IS 3025-58 (2006): Methods of sampling and test (physical and chemical) for water and wastewater, Part 58: Chemical oxygen demand (COD) [CHD 32: Environmental Protection and Waste Management]

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भारतीय मानक

जल और अपशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियाँ

भाग 58 रसायन ऑक्सीजन माँग (सीओडी)

(पहला पुनरीक्षण)

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 58 CHEMICAL OXYGEN DEMAND (COD)

(First Revision)

ICS 13.060.50

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

February 2006

Price Group 2

FOREWORD

This Indian Standard (Part 58) (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Environment Protection and Waste Management Sectional Committee had been approved by the Chemical Division Council.

The chemical oxygen demand (COD) determines the amount of oxygen required for chemical oxidation of organic matter using a strong chemical oxidant, such as, potassium dichromate under reflux conditions. This test is widely used to determine:

a) Degree of pollution in water bodies and their self purification capacity,

b) Efficiency of treatment plants,

c) Pollution loads, and

d) Provides rough idea of biochemical oxygen demand (BOD) which can be used to determine sample volume for BOD estimation.

The limitation of the test lies in its inability to differentiate between the biologically oxidizable and biologically inert material.

COD determination has an advantage over BOD test in that the results can be obtained in less than 5 h where as BOD determination requires 3 or 5 days. Further the test is relatively easy and precised. Also there are not many interferences as in the case of BOD.

In the preparation of this standard, considerable assistance has been derived from ISO 6060 : 1989 'Water quality — Determination of the chemical oxygen demand and standard methods for the examination of water and wastewater', 19th Edition — 1995, published by the American Public Health Association, Washington, U.S.A. The method prescribed in this standard is principally same as that of ISO 6060 : 1989 except that it specifies two procedures one for high COD and other for low COD against a single procedure specified in ISO 6060 : 1989.

The committee responsible for the formulation of this standard had decided to revise this standard and publish it as separate parts. This standard supersedes **52** of IS 3025 : 1964 and **4** of IS 2488 (Part 5) : 1976 'Methods of sampling and test for industrial effluents, Part 5'.

The composition of the Committee responsible for formulation of this standard is given at Annex A.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 58 CHEMICAL OXYGEN DEMAND (COD)

(First Revision)

1 SCOPE

This standard (Part 58) prescribes the method for determination of chemical oxygen demand (COD) in water and wastewater.

2 REFERENCES

The standards listed below contain provisions which through reference in this text constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
3025 (Part 1) : 1986	Methods of sampling and test (physical and chemical) for water and wastewater: Part 1 Sampling (*first revision*)
7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents, Part 1
7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents, Part 2

3 TERMINOLOGY

For the purpose of this standard, definitions given in IS 7022 (Part 1) and IS 7022 (Part 2) shall apply.

4 SAMPLING AND PRESERVATION

Sampling and sample preservation shall be done as prescribed in IS 3025 (Part 1).

5 PRINCIPLE

Most of the organic matters are destroyed when boiled with a mixture of potassium dichromate and sulphuric acid producing carbon dioxide and water. A sample is refluxed with a known amount of potassium dichromate in sulphuric acid medium and the excess of dichromate is titrated against ferrous ammonium sulphate. The amount of dichromate consumed is proportional to the oxygen required to oxidize the oxidizable organic matter.

6 INTERFERENCE

Straight-chain aliphatic compounds, aromatic hydrocarbon fatty acids, chlorides, nitrites and iron are the main interfering radicals.

The interference caused by chlorides can be eliminated by the addition of mercuric sulphate to the sample prior to addition of other reagents. About 0.4 g $HgSO_4$ is adequate to complex 40 mg Cl ions in the form of poorly ionized HgCl.

Nitrite exerts a COD of 1.1 mg/mg N, hence 120 mg of sulphamic acid is added to potassium dichromate solution to avoid interference caused by nitrite (NO_2). When 20 ml sample and 10 ml dichromate is taken, this can take care of concentrations up to 6 mg/l NO_2-N.

Silver sulphate is added to concentrated H_2SO_4 (22 g/4 kg acid) as a catalyst. This accelerates the oxidation of straight-chain aliphatic and aromatic compounds.

For complete and better oxidation of organic matter it is necessary to maintain the final concentration of H_2SO_4 at 18 N.

7 APPARATUS

7.1 Reflux Apparatus — Consisting of series of flat bottom, 150 to 250 ml capacity tubes with glass joint and a long condenser.

7.2 Hot Plate — A digester block on which a series of refluxing sets are connected to provide uniform heating to all the tubes.

