

Chapter 6

BOD and COD

1. Biochemical Oxygen Demand (BOD)

I. Principle

Biochemical oxygen demand (BOD) is a term used to indicate the amount of oxygen used to break down biodegradable organic matter through biochemical processes. BOD is measured using a manometric method (pressure measurement in a closed system) based on the Warburg respirometer, in which biomass respiration is directly measured. A sample volume is placed in ground-glass stoppered flasks.

A quantity of water is poured into a 510 mL incubation bottle, sealed with a stopper equipped with a pressure sensor (oxytop). The volume chosen depends on the desired measurement range. The measuring device, of the OxiDirect type (BSB BOD), is placed in a refrigerator maintained at 20 °C. Oxygen consumption, indicated by a decrease in air pressure, is then monitored over time, daily for 5 days for BOD5. The oxidation of organic matter causes the formation of CO₂, which is trapped by a potassium hydroxide (KOH) solution in the bottle's rubber seal. This creates a vacuum inside the bottle.

The addition of the nitrification inhibitor (ATH: 2-allyl thiourea) helps to slow down nitrification, because the oxidation of ammonia derivatives and nitrites to nitrates also absorbs oxygen. This amine acts as an inhibitor.

I.1. Matériels nécessaires



Figure 1 : BOD bottles **Figure 2** : Incubator

I.3. Workbench

- 4 bottles of 500 ml
- Oven 20°C
- 1'allyl 2 thiourea: C₄H₈N₂S
- KOH

Operating procedure

- Evaluate the measurement range of the sample to be analyzed and choose the sample volume according to the table below.
- Measure the exact sample volume using the overflow flask and pour it into a BOD bottle (using a funnel if necessary).
- Insert a stirring bar into the BOD bottle
- Add the required number of drops of ATH (see table below) to the bottle
- Screw the BOD probe onto the bottle
- Place the sample on the bottle holder.
- Turn the device on by pressing the ON/OFF button
- Incubate the sample at 20°C.
- Record the values after 5 days.

Table I.1: Sample volume as a function of the BOD₅ range

BOD ₅ range (mg O ₂ /L)	Sample volume (mL)	Dosage (ATH)
0 – 40	428	10 drops
0 – 80	360	10 drops
0 – 200	244	5 drops
0 – 400	157	5 drops
0 – 800	94	3 drops
0 – 2000	56	3 drops
0 – 4000	21.7	1 drop

2. CHEMICAL OXYGEN DEMAND (COD)

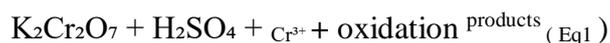
I. Principle

The chemical oxygen demand (COD) reflects the oxygen requirements of oxidizable substances present in wastewater. These are largely organic materials that will be oxidized during enzymatic reactions, or oxidizable ions (ferrous iron, chlorides, sulfides, nitrites, etc.). COD helps to understand the effectiveness of the treatment applied and to assess the environmental impact of discharges.

COD corresponds to the amount of oxygen released from potassium dichromate reacting, under the operating conditions of the indicated process, with the oxidizable substances contained in 1 L of water. 1 mol of $K_2Cr_2O_7$ corresponds to 1.5 mol of O_2 . COD is expressed in mg/L (= mg/L of O_2).

The reactions can be summarized as follows:

- ❖ *Oxidation of substances (s^*) present in water*



- ❖ Intervention by a masking agent

To prevent the oxidation of chloride ions to chlorine, mercury(II) sulfate is used, which complexes the Cl^- ions:



- ❖ Titration reaction



I.2. Products and equipment

I.2.1. Products

- Concentrated sulfuric acid $d = 1.83$ g/l (dangerous);
- Diluted sulfuric acid 4 M;
- Solution of silver sulfate in concentrated sulfuric acid, (dangerous);
- 0.12 M ammonium iron sulfate solution;
- Mercury sulfate crystals;
- Potassium dichromate solution 0.04 M;
- Aqueous solution of tris(1,10-phenanthroline)iron(II) sulfate (ferroin).

1.2.2. Equipment

- Reflux device;
- 250 ml balloons;
- 5 ml graduated pipette;
- 25 ml burette;
- 10 ml and 20 ml test tubes;
- Heating ramp;
- Magnetic stirrer .



Figure 1: Reflux device

1.3. Operating Protocol

❖ Determination of the exact quality of Mohr salt

- In a 250 ml Erlenmeyer flask, introduce 10 ml of 0.25 N $K_2Cr_2O_7$ solution and 90 ml of distilled water . Slowly add 30 ml of concentrated H_2SO_4 . Cool .
- Add 3 drops of ferroin.
- Titrate using Mohr's salt contained in the burette.
- Observe the changes in colour.
- The equivalent point corresponds to the change from blue-green to red-brown.
- Note the volume of Mohr's salt in the VSDM burette and deduce the concentration of the solution.

❖ Oxidation (2 hours of reaction)

- In a 250 ml ground glass tube, introduce 0.4 g of mercuric sulfate, then 20 ml of sample, 10 ml of the dichromate solution and (slowly) 30 ml of the mixture of sulfuric acid and silver sulfate.
- Stir well to homogenize and add one or two pumice stones before heating.
- Set up the reflux. Do not use silicone grease as it may reduce the dichromate. A Teflon rod is preferred. Neither sulfuric acid nor dichromate is volatile. There are six simultaneous positions.
- We will therefore prepare simultaneously: a distilled water blank and 5 samples. Given the back titration method, it is essential to ensure that the dichromate is in excess, but not too much. The amount of dichromate cannot be changed.

Therefore, we will need to perform several dilutions of a completely unknown sample.

❖ *Dosage*

- Carefully and unhurriedly collect the entire assembly after two hours of heating, rinsing and gathering all residues thoroughly.
- Allow the system to cool slightly before handling it. There is a very serious danger of splashing boiling acid dichromate. Take particular care to avoid contact with the eyes. Skin contact will cause permanent burns (deep burns).
- We need to reach a volume of approximately 140 mL which is titrated with Mohr's salt in the presence of ferroin.
- Warning, the dosage cannot be repeated!