IS 3025 (Part 58) (2006): Method of Sampling and Test (Physical and Chemical) for Water and Wastewater, Part 58: Chemical Oxygen Demand (COD) First Revision). ICS 13.060.50

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
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NEW DELHI 110002

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Environment Protection and Waste Management Sectional Committee, CHD 32

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***)
Bhabha Atomic Research Centre, Mumbai	DR (SHRIMATI) G. G. PANDIT DR I. V. SARADHI (*Alternate*)
Bharat Heavy Electricals Limited, Haridwar	DR N. G. SHRIVASTAVA
Cement Manufacturers' Association, New Delhi	DR K. C. NARANG
Central Fuel Research Institute, Dhanbad	DR L. C. RAM
Central Leather Research Institute, Chennai	DR S. RAJAMANI
Central Mining Research Institute, Dhanbad	DR B. K. TEWARY
Central Pollution Control Board, New Delhi	DR S. D. MAKHIJANI DR C. S. SHARMA (*Alternate*-I) DR S. K. TYAGI (*Alternate*-II)
Confederation of Indian Industries, New Delhi	SHRI A. K. GHOSE SHRI R. P. SHARMA (*Alternate*)
Crop Care Federation of India, New Delhi	SHRI P. N. PARMESHAWARAN
Indian Institute of Technology, Department of Civil Engineering, New Delhi	DR MUKESH KHARE DR ATUL MITTAL (*Alternate*-I) DR ARVIND NEMA (*Alternate*-II)
Department of Science and Technology (TIFAC), New Delhi	DR P. SANJEEVA RAO DR G. SRINIVASAN (*Alternate*)
Delhi College of Engineering, Delhi	DR RAKESH MEHROTRA SHRI V. K. MINOCHA (*Alternate*-I) DR (SHRIMATI) A. MANDAL (*Alternate*-II)
Directorate General Factory Advice Service and Labour Institute, Mumbai	SHRI S. S. GAUTAM SHRI M. R. RAJPUT (*Alternate*)
Directorate General of Health Services, New Delhi	DR (SHRIMATI) MADHURI SHARMA
Engineers India Limited, New Delhi	SHRI B. B. LAL SHRI SUSHEEL SADH (*Alternate*)
Envirotech Instruments Private Limited, New Delhi	SHRI RAKESH AGARWAL DR RAJENDRA PRASAD (*Alternate*)
Food Research & Analysis Centre, New Delhi	DR S. K. SAXENA DR R. PRABHAKARAN (*Alternate*)
Gujarat Pollution Control Board, Ahmedabad	KUMARI P. S. SHAH
Hindustan Lever Limited, Mumbai	SHRI B. B. DAVE SHRI ADITYA JHAVAR (*Alternate*)
Indian Chemical Manufacturers' Association, Mumbai	SHRI V. N. DAS SHRI A. A. PANJWANI (*Alternate*)
Indian Council of Agricultural Research, New Delhi	DR R. C. MAHESHWARI
Indian Council of Medical Research, New Delhi	SHRI H. N. SAIYAD
Indian Institute of Packaging, Mumbai	SHRI S.C. ADAK
Indian Oil Corporation Limited, Faridabad	DR M. P. SINGH
IPCL, Vadodara	SHRI ANUPAM DESAI SHRI MIHIR BANERJI (*Alternate*)
Industrial Toxicology Research Centre, Lucknow	DR S. K. BHARGAVA
Ministry of Defencce (R & D), DRDO, New Delhi	SHRI J. C. KAPOOR
Ministry of Environment and Forests, New Delhi	REPRESENTATIVE
Ministry of Non-conventional Energy Sources, New Delhi	SHRI VINOD KUMAR JAIN
Town and Country Planning Organization, Ministry of Urban Development, New Delhi	SHRI K. K. JOADDER DR SANTOSH VIDHYA DHARAN (*Alternate*)
Municipal Corporation of Greater Mumbai, Mumbai	DEPUTY CITY ENGINEER CIVIL (ENVT) DEPUTY EXECUTIVE ENGINEER (EMISSION INVENTORY GROUP) (*Alternate*)
National Institute of Occupational Health (ICMR), Ahmedabad	DR V. KRISHNA MURTHY DR A. K. MUKHERJEE (*Alternate*)
National Environmental Engineering Research Institute, Nagpur	DR V. I. PANDIT DR TAPAN NANDY (*Alternate*)
National Productivity Council, New Delhi	SHRI R. C. MONGA DR A. K. SAXENA (*Alternate*)

Organization	*Representative(s)*
National Thermal Power Corporation Limited, New Delhi	SHRI R. GOPAL
NCCBM, New Delhi	SHRI M. S. BHAGWAT
	DR S. N. PATI (*Alternate*)
Reliance Industries Limited, Mumbai	DR E. SUNDERASAN
	DR U. K. SAROOP (*Alternate*)
Shriram Institute of Industrial Research, New Delhi	SHRI V. G. K. NAIR
	DR JAGDISH KUMAR (*Alternate*)
SGS India Limited, Chennai	SHRI S. RAVI
Steel Authority of India Limited, New Delhi	SHRI J. KUMAR
	DR MEENAKSHI KAKKAR (*Alternate*)
Thapar Centre for Industrial Research and Development, Patiala	DR MAHESHWAR ROY
	DR S. K. CHAKRABORTY (*Alternate*)
The Fertilizer Association of India, New Delhi	DR (SHRIMATI) B. SWAMINATHAN
	DR S. NAND (*Alternate*)
BIS Directorate General	DR U. C. SRIVASTAVA, Director & Head (CHD) [Representing Director General (*Ex-officio Member*)]

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