BANK OR DRAIN

Pollution Prevention Pays in Food Processing

Using COD to Measure Lost Product

BOD$_5$ and COD Values of Dairy Products

Product	BOD$_5$ (mg/l)	COD (mg/l)	BOD$_5$/COD
Milk	104,600	173,000	0.60
Ice cream (10% fat)	292,000	540,000	0.54
Whey (acid)	32,000	70,000	0.54

Food processing plants produce various types of waste materials (solid, liquid, and gaseous) during routine operations. Indiscriminate or improper disposal of these waste materials or discharge of improperly treated waste materials can harm the environment and can result in surcharges, fines, or civil and criminal penalties.

As environmental regulations become stricter and the food industry expands, it becomes important for processors to have methods for sampling waste streams. Routine sampling and testing will enable a food processor to determine which activities and products produce the greatest waste streams.

What Are BOD$_5$ and COD?

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD$_5$) are measurements commonly used to determine water quality. Many of the wastes in the effluent from food processing plants are organic compounds, primarily lost product. As these substances oxidize or stabilize, they combine with some of the oxygen dissolved in the water. The amount of oxygen used is therefore a good indicator of the amount of organic waste present. The BOD$_5$ and COD values for three dairy products are shown in the table above. The values indicate the amount of oxygen (in milligrams per liter of product) needed to oxidize or stabilize these products when they appear in wastewater.

COD and BOD$_5$ are of special interest to the food processing industry as they can be a useful tool for indicating lost product and wasteful practices. High BOD$_5$ and COD levels indicate increased amounts of product lost to the waste stream.

Greater numbers of food processing plants are taking steps to reduce waste and save water because of rising treatment costs and increased environmental standards. BOD$_5$ and COD measurements can help isolate areas of severe waste.

Why COD?

Although regulatory agencies require the monitoring and reporting of BOD$_5$ levels, the COD test has several advantages for the plant’s operation staff. Time (speed) is the major advantage: a COD 2-hour reflux test is standard. A COD test of easily oxidized waste may take even less time. The BOD$_5$ test is time consuming, requiring a standard 5-day incubation period. The rapid test results of the COD procedure provide an advantage to the processor monitoring daily waste production and wastewater discharge.

Another advantage of the COD test is that strong oxidizing conditions are somewhat independent of variations in experimental conditions and procedures. This is not true for the BOD$_5$, test, which is sensitive to test conditions and can vary depending upon the seed (microbial) culture used. In addition, the BOD_5 test, unlike the COD test, does not measure biologically resistant compounds

Are COD and BOD_5 Interrelated?

At any point in a particular food processing operation, the relationship between BOD_5 and COD is fair] y consistent, The ratio of these two measures varies widely with the type of product, however, Typical BOD_5 and COD values for the wastewatcr from seven types of food processing operations are shown in the table on this page. For example, a bakery product having a COD of 7,000 mg/1 would have a corresponding BOD_5 of 3,200 mg/l. The ratio of BOD_5 to COD, shown in the right column, ranges from 0.46 to 0.83. The ratio also depends on where the measurements are made in the processing operation or in the wastewater treatment process.

COD values are greater than BOD_5 values because of the nature of the measurement procedure. With the bichromate refluxing procedure used to measure COD, almost all organic compounds will oxidize. With the BOD_5 measurement procedure, some of these compounds do not fully oxidize, making the oxygen demand lower. The BOD_5 value may be much lower than the COD value when a substantial amount of biologically resistant organic matter is present. In addition, a few chemical interferences —- primarily from chlorides and certain nitrogen compounds — can affect the test results. For further information, see “Elimination of Interference .“

Values of BOD_5 and COD for Food Plant Wastewaters

Type of Processor	BOD_5 (mg/1)	COD (mg/1)	BOD_5/COD
Poultry processor	1,306	1,581	0.63
Frozen bakery products	3,200	7,000	0.46
Meat specialties	530	800	0.59
Jams and jellies	2,400	4,000	0.60
Meat packing	1,433	2,746	0.52
Dairy processing	2,700	4,700	0.57
Gulf shrimp canning	1,081	2,296	0.47

Bichromate Reflux Technique Standard Method

Equipment Required

1. 500-milliliter (ml) Erlenmeyer flask with standard (24/40) tapered glass joints
2. Friedrichs reflux condensers (12-inch) with standard (24/40) tapered glass joints
3. Electric hot plate or six-unit heating, shelf
4. Volumetric pipets (10, 25, and 50-ml capacity)
5. Buret, 50 ml +/- 0.1 ml accuracy
6. Buret stand and clamp
7. Analytical balance, accuracy 0.001 gram (g)
8. Spatula
9. Volumetric flasks (1,000 ml capacity)

1(). Boiling beads, glass

11. Magnetic stirrer and stirring bars

Chemicals Required

1. Potassium bichromate ($K_2Cr_2O_7$) 0.25 N
2. Sulfuric acid (H_2SO_4)–silver sulfate (Ag_2SO_4) solution
3. Mercuric sulfate ($HgSO_4$) crystals
4. Ferrous ammonium sulfate (FAS) $[Fe(NH_4)_2(S0_4)_2]$, approximately 0.01 N
5. Ferroin indicator (1, 10-phenanthroline and ferrous ammonium sulfate)

Caution: In carrying out the following procedures, use proper safety measures, including protective clothing, eye protection, and a fume hood. Reagents containing heavy metals ($HgS0_4$) and Ag_2S0_4) should be disposed of as toxic wastes.

Chemical Preparation

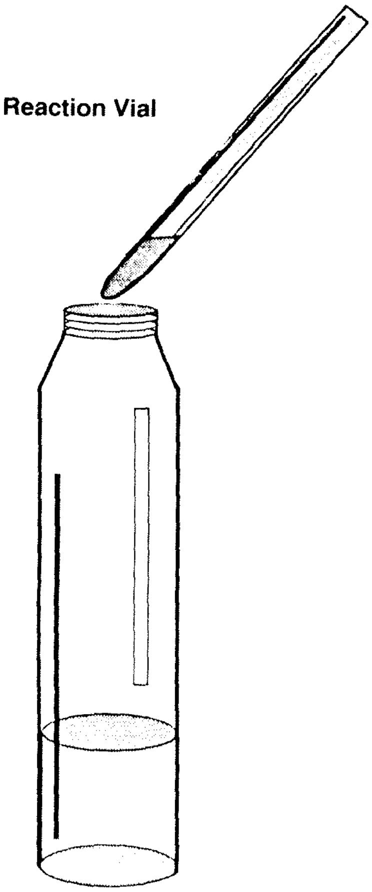
1. Dissolve 12.259 g of oven-dried (primary standard grade dried 103^{o}C to a constant weight) potassium bichromate in distilled water and dilute to 1-liter volume in a volumetric flask.
2. Add 22 g of reagent grade silver sulfate to a 4-kg bottle of concentrated sulfuric acid (H_2S0_4) and mix until the silver sulfate goes into solution.
3. Use 1 g of mercuric sulfate ($HgSO_4$) to complex 100 mg chloride (2,000 mg/l).
4. Dissolve 1.485 g of 1, 10-phenanthroline monohydrate and 0.695 g of ferrous ammonium sulfate heptahydrate in distilled water and dilute to approximate] y 100 ml. (Alternatively, this indicator may be purchased from most scientific supply houses.)
5. Dissolve 39 g reagent grade ferrous ammonium sulfate hexahy - drate in distilled water. Add 20 ml of concentrated sulfuric acid (H_2SO_4). Cool and dilute to exactly 1 liter in a volumetric flask using distilled water. The ferrous ammonium sulfate (FAS) titrant must be standardized daily by the following procedure. Dilute 10 ml of standard potassium bichromate ($K_2Cr_20_7$) solution to 100 ml with distilled water. Slowly add 30 ml of concentrated sulfuric acid and cool to

1. Place approximately 500 ml of sample in a clean blender bowl and homogenize at high speed for 2 minutes. This ensures a uniform distribution of suspended solids and improves both accuracy and repeatability.

2. Preheat COD reactor to 150°C. Place a towel around a COD digestion reagent vial of desired range and remove the cap. Carefully pipet 2.00 ml of sample with a large-bore pipet into the vial while holding the vial at a 45-degree angle directed away from you.

Caution: Do not use vials that have reagent spilled or leaked because the test accuracy wilI be affected and reagents may be hazardous to the skin.

3. Using a dry towel wrapped around the vial, cautiously replace and tighten cap. Hold vial by the cap over an empty sink and invert several times to mix contents.



Caution: Vial will become hot during mixing procedure and the towel will decrease heat transfer.

4. Have plastic shield in place on heater block and insert vial in preheated COD reactor.

5. Prepare a reagent blank by substituting 2.00 ml of distilled or demineralized water for the wastewater sample and follow steps 1 through 4.

6. Heat vials at 150°C for 2 hours. Turn off the reactor and allow vials to cool to 120°C or less (requires approximate] y 20 minutes). Invert each vial several times while still warm

7. Place vials in cooling rack and allow cool to touch touch.

8. Measure COD by the titrametric or calorimetric method. One blank from same vial lot should be tested with each set of samples.

9. COD standard solutions can be used to replace wastewater samples to monitor accuracy.

Calorimetric Measurement (O to 150 mg/l COD)

1. Place the COD vial adapter in the cell holder of the spectrophotometer with the raised marker to the left. Insert the vial containing the reagent blank into the adapter and install the cover. Insert the oxygen demand, chemical low-range meter scale into the meter and adjust the wavelength dial to 600 nm.

2. Set mode switch to LEFT SET and adjust the LEFT SET control to align the meter needle with the extreme left mark of the meter scale arc.

3. Set the mode switch to NORM and adjust the RIGHT SET control for a meter reading of O mg/1.

4. Place the vial containing the test sample in the adapter, replace light shield, and read mg/l from the meter scale.

Modification of Alternative Procedures

Modification of alternative procedures can result in a cost savings. Changes that produce similar results but utilize available equipment can show a sizable savings in the initial or start-up costs. The following modifications can be utilized for cost or time savings once a procedure is found that produces desired results. Modifications include:

- Using an oven that maintains 150°C ± 2°C instead of purchasing a manufacturer’s heating control.

Caution: Maintain precise temperature and ensure a pressure tight seal on the digestion vials. (A shield should be provided to protect against explosion when heating vials).

- Snap-off glass vials can be heat sealed with a propane torch.

Caution: Prevent boiling the digestion mixture by applying heat to tip or end of sealing neck.

A colorimetric procedure may be accomplished with the use of any spectrophotometer that can produce a 600-nm wavelength and has a 1 -cm light path. A standard curve can be prepared by digestion of known COD value samples and plotting concentration versus percent transmittance. A sample of 850 mg of potassium acid phthalate dried to a constant weight at 10°C diluted to 1 liter with carbon dioxide (CO_2) free distilled water will produce 1,000 mg/1 COD.

A titrametric procedure can be accomplished by quantitative] y transferring the contents of the digestion vials to an Erlenmeyer flask and diluting it to approximately 200-ml final volume with distilled water. Titrate to the “ferroin” endpoint with 0.015 N ferrous ammonium sulfate.

1. Place approximately 500 ml of sample in a clean blender bowl and homogenize at high speed for 2 minutes. This ensures a uniform distribution of suspended solids and improves both accuracy and repeatability.

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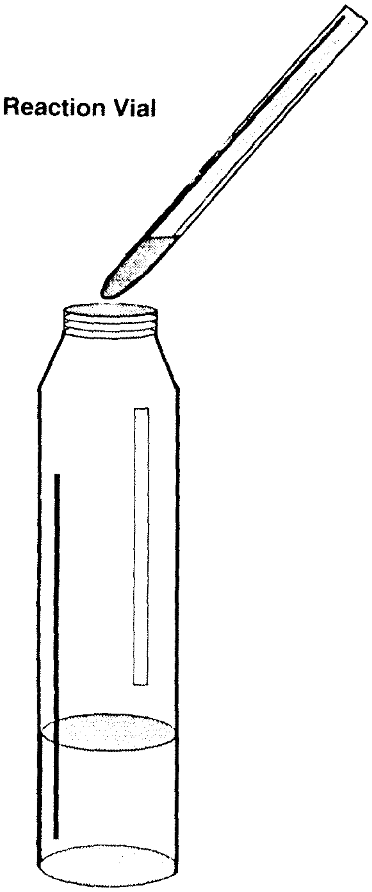

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Elimination of Interference

One gram of mercuric sulfate ($HgSO_4$) will complex 100 mg of chloride in a 50-ml sample (2,000 mg/l). For samples higher in chloride more $HgS0_4$ should be used in the ratio of 10:1 $HgSO_4$

Interference from nitrites can be prevented by the addition of 10:1 ratio of sulfamic acid: nitrite. The addition of the silver sulfate ($AgSO_4$) concentrated sulfuric acid (HSO_4) refluxing acid will aid in the oxidation of some organic nitrogen compounds, but aromatic hydrocarbons and pyridine are not oxidized to any appreciable amount.