8 REAGENTS

8.1 Standard Potassium Dichromate, 0.25 N — Dissolve 12.259 g potassium dichromate previously dried at 105 ± 2°C for 24 h, in distilled water. Add 120 mg sulphamic acid to this. Dilute to 1 litre.

8.2 Sulphuric Acid Concentrate — Add 22 g silver sulphate to 4 kg (10.12 g silver sulphate/l) concentrated

H_2SO_4 bottle. Keep overnight for dissolution. Shake well after dissolution.

8.3 Standard Ferrous Ammonium Sulphate 0.1 N — Dissolve 39 g Fe $(NH_4)_2$ $(SO_4)_2$. $6H_2O$ in distilled water. Add 20 ml concentrated H_2SO_4, cool, and dilute to 1 litre. Standardize this solution daily against standard $K_2Cr_2O_7$.

8.4 Ferroin Indicator — Dissolve 1.485 g 1.10-Phenanthroline monohydrate and 695 mg $FeSO_4$. $7H_2O$ in water and dilute to 100 ml.

NOTE — Already prepared indictor is also available in the market.

8.5 Mercuric Sulphate, $HgSO_4$ Crystals

9 PROCEDURE

9.1 Procedure for High-COD Sample (≥ 50 mg/l)

Place 0.4g $HgSO_4$ in a reflux tube. Add 20 ml or an aliquot of sample diluted to 20 ml with distilled water. Mix well, so that chlorides are converted into poorly ionized mercuric chloride. Add 10 ml standard $K_2Cr_2O_7$ solution and then add slowly 30 ml sulphuric acid which already containing silver sulphate. Mix well, if the colour turns green, take fresh sample with smaller aliquot. Final concentration of concentrated. H_2SO_4 should be always 18 N.

Connect the tubes to condensers and reflux for 2 h at 150±2°C. Cool and wash down the condensers with 60 ml distilled water. Cool and titrate against standard ferrous ammonium sulphate using ferroin as indicator. Near the end of the titration colour changes sharply from green blue to wine red. Reflux a reagent blank simultaneously with the sample under identical conditions.

NOTE — This slow addition along with swirling prevents loss of volatile materials such as fatty acids, in the sample.

9.2 Alternate Procedure for Low-COD Samples (Up to 160 mg/l)

The method is same as for the high-COD samples (*see* **9.1**) except that the concentration of $K_2Cr_2O_7$ and ferrous ammonium sulphate is reduced to 0.05 N and 0.02 N respectively in this case. COD values up to 160 mg/l can be estimated by this procedure.

9.3 Standardization of Ferrous Ammonium Sulphate

Dilute 10.00 ml standard $K_2Cr_2O_7$ solution to about 100 ml. Add 30 ml concentrated H_2SO_4 and cool. Add 3-4 drops of ferroin indicator and titrate with ferrous ammonium sulphate till the colour changes to wine red.

$$\text{Normality of ferrous ammonium sulphate} = \frac{10 \times 0.25}{V}$$

where

V = volume of Fe $(NH_4)_2$ $(SO_4)_2$ required for titration, in ml.

10 CALCULATION

$$\text{COD, mg/l} = \frac{(V_1 - V_2)\, N \times 8\,000}{V_0}$$

where

V_1 = volume of Fe $(NH_4)_2$ $(SO_4)_2$ required for titration against the blank, in ml;

V_2 = volume of $Fe(NH_4)_2$ $(SO_4)_2$ required for titration against the sample, in ml;

N = Normality of $Fe(NH_4)_2$ $(SO_4)_2$; and

V_0 = volume of sample taken for testing, in ml.

11 EXPRESSION OE RESULTS

Results are expressed as mg/l of O_2. Report to the nearest whole number.

12 PRECISION AND ACCURACY

Precision and accuracy both depends upon the COD value. For the high COD values (≥ 400 mg/l) precision up to 2 percent is expected from a good analyst. As the COD value goes on decreasing, precision also become poorer and poorer that is percentage goes on increasing.

Precision for the low COD samples may be improved by using alternate method where diluted reagents are used.

ANNEX A

(Foreword)

COMMITTEE COMPOSITION

Environment Protection and Waste Management Sectional Committee, CHD 32

Organization	*Representative(s)*
In personal capacity (*40/14, C.R. Park, New Delhi-110019*)	PROF DILIP BISWAS (***Chairman***)
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	[Representing Director General (*Ex-officio Member*)]

Member Secretary
SHRI N. K. PAL
Director (Chemical), BIS

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Amendments Issued Since Publication

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