*भारतीय मानक*

*Indian Standard*

**IS 3025 (Part 28) : 2024**

# जल एवं अपिशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियाँ

## भाग 28 सल्फाइट्स

*( दूसरा पुनरीक्षण )*

# Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater

## Part 28 Sulphites

*( Second Revision )*

ICS 13.060.50

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**April 2024** **Price Group 5**

Water Quality Sectional Committee, CHD 36

## FOREWORD

This Indian Standard (Part 28) (Second Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Water Quality Sectional Committee had been approved by the Chemical Division Council.

Sulphites may occur in natural waters or wastewaters as a result of industrial pollution and in treatment plant effluents dechlorinated with sulphur dioxide. Control of sulphite ion in wastewater treatment and discharge may be important environmentally, mainly because of its toxicity to fish and other aquatic life and its rapid oxygen demand. The presence of other oxidizable materials, such as sulphide, thiosulphate, ferric ions can apparently give higher readings of sulphites. Some metal ions like $Cu^{2+}$ may catalyze the oxidation of sulphite.

The Committee responsible for formulation of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' decided to revise the standard and publish it in separate parts. This standard was one of the different parts published under IS 3025 series of standards and superseded **21** of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry'. The first revision was published in 1986.

In this second revision following changes have been incorporated:

a) Phenanthroline method has been incorporated;
b) References, ICS No. have been updated; and
c) Other editorial changes have been done to bring the standard in the latest style and format of Indian Standards.

In the preparation of this standard, considerable assistance has been derived from the method no. 4500 $SO_3^-$ A and B of Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association, Washington, USA, 23nd edition, 2017.

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

In reporting the results of a test or analysis 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 : 2022 'Rules for rounding off numerical values (*second revision*)'.

*Indian Standard*

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

## PART 28 SULPHITES

*( Second Revision )*

## 1 SCOPE

This standard (Part 28) prescribes the following methods for determination of sulphites in water and wastewater:

a) Iodometric method (applicable to minimum detectable concentration of 2 mg/l); and
b) Phenanthroline method (applicable to minimum detectable concentration of 0.01 mg/l).

## 2 REFERENCES

The standards given 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 edition of these standards:

| *IS No.* | *Title* |
|---|---|
| IS 7022 (Part 1) : 1973 | Glossary of term relating to water, sewage and industrial effluents: Part 1 |
| IS 7022 (Part 2) : 1979 | Glossary of term relating to water, sewage and industrial effluents: Part 2 |
| IS 17614 | Water quality — Sampling: |
| (Part 1) : 2021/ ISO 5667-1 : 2020 | Guidance on the design of sampling programmes and sampling techniques |
| (Part 3) : 2021/ ISO 5667-3 : 2018 | Preservation and handling of water samples |

## 3 TERMINOLOGY

For the purpose of this standard, the 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 17614 (Part 1) and IS 17614 (Part 3). Highly polluted or contaminated samples should be stored at low temperature, allowing as little contact with air as possible. Since at *p*H 8.0 or above sulphite may be oxidised to sulphate, *p*H should, therefore be adjusted below 8.0. Fix the sample (at about 50 °C) immediately by adding 1 ml ETDA solution for each 100 ml of sample.

## 5 IODOMETRIC METHOD

### 5.1 Theory and Principle

Acidified water sample containing sulphite reduces iodate to iodine. Any excess of iodate added after all the sulphite is used up, oxidizes iodide to free iodine under acidic *p*H condition. Iodine oxidizes sulphite to sulphate. Any excess iodine results in the formation of blue colour in presence of starch indicator.

### 5.2 Interferences

**5.2.1** Generally, sulphide and thiosulphate are encountered in samples containing industrial discharge but it must be accounted. Interferences due to the presence of sulphides may be removed by the addition of zinc acetate.

**5.2.2** Copper ions rapidly accelerate the oxidation of sulphite ions. Certain heavy metals may also react in a similar manner as copper. Proper sampling and immediate fixing by acid addition should 3 in size such difficulties.

**5.2.3** Addition of sulphamic acid helps to eliminate interference due to nitrate.

### 5.3 Reagents

**5.3.1** *Sulphuric Acid* — 1 + 1

**5.3.2** *Starch Indicator Solution*

Take 5 g starch in motar, to this add little cold distilled water and grind and form paste. Dilute to 1 litre and boil for a few minutes and let settle overnight. Use the clear supernatant liquid. Add combination of either 1.3 gm of salicylic acid and 4 gm of zinc chloride or 4 gm of sodium propionate and 2 gm of sodium azide in 1 litre of starch solution to preserve the indicator.

**5.3.3** *Standard Iodide-Iodate Solution* (0.012 5 M)

Dissolve 0.445 8 gm primary grade potassium iodate (dried for 4 h at 120 °C), 4.35 g of potassium iodide and 310 mg sodium bicarbonate in distilled water and dilute to 1 000 ml (1 ml = 500 µg of sulphite).

**5.3.4** *Sulphamic Acid* — crystalline

**5.3.5** *Ethylenediamine Tetraacetic Acid* (*EDTA*) *Reagent*

Dissolve 2.5 g of disodium EDTA in 100 ml of distilled water.

