

COMENIUS BILATERAL PARTENARIATE 2012/2014

WATER POLLUTION IN URBAN AREAS:

ANALYSIS AND TREATMENT

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DETERMINATION OF CHEMICAL OXYGEN DEMAND COD



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EXPERIMENT ON DETERMINATION OF CHEMICAL OXYGEN DEMAND

PREAMBLE:

“How to determine chemical oxygen demand in Water and Wastewater”. Test procedure is in accordance to IRSA-CNR (Method 5130) – 1994 Edition.

In addition to our Italian Standard, we also discuss in brief regarding the procedure stated in:

- (1) Metodi Analitici per le acque IRSA-CNR - 1994 Edition. Method 5130.
- (2) Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003a.

1 AIM

To determine chemical oxygen demand in the given water sample with the stipulations as per IRSA-CNR (Method 5130) – 1994 Edition.

2 INTRODUCTION

Before performing this experiment, few questions may arise to the learners:

- What is meant by chemical oxygen demand?
- Why do we need to determine COD?
- What are the methods available to measure COD?
- Is it measured in water or wastewater?
- Whether is it mandatory to determine COD as per our codal provision?

The chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution.

COD is the measurement of the amount of oxygen in water consumed for chemical oxidation of pollutants.

COD determines the quantity of oxygen required to oxidize the organic matter in water or waste water sample, under specific conditions of oxidizing agent, temperature, and time.

This method covers the determination of COD in ground and surface waters, domestic and industrial wastewaters. The applicable range is 3-900 mg/L.

2.1 ENVIRONMENTAL SIGNIFICANCE

COD values are particularly important in the surveys designed to determine and control the losses to sewer systems.

The ratio of BOD to COD is useful to assess the amenability of waste for biological treatment. Ratio of BOD to COD greater than or equal to 0.8 indicates that wastewater highly polluted and amenable to the biological treatment.

It is useful to assess strength of wastes, which contain toxins and biologically resistant organic substances.



COD can be related to TOC, however, does not account for oxidation state of the organic matter.

BOD value is always lower than COD value. For domestic and some industrial wastewater, COD value is about 2.5 times BOD value.

3 PRINCIPLE

The organic matter present in sample gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) in the presence of sulphuric acid (H_2SO_4), silver sulphate ($AgSO_4$) and mercury sulphate ($HgSO_4$) to produce CO_2 and H_2O . The sample is refluxed with a known amount of potassium dichromate ($K_2Cr_2O_7$) in the sulphuric acid medium and the excess potassium dichromate ($K_2Cr_2O_7$) is determined by titration against ferrous ammonium sulphate, using ferroin as an indicator. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidize the organic matter.

