भारतीय मानक

(Reaffirmed 1998)

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

भाग 43 फिनौल

(पहला पुनरीक्षण)

Indian Standard

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

PART 43 PHENOLS

(First Revision)

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Price Group 2

FOREWORD

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

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclii may occur in domestic and industrial wastewaters, natural waters and portable water supplies. Chlorination of such waters may produce odouriferous and objectional tasting chlorophenols. Phenol removal processes in water treatment include super chlorination, chlorine dioxide or chloramine treatment, ozonation and activated carbon adsorption. This standard supersedes 57 of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry'. In the preparation of this standard, considerable assistance has been derived from Standard Methods for the Examination of Water and Wastewater, 17th edition published by American Public Health Association, Washington (USA), 1989 and EPA-1979 'Methods for Chemical Analysis of Water and Wastewater.'

In reporting the result 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 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 43 PHENOLS

(First Revision)

1 SCOPE

1.1 This standard prescribes two spectrophotometric methods for the determination of phenol in natural waters, potable water supplies, domestic and industrial wastewaters.

a) 4 Amino-antipyrine method without chloroform extraction, and

b) 4 Amino-antipyrine method with chloroform extraction.

1.2 It does not apply to differentiate between various kinds of phenols.

2 REFERENCES

The following Indian standards are the necessary adjuncts to this standard:

IS No.	*Title*
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) : 1973 and IS 7022 (Part 2) : 1979 shall apply.

4 SAMPLE PRESERVATION AND STORAGE

4.1 Phenol concentration usually encountered in wastewaters are subject to biological and chemical oxidation. Preserve and store samples at 4°C or lower but do not allow to freeze unless analysed within 4 hours after collection.

4.2 After acidification with phosphoric acid to *p*H 4 or slightly below the sample can be stored upto 4 weeks at 4°C.

5 4-AMINOANTIPYRINE METHOD WITHOUT CHLOROFORM EXTRACTION

5.1 Principle

Most phenols react with 4-aminoantipyrine at *p*H 7·9 ± 0·1 in the presence of potassium ferricyanide to form a coloured antipyrine dye. This dye is kept in aqueous solution and the absorbance is measured at 460 nm.

This method is recommended for concentrations more than 1 mg/l phenol which does not require chloroform extraction technique.

5.2 Interferences

To eliminate or minimize the interferences, use steam distilled sample. Phenols are distilled from non-volatile impurities. Because the volatilization of phenols is gradual, the distilate volume shall ultimately equal that of the original sample.

5.2.1 *Preliminary Step of Steam Distillation*

5.2.1.1 Measure 500 ml of sample into a beaker. Lower the *p*H to approximately 4·0 with 8·5 percent phosphoric acid. If the sample was already preserved using phosphoric acid, omit the addition of phosphoric acid again. Transfer to the distillation apparatus made up of glass, consisting of a 1 litre borosilicate glass distilling apparatus with Graham condenser.

5.2.1.2 Distil 450 ml of sample and stop the distillation. When boiling ceases, add 50 ml of warm distilled water to the distilling flask and resume distillation until 500 ml have been collected.

5.2.1.3 If the distillate is turbid, filter through a pre-washed membrane filter.

5.3 Apparatus

5.3.1 *Spectrophotometer*

For use at 460 nm equipped with light path 1 to 5 cm.

5.3.2 *p*H *Meter*

5.4 Reagents

All reagents should be prepared with distilled water free from phenols and chlorine.

5.4.1 *Stock Phenol Solution*

Dissolve 1·0 g phenol in freshly boiled and cooled distilled water and dilute to 1 000 ml.

CAUTION — ' TOXIC; HANDLE WITH CARE '.

5.4.1.1 Standardize the stock phenol solution as follows:

To 100 ml water in a 500-ml glass stoppered conical flask, add 50·0 ml stock phenol solution and 10·0 ml 0·1 N bromate-bromide solution. Immediately, add 5 ml concentrated hydrochloric acid and swirl gently. If brown colour of free bromine does not persist, add 10·0-ml portions of bromate-bromide solution until it does. Keep flask stoppered and let stand for 10 minutes, then add approximately 1 g KI. Usually four 10-ml portions of bromate-bromide solution are required if the stock phenol solution contains 1 000 mg phenol/l.

Prepare a blank in exactly the same manner, using distilled water and 10·0 ml 0·1 N bromate bromide solution. Titrate blank and sample with 0·025 N sodium thiosulphate, using starch solution indicator.

Calculate the cencentration of phenol solution as follows:

$$\text{Phenol, mg/l} = 7{\cdot}842\,(A \times B) - C$$

where

A = thiosulphate for blank in ml;

B = bromate-bromide solution used for sample divided by 10 in ml; and

C = thiosulphate used for sample in ml.

5.4 2 *Intermediate Phenol Solution*

Dilute 10·0 ml of the stock phenol solution in freshly boiled and cooled distilled water to 1 000 ml; 1 ml = 10 μg pnenol. Prepare daily.

5.4.3 *Standard Phenol Solution*

Dilute 50·0 ml of intermediate phenol solution to 500 ml with freshly boiled and cooled distilled water; 1 ml = 1·0 μg phenol. Prepare within 2 hours of use.

5.4.4 *Ammonium Hydroxide* — 0·5 N.

Dilute 35 ml of fresh concentrated ammonium hydroxide to 1 litre with distilled water.

5.4.5 *Phosphate Buffer Solution*

Dissolve 104·5 g of potassium hydrogen phosphate (K_2HPO_4) and 72·3 g of potassium dihydrcgen phosphate (KH_2PO_4) in distilled water and dilute to 1 litre. The *p*H of the resulting solution should be 6·8.

5.4.6 *4-Aminoantipyrine Solution*

Dissolve 2·0 g of 4-aminoantipyrine in distilled water and dilute to 100 ml. Prepare daily.

5.4.7 *Potassium Ferricyanide Solution*

Dissolve 8·0 g of potassium ferricyanide [$K_3Fe(CN)_6$] in distilled water and dilute to 100 ml. Store in a brown glass bottle. Prepare fresh weekly.

5.4.8 *Sodium Sulphate* — Anhydrous.

5.5 Procedure

5.5.1 Place 100 ml of distillate or a portion containing not more than 0·5 mg of phenol diluted to 100 ml in a 250 ml beaker. Prepare a 100 ml distilled water blank. Prepare a series of 100 ml phenol standards containing 0·1, 0·2, 0·3, 0·4 and 0·5 mg phenol. Treat sample, blank and standards as follows:

Add 2·5 ml of 0·5 N ammonium hydroxide solution and adjust to *p*H 7·9 + 0·1 with phosphate buffer. Add 1·0 ml of 4-amino-antipyrine solution, mix well, add 1 ml of potassium ferricyanide solution and mix well. Let it stand for 15 minutes. Read absorbance of sample and standards against the bank at 460 nm.

5.5.2 *Calibration Curve*

Prepare a standard curve by plotting the absorbance values of standards versus corresponding phenol concentrations.

5.6 Calculation

After obtaining the absorbance values, depending upon the volume of sample chosen for test, calculate the amount of phenol present in 1 000 ml as given below:

Using calibration curve:

$$\text{phenol, } \mu\text{g/l} = \frac{C}{V} \times 1\,000$$

where

C = concentration of phenol in μg in sample from the calibration curve, and

V = voulme in ml of original sample.

6 4-AMINOANTIPYRINE METHOD WITH CHLOROFORM EXTRACTION

6.1 Principle

Most phenols react with 4-aminoantipyrine at *p*H 7·9 + 0·1 in the presence of potassium ferricyanide to form a coloured antipyrine dye. This dye is extracted from water with chloroform and the absorbance is measured at 460 nm. The minimum detectable quantity is 1 μg of phenol/litre in 460 ml distilate.

This method is more sensitive and is adoptable for use in water sample containing less than 1 mg of phenol/litre.

6.2 Interferences

6.2.1 Interferences such as phenol decomposing bacteria, oxidizing and reducing substances, and alkaline *p*H values are dealt with by acidification. If the sample has been preserved as mentioned in **4**, further acidification is not required. The interferences may be eliminated as follows.

6.2.1.1 *Oxidizing agents, such as chlorine*

Remove immediately after sampling by adding excess ferrous sulphate.

6.2.1.2 *Sulphur compounds*

Remove by acidifying to *p*H 4·0 with phosphoric acid and aerating briefly by stirring. This eliminates interference of gases like hydrogen sulphite and sulphur dioxide.

6.2.1.3 *Oils and tars*

Make an alkaline extraction by adjusting *p*H to 12 to 12·5 with sodium hydroxide pellets. Extract oil and tar from aqueous solution with 50 ml chloroform in three steps. Discard oil and tar containing layer. Remove excess chloroform in aqueous layer by warming on a water bath before proceeding with the distillation step.

6.3 Preliminary Step of Steam Distillation

6.3.1 Measure 500 ml of sample into a beaker. Lower the *p*H to approximately 4·0 with 8·5 percent phosphoric acid. If the sample was already preserved using phosphoric acid, omit the addition of phosphoric acid again. Transfer to the distillation apparatus made up of glass, consisting of a 1 litre borosilicate glass distilling apparatus with Graham condenser.

6.3.2 Distil 450 ml of sample and stop the distillation. When boiling ceases, add 50 ml of warm distilled water to the distilling flask and resume distillation until 500 ml have been collected.

6.3.3 If the distillate is turbid, filter through a pre-washed membrane filter.

6.4 Apparatus

6.4.1 *Spectrophotometer*

For use at 460 nm and equipped with 1 to 10 cm cells.

6.4.2 *Filter Funnels*

Buchner type with fritted disc.

6.4.3 *Filter Paper*

Alternative to buchner type funnel, use Whatman No. 40 filter paper and anhydrous sodium sulphate for filtration of chloroform phase.

6.4.4 *p*H *Meter*

6.4.5 *Separating Funnel*

1 000 ml capacity with ground glass stoppers and TFE stop cock.

6.5 Reagents

All reagents should be prepared with distilled water free from phenols and chlorine.

6.5.1 *Phenol Stock Solution*

Dissolve 1·0 g phenol in freshly boiled and cooled distilled water and dilute to 1 000 ml.

CAUTION — ' TOXIC, HANDLE WITH CARE '.

6.5.2 *Intermediate Phenol Solution*

Dilute 10·0 ml of stock phenol solution in freshly boiled and cooled distilled water to 1 000 ml. 1 ml = 10·0 µg of phenol. Prepare daily.

6.5.3 *Standard Phenol Solution*

Dilute 50·0 ml of intermediate phenol solution to 500 ml with freshly boiled and cooled distilled water. 1 ml of this solution is equivalent to 1·0 µg of phenol. Prepare this solution within 2 hours of use.

6.5.4 *Ammonium Hydroxide* — 0·5 N.

Dilute 35 ml of fresh concentrated ammonium hydroxide to 1 litre with distilled water.

6.5.5 *Phosphate Buffer Solution*

Dissolve 104·5 g of potassium hydrogen phosphate (K_2HPO_4) and 72·3 g of potassium dihydrogen phosphate (KH_2PO_4) in distilled water and dilute to 1 litre. The *p*H of the resulting solution should be 6·8.

6.5.6 *4-Aminoantipyrine Solution*

Dissolve 2·0 g of 4-aminoantipyrine in distilled water and dilute to 100 ml. Prepare daily.

6.5.7 *Potassium Ferricyanide Solution*

Dissolve 8·0 g of material in water and dilute to 100 ml. Filter, if necessary and store in brown glass bottle. Prepare fresh weekly.

6.5.8 *Chloroform*

6.5.9 *Sodium Sulphate* — Anhydrous.

6.6 Procedure

6.6.1 Place 500 ml of distillate or a suitable portion containing not more than 50 μg phenol, diluted to 500 ml, in a 1-litre beaker. Prepare a 500 ml distilled water blank and a series of 500 ml phenol standards containing 5, 10, 20, 30, 40 and 50 μg phenol. Treat sample, blank, and standards as follows:

Add 12·0 ml of 0·5 N ammonium hydroxide and adjust *p*H to 7·9 ± 0·1 with phosphate buffer (10 ml may be sufficient). Transfer to a 1 litre separating funnel, add 3·0 ml aminoantipyrine solution, mix well and add 3·0 ml of potassium ferricyanide and let colour develop for 3 minutes. The solution should be clear and light yellow. Extract immediately with chloroform using 25 ml for 1 to 5 cm cells and 50 ml for 10 cm cell. Let chloroform settle, shake again for 10 minutes add let the chloroform settle again. Filter each chloroform extract through filter paper or fritted glass funnels containing a 5 g layer of anhydrous sodium sulphate. Make up the volume to 25 ml or 50 ml as the case may be. Read absorbance of sample and standards against the blank at 460 nm.

6.6.2 *Calibration Curve*

Prepare a standard curve by plotting the absorbance values of standards versus corresponding phenol concentrations.

6.6.3 For infrequent analysis, prepare only one standard phenol solution. Prepare 500 ml standard phenol solution of a strengh approximately equal to the phenolic content of that portion of original sample used for final analysis. Also prepare a 500 ml distilled water blank. Measure absorbance of sample and standard phenol solution against the blank at 460 nm following procedure given in **6.6.1**.

6.7 Calculation

After obtaining the absorbance values, depending upon the volume of sample chosen for test, calculate the amount of phenol present in 1 000 ml as given below:

Using calibration curve:

$$\text{phenol, } \mu g/l = \frac{C}{V} \times 1\,000$$

where

C = concentration of phenol in μg in sample from the calibration curve, and

V = volume in ml of original sample.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 1986 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Handbook' and 'Standards : Monthly Additions'.

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TO
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PART 43 PHENOLS

(First Revision)

(*Page* 2, *clause* 5.4.1.1, *line* 23) — Substitute the following for the existing:

'Phenol, mg/l = 7.842 [$(A \times B) - C$]'

(CHD 12)

Reprography Unit, BIS, New Delhi, India

AMENDMENT NO. 2 MARCH 2003
TO
IS 3025 (Part 43) : 1992 METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 43 PHENOLS

(First Revision)

(*Page* 3, *clause* **6.5.2**, *line* 3) — Substitute '10.0 µg' *for* '10 0 µg'.

(CHD 32)

Reprography Unit, BIS, New Delhi, India