³ concentrated sulphuric acid, for each litre of sample taken, using a glass pipette and pipette filler. Mix. Check the sample pH to be sure the pH is 2 or less. Add more acid if necessary. Samples preserved in this manner can be stored at 4°C for up to 28 days.

5.2 Digestion of the samples

Preheat the COD reactor to 150°C. Cautiously remove the cap from a high or a low range vial and carefully pipette 2 cm³ of the effluent sample to be tested for COD into the appropriate vial. The choice of using high or low range depends on the experience of the analyst. If the result is out of the chosen range the test has to be repeated using the other range. Spilled reagent will affect the test accuracy and is hazardous to the skin and other materials. Do not run the COD test with vials that have had reagents spilled from them. Replace the caps. To avoid vapour loss and accidental spillage, be sure caps are well tightened.

Swirl the vials until the contents are mixed. Place the vials in the preheated COD reactor. The plastic safety shield should be in place on the heater block before vials are placed in the reactor. Prepare a reagent blank by substituting 2 cm³ of distilled water in place of the effluent sample added to a high or low range vial. Heat the vials for 2 hours at 150°C. Turn the reactor off and allow the vials to cool to 120°C or less. The cooling will require about 20 minutes. Place vials in a cooling rack and allow to cool to touch.

At least one blank should be run with each set of samples.

5.3 Colorimeter check

The accuracy of the low range of the instrument can be checked by diluting 10 cm³ of the 1 000 mg/litre COD standard solution to 100 cm³ to produce a 100 mg/litre standard. The expected result will be 100 mg/litre COD (± 5). Use 2 cm³ as the sample volume.

The accuracy of the high range can be checked by using the 1 000 mg/litre standard. The expected result will be 1 000 mg/litre COD (± 29). Use 2 cm³ as the sample volume. Perform an accuracy check on each new batch of vials.

5.4 Colorimetric measurement (0 - 1 500 mg/litre COD range)

Install module 61.01 in the colorimeter. Press I/O. The display will show 610 nm and module number 61.01. After two seconds, the display will show a program number, the concentration units and the zero prompt. If necessary, press the up arrow key until the lower display shows program number 61.08.1. Fully insert a COD vial adaptor into the cell holder with the tabs in the square slot. Clean the outside of the blank with a towel. Place the blank into the adaptor with the Hach logo facing the front of the instrument. Press zero. The display will count down to zero. Then the display will show 0.00 mg/litre, and the zero prompt will turn off. Clean the outside of the sample vial with a towel. Place the sample vial in the adaptor with the Hach logo facing the front of the instrument. Press read. The display will count down to zero after which the display will show the results in mg/litre COD.

5.5 Colorimetric measurement (0 - 150 mg/litre COD range)

Install module 42.01 in the colorimeter. Press I/O. The display will show 420 nm and module number 42.01. After two seconds, the display will show a program number, the concentration units and the zero prompt. If necessary, press the up arrow key until the lower display shows program number 42.06.1. Fully insert a COD vial adaptor into the cell holder with the tabs in the square slot. Clean the outside of the blank with a towel. Place the blank into the adaptor with the Hach logo facing the front of the instrument. Press zero. The display will count down to zero. Then the display will show 0.00 mg/litre, and the zero prompt will turn off. Clean the outside of the sample vial with a towel. Place the sample vial in the adaptor with the Hach logo facing the front of the instrument. Press read. The display will count down to zero after which the display will show the results in mg/litre COD.

6. Expression of Results

If a pure green colour is obtained in a reacted sample, all the dichromate has been reduced to the chromic state. It will be necessary to repeat the digestion with a diluted sample.

The blank has been found to be stable when kept in the dark. It can be monitored for decomposition by using the absorbance scale and reading the absorbance at 420 nm and 610 nm for the low and high range vials, respectively, after zeroing the meter using a vial containing 5 cm³ of distilled water. Prepare a new blank when the absorbance has changed by about 0.01 absorbance units.

The permissible COD level for discharging into a public watercourse is 75 mg/litre.

Express the result as mg COD/litre effluent.

7. References

Hach DR/700 Dedicated Colorimeter Manual.

Purchase BS and Proudfoot S (1985). An improved method for chemical oxygen demand (COD) analyses. *SMRI Technical Report* No. 1420, 9 pp.

SMRI (1997). Determination of the chemical oxygen demand in effluent by the semi-micro method. *SMRI Test Methods*, TM201.