4 MATERIALS REQUIRED

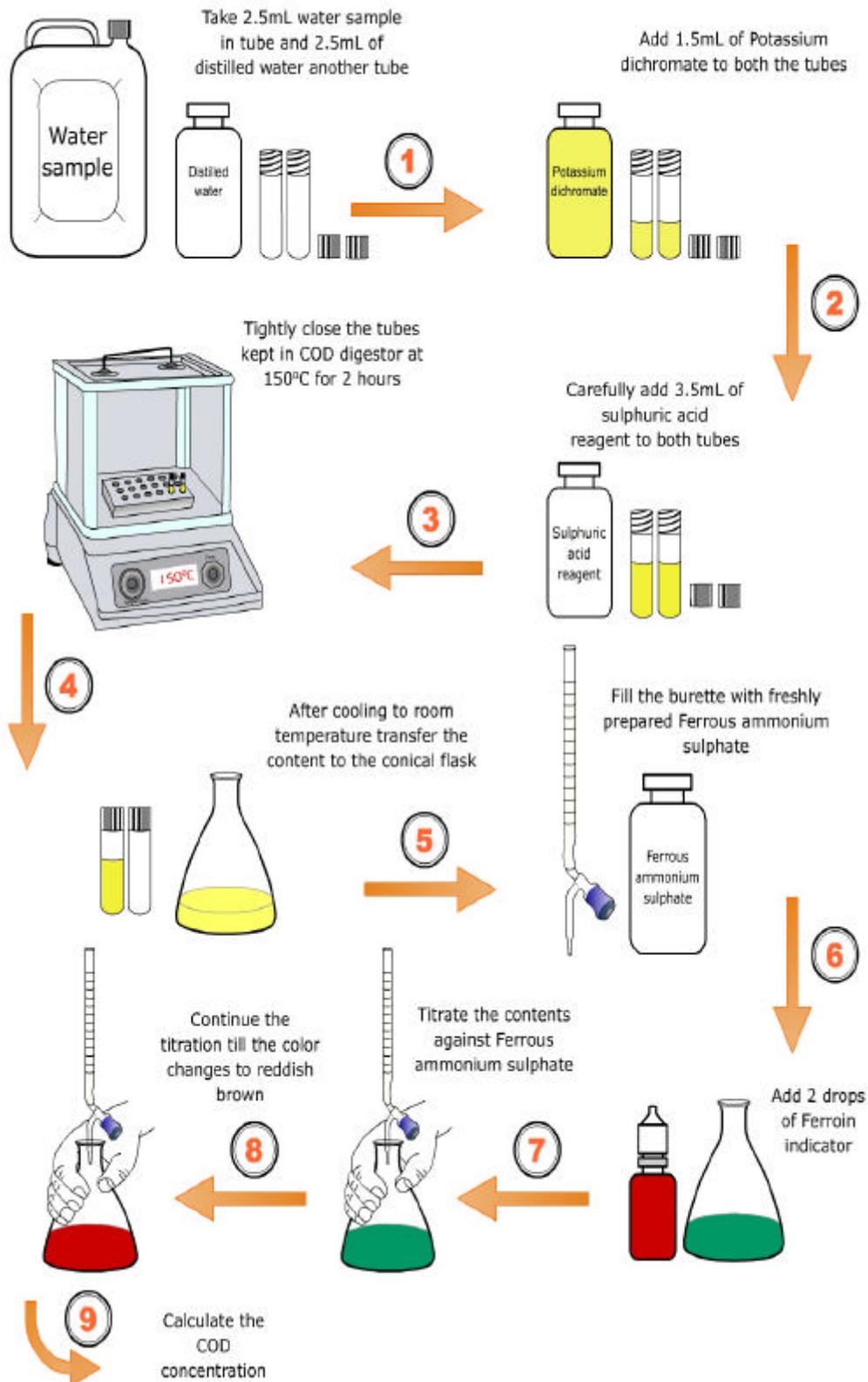
4.1 APPARATUS REQUIRED

1. COD Digester
2. Burette & Burette stand
3. COD Vials with stand
4. 250 mL conical flask (Erlenmeyer Flask)
5. Pipettes
6. Pipette bulb
7. Tissue papers
8. Wash Bottle

4.2 CHEMICALS REQUIRED

1. Potassium dichromate
2. Sulfuric acid
3. Ferrous ammonium sulphate
4. Silver sulphate
5. Mercury sulphate
6. Ferroin indicator
7. Organic free distilled water

PROCEDURE CHART





5 SAMPLE HANDLING AND PRESERVATION

Samples are collected in glass bottles. Use of plastic containers is permitted if it is known that there is no organic contaminants present in it.

Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

Samples should be preserved with sulphuric acid to a pH < 2 and maintained at 4o C until analysis.

Do not allow the samples to freeze.

5.1 PRECAUTIONS

The following precautions should be observed while performing the experiment:

- Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex the chlorides so that it does not interfere in the determination.
- Nitrites also interfere in the determination of COD and hence during the determination of samples with high concentration of nitrites, 120 mg of sulphuric acid is added to the potassium dichromate solution.
- Traces of organic material either from the glassware or atmosphere may cause a positive error. Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.



6 PROCEDURE

For testing the given sample, first the reagents are required to be prepared.

6.1 PREPARATION OF REAGENTS

a) Standard Potassium Dichromate Reagent - Digestion Solution

Weigh accurately 4.913 g of potassium dichromate, previously dried at 103 °C for 2 - 4 hours and transfer it to a beaker.

Weigh exactly 33.3g of mercuric sulphate and add to the same beaker. Measure accurately 167 mL of concentrated sulphuric acid using clean dry measuring cylinder and transfer it to the beaker. Dissolve the contents and cool to room temperature. (If not dissolved keep it over night).

Take 1000 mL standard measuring flask and place a funnel over it.

Carefully transfer the contents to the 1000 mL standard flask and make up to 1000 mL using distilled water.

This is the standard potassium dichromate solution to be used for digestion.

b) Sulphuric Acid Reagent - Catalyst Solution

Weigh accurately 5.5 g silver sulphate crystals to a dry clean 1000 mL beaker. To this carefully add about 500 mL of concentrated sulphuric acid and allow to stand for 24 hours (so that the silver sulphate crystals dissolve completely).

c) Standard Ferrous Ammonium Sulphate solution (FSA)

Weigh accurately 39.2g of ferrous ammonium sulphate crystals and dissolve it in distilled water.

Take 1000 mL standard measuring flask and place a funnel over it.

Carefully transfer the contents to the 1000 mL standard flask and make up to 1000 mL mark using distilled water.

6.2 TESTING OF SAMPLE

- Take three COD vials with stopper (two for the sample and one for the blank).
- Add 2.5 mL of the sample to each of the two COD vials and the remaining COD vial is for blank; to this COD vial add distilled water.
- Add 1.5 mL of potassium dichromate reagent - digestion solution to each of the three COD vials.
- Add 3.5 mL of sulphuric acid reagent - catalyst solution in the same manner.
- **CAUTION:** COD vials are hot now.
- Cap tubes tightly. Switch on the COD Digester and fix the temperature at 150° C and set the time at 2 hours.
- Place the COD vials into a block digester at 150°C and heat for two hours.



- The digester automatically switches off. Then remove the vials and allow it to cool to the room temperature.
- Meanwhile, get ready with the burette for the titration.
- Fill the burette with the ferrous ammonium sulphate solution, adjust to zero and fix the burette to the stand.
- Transfer the contents of the blank vial to conical flask.
- Add few drops of ferroin indicator. The solution becomes bluish green in colour.
- Titrate it with the ferrous ammonium sulphate taken in the burette.
- End point of the titration is the appearance of the reddish brown colour.
- Note down the volume of ferrous ammonium sulphate solution added for the blank (A) is **14.1 mL**.
- Transfer the contents of the sample vial to conical flask.
- Add few drops of ferroin indicator. The solution becomes green in colour.
- Titrate it with the ferrous ammonium sulphate taken in the burette.
- End point of the titration is the appearance of the reddish brown colour.
- Note down the volume of ferrous ammonium sulphate solution added for the sample (B) is **13.2 mL**.



7 CALCULATION

For determining the Chemical Oxygen Demand in the given water sample, the readings should be tabulated.

7.1 TABLE

ID	Sample	Volume of Sample (mL)	Burette Reading (mL)		Volume of 0.1 N FAS (mL)
			Initial	Final	
1.					
2.					
3.					

Burette Solution: Ferrous Ammonium Sulphate

Pipette Solution: Sample

Indicator: Ferroun Indicator

End point: Appearance of reddish brown color

- For the blank titration the volume of sample taken is 2.5 mL.
- Ferrous Ammonium Sulphate is taken in the burette.
- The obtain reading is 14.1 mL. Similarly for sample one the volume of sample taken is 2.5 mL.
- Ferrous Ammonium Sulphate is taken in the burette
- The initial reading is 0 mL and the final reading is 13.2 mL. Volume of Ferrous Ammonium Sulphate consumed to get the end point is 13.2 mL.
- For sample two the initial reading is 0 mL and the final reading is 13.2 mL.
- The volume of Ferrous Ammonium Sulphate consumed to get the end point is 13.2 mL.
- For sample 1 and 2 the reading as same so we can go for the calculations



7.2 DATA SHEET

DETERMINATION OF CHEMICAL OXYGEN DEMAND DATA SHEET

Date Tested : August 30, 2010

Tested By : 5AC Class, Group A

Project Name : CEM, NITTTTR Lab

Sample Number : BH1

Sample Location : Perungudi (Lat 12' 57" 31.74 & Long 80'14" 8.82)

Sample Description : Surface water

ID	Sample	Volume of Sample (mL)	Burette Reading (mL)		Volume of 0.1 N FAS (mL)
			Initial	Final	
1.	Blank	2.5	0	14.1	14.1
2.	Sample 1	2.5	0	13.2	13.2
3.	Sample 2	2.5	0	13.2	13.2

Specimen Calculation:

Volume of Ferrous Ammonium sulphate for blank (A) = 14.1 mL

Volume of Ferrous Ammonium sulphate for Sample (B) = 13.2 mL

Normality of Ferrous Ammonium sulphate N = 0.1 N

Volume of Sample V = 2.5 mL

Chemical Oxygen Demand :

$$COD = \frac{(A - B) \cdot N \cdot 8 \cdot 1000}{\text{Volume of sample taken}}$$

To convert the sample size from mL to L, multiply the result by 1000 mL/L

$$COD = \frac{(14.1 - 13.2) \cdot 0.1 \cdot 8 \cdot 1000}{2.5} = 288 \text{ mg/L}$$



8 INTERPRETATION OF RESULTS

The COD of the given sample of water = **288 mg/L**.

9 INFERENCE

Chemical oxygen demand does not differentiate between biologically available and inert organic matter, and it is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. COD values are always greater than BOD values. For domestic and some industrial wastewater COD is about 2.5 times BOD.

10 EVALUATION

1. Potassium dichromate is considered as the best
 - a) Oxidizing agent
 - b) Reducing agent
 - c) Redox agent
 - d) Chemical agent

2. Mercury Sulphate is added to reduce the interference of
 - a) Chlorides.
 - b) Sulphates
 - c) Organic pollutants
 - d) Hardness

3. Silver Sulphate is added as
 - a) Oxidizing agent
 - b) Reducing agent
 - c) Redox agent
 - d) Catalyst

4. Ferroin indicator is
 - a) Phenanthroline mono hydrate
 - b) Ferric sulphate
 - c) Phenanthroline mono hydrate and Ferric Sulphate
 - d) Ferrous Sulphate



5. After refluxing, _____ solution is titrated against FAS.
- excess potassium dichromate
 - consumed potassium dichromate
 - initially added potassium dichromate
 - potassium dichromate and silver sulphate
6. H_2SO_4 is added to FAS solution
- as it is a component of the reagent
 - to prevent hydrolysis of ferrous sulphate into ferrous hydroxide
 - to provide acidic medium
 - to neutralise the medium
7. The products formed after COD analysis are _____.
- Carbon di oxide and water
 - Water alone
 - Carbon di oxide alone
 - Carbon monoxide and water
8. In industrial waste water, COD value is about _____ BOD value.
- 2.5 times
 - 3.5 times
 - 4.5 times
 - 5.5 times
9. Sulphuric acid is added
- as it assists in oxidizing the nitrogen compounds
 - to provide acidic medium
 - to neutralise the medium
 - as catalyst
10. A blank solution is
- identical in all respects to the test solution except for the absence of test solute
 - identical in all respects to the test solution
 - a solution without any reagents
 - a solution without distilled water



KEY TO ITEMS:

- 1) a
- 2) a
- 3) d
- 4) c
- 5) a
- 6) b
- 7) a
- 8) a
- 9) a
- 10) a