HACH Semimicro- Alternate Procedures

Equipment and Chemicals Required

1. **HACH COD** test system kit including:

a) Sample vials with caps

b) Pipets (2-ml capacity)

c) COD reactor block heating unit

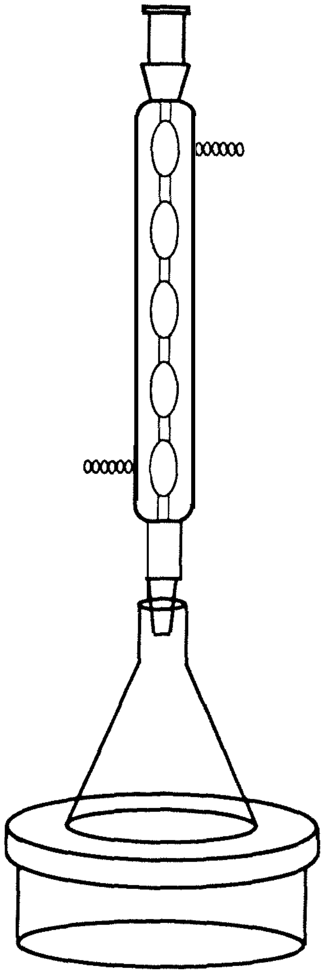
d) Spectrophotometer, wavelength setting 600 nm

Procedure HACH Semimicro

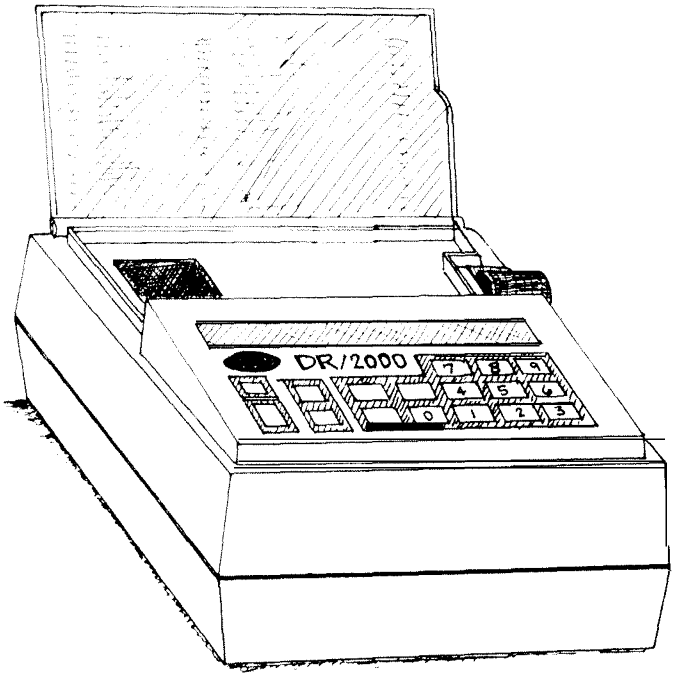
WARNING

1. Vials contain hazardous materials (sulfuric acid and mercuric salts) and are heated to 150^{o}C (302^{0}F). The aluminum block heater could cause severe burns if touched, and a glass vial could burst. Wear protective clothing (gloves, goggles, or face mask) when performing the test. Wipe up spills immediately and rinse any skin area contacted with cool water.

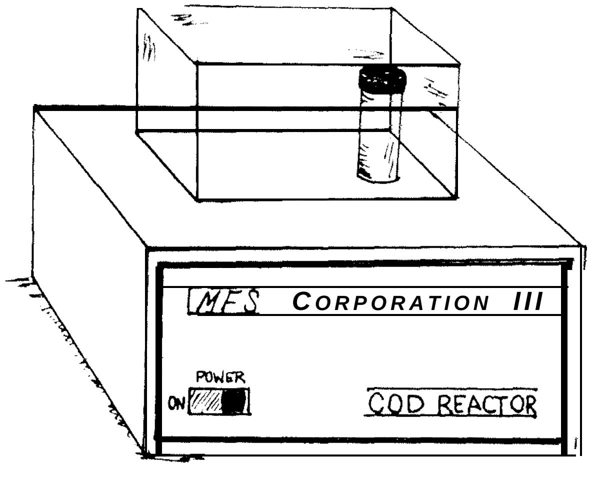
2. Bare terminals on the reactor could cause severe shock if touched. Always disconnect power before removing the reactor cover.



Erlenmeyer flask with Friedrichs Reflux Condenser



Spectrophotometer



COD Reactor

room temperature. Titrate with ferrous ammonium sulfate titrant, using 2 to 3 drops (0.10 to 0.15 ml) of ferroin indicator.

$$\text{Normality of FAS} = \frac{(\text{ml K,Cr,0}_7)(0.25)}{\text{ml FAS required}}$$

The deterioration of FAS can be decreased if it is stored in a dark bottle.

Procedure

1. Place a 50-ml sample or an aliquot diluted to 50 ml in a 500-ml refluxing flask. The blank is prepared using 50 ml of distilled water. This is a precise measurement and a 50-ml volumetric pipet should be used. (Refer to “COD Range and Sample Size” below for dilution.)

2. Add 5 to 7 glass boiling beads.

3. Add 1 g of mercuric sulfate ($HgSO_4$), 5 ml of concentrated sulfuric acid, mercuric sulfate solution, and mix until the $HgSO_4$) is in solution. The function of the mercuric sulfate is to bind or complex chlorides. One gram may not be required if the chloride concentration is low. (Refer to “Elimination of Interference.” p.4)

Caution: Always add acid slowly down the side of the flask while mixing to avoid overheating. It may be necessary to use gloves because of the heat generated.

4. Add 25 ml of 0.25 N potassium dichromate ($K_2Cr_2O_7$) and mix.

5. Add while mixing an additional 70 ml of concentrated sulfuric acid-silver sulfate solution.

6. After thorough mixing, attach the flask to the reflux condenser, apply heat, and reflux for 2 hours. Refluxing time can be decreased depending on the ease of oxidation of organic materials. This time may be determined by refluxing for periods from 15 minutes to 2 hours and comparing the results.

7. A reagent blank containing 50 ml of distilled water treated with the same reagent as the sample should be refluxed with each set of samples.

8. Cool the apparatus to room temperature after the refluxing period. Wash down the interior of the condenser and flask twice with approximately 25-ml portions of distilled water.

9. Remove flask from the condenser and dilute to a final volume of approximately 350 ml with distilled water.

10. Add 4 to 5 drops of ferroin indicator and a magnetic stirring bar.

11. Place flask on a magnetic stirrer and rapidly titrate with 0.1 N ferrous ammonium sulfate to the first red brown endpoint.

Caution: Use care in titration. The endpoint is very sharp and may be reached rapidly.

12. Formula to determine COD

$$\text{COD (m/l)} = \frac{(a-b)(N) \text{ x } 8{,}000}{\text{sample size (ml)}}$$

a = ml $Fe(NH_4)_2(SO_4)$ used for blank

b = ml $Fe(NH_4)_2(SO_4)$ **used** for sample

N = normality of ferrous ammonium sulfate (FAS) $Fe(NH_4)_2(SO_4)$:

ml sample = the actual volume of sample used before dilution

Sources of Error

1. The largest error is caused by using a nonhomogeneous sample. Every effort should be made to blend and mix the sample so that solids are never excluded from any aliquot.

2. Always use the largest sample practical and use the largest glassware that is in keeping with good laboratory practice.

3, Use volumetric flasks and volumetric pipets with a large bore.

4. The K_2CrO_7 oxidizing agent must be precisely measured. Use a volumetric pipet and use the same one each time if possible.

5. When titrating, be certain that the buret is clean and free of air bubbles.

6. Always read the bottom of the meniscus and position the meniscus at eye level.

COD Range and Sample Size

COD Range(mg/1)	**50-800**	**100-1,500**	**240-8,700**	**480-7,500**	**1,200-18,800**	**2,400-3,706**	**24,000-375,000**
Volume of Sample (ml)	**50**	**25**	**10**	**5**	**2**	**1**	**0.1**

All samples high in solids should be blended for 2 minutes at high speed and stirred when an aliquot is taken. Sample volumes less than 25 ml should not be pipetted directly, but serially diluted and then a portion of the diluent removed:

(1) 500 ml of sample diluted to 1,000 ml= 0.5 ml sample/ml of diluent,.: 50 ml of diluent = 25 ml of sample.

(2) 100 ml of sample diluted to 1,000 ml= 0.1 ml sample/ml diluent,.: 50 ml of diluent = 5 ml of sample.

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