### 5.4 Procedure

**5.4.1** Add 1 ml sulphuric acid and about 0.1 g of sulphamic acid crystals into a 250 ml long necked flask.

**5.4.2** Measure a suitable volume of ETDA stabilized sample (50 ml to 100 ml) and transfer to the flask keeping the tip of the pipette below the surface of liquid. Add 1 ml of starch indicator solution (*see* 5.3.2).

**5.4.3** Titrate immediately with postassium iodide-iodate standard solution until a faint permanent blue colour develops (view the colour change against a white background). Carry out a blank, using distilled water instead of sample.

### 5.5 Calculation

$$SO_3^{2-} = \frac{(A - B) \times \mathrm{N} \times 40\,000}{V} \text{ (mg/l)}$$

where

$A$ = volume, in ml, of standard iodide-iodate solution used for sample;

$B$ = volume, in ml, of standard iodide-iodate solution used in blank;

N = normality of potassium iodide-iodate solution; and

$V$ = volume, in ml, of sample taken for the test.

## 6 PHENANTHROLINE METHOD

### 6.1 Principle

Purge the nitrogen gas in acidified solution. Liberated sulphur dioxide is absorbed in the solution containing ferric iron and 1, 10 phenanthroline. Sulphur dioxide reduces ferric iron to ferrous iron, producing the orange tris (1,10-phenanthroline) iron (II) complex. Remove excess ferric iron with ammonium bifluoride, and measure the phenanthroline complex at 510 nm.

### 6.2 Interferences (*see* 5.2)

### 6.3 Apparatus

**6.3.1** *Apparatus for Evolution of Sulphur Dioxide*

**6.3.1.1** *Gas flow meters* — flow rate of 2 l/min

**6.3.1.2** *Gas washing bottle* — 250 ml with coarse porosity, 12 mm diameter fritted cylinder gas dispersion tube

**6.3.1.3** *Tubing connector* — polypropylene

**6.3.1.4** *Tubing* — poly vinyl chloride (PVC)

**6.3.1.5** *Nessler tube* — 100 ml

**6.3.2** *Spectrophotometer* — for use at 510 nm, providing a light path of 1 cm

### 6.4 Reagents

**6.4.1** 1, 10 - *Phenanthroline Solution* — 0.03 M

In 100 ml 95 percent ethanol dissolve 5.95 g of 1, 10-phenanthroline solution. Dilute it to 1 litre with distilled water. Discard if solution becomes coloured.

**6.4.2** *Ferric Ammonium Sulphate Solution* — 0.01 M

To 1 000 ml of distilled water add 1 ml of concentrated sulphuric acid to reduce probability of ferric hydrolysis, than dissolve ferric ammonium sulphate ($NH_4Fe(SO_4)_2.12H_2O$) in it. Filter through a glass fibre filter, if any insoluble matter is visible. If required, adjust volume of acid so as a mixture of 10 parts of phenanthroline solution and one part of ferric ammonium sulphate solution has *p*H in range of 5 and 6.

**6.4.3** *Ammonium Bifluoride* — 5 percent

In 500 ml distilled water dissolve 25 g of ammonium bifluoride. Store in a polyethylene bottle and dispense with a plastic pipettte.

**6.4.4** *Potassium Tetrachloromercurate* (TCM) ($K_2HgCl_4$) — 0.04 M

Dissolve 10.86 g of $HgCl_2$, 5.96 g of KCl, 0.066 g of disodium EDTA (*see* **5.3.5)** in distilled water. Add water to make up volume to 1 000 ml. Adjust *p*H to 5.2.

This reagent is stable for 6 months, but discard if a precipitate forms.

**6.4.5** *Dilute TCM -Stabilized Sulphite Standard*

Dissolve 0.5 g sodium sulphite ($Na_2SO_3$) in 500 ml distilled water. Standardization on day of preparation, wait for 30 min to allow the rate of oxidation to slow. Titrate with 0.012 5 M standard iodide-iodate solution using starch indicator (*see* 5.3.2). Calculate molarity of working standard as follows:

$$\text{Molarity of } SO_3^{2-} = \frac{(A - B) \times M}{V}$$

where

$A$ = volume, in, ml, of titrant of sample;

$B$ = volume, in ml, of titrant for blank;

M = molarity of standard iodide-iodate solution; and

$V$ = volume, in ml, of sample.

As stock sodium sulphite ($Na_2SO_3$) solution is unstable, immediately after standardization. Pipet 10 ml into 100 ml volumetric flask partially filled with TCM and dilute to mark with TCM.

Calculate the concentration of this dilute sulphite solution by multiplying the stock solution concentration by 0.02. This TCM-stabilized standard is stable for 30 days if stored at 5 °C. Discard as soon as any precipitate is noticed at the bottom.

**6.4.6** *Standard Iodide-Iodate Solution* (0.012 5 M) — *see* 5.3.3

**6.4.7** *Hydrochloric Acid* — 1 + 1

**6.4.8** *Octyl Alcohol* — reagent grade

**6.4.9** *Sulphamic Acid* — 10 percent

In 100 ml distilled water dissolve 10 g of sulphamic acid ($NH_2SO_3H$). Avoid exposure to air and is stored for few days.

**6.4.10** *EDTA* — *see* 5.3.5

### 6.5 Procedure

**6.5.1** *Sample Collection*

Collect a fresh sample, taking care to minimize contact with air. Add 1 ml of EDTA to each of 100 ml of cooled samples < 50 °C.

**6.5.2** $SO_2$ *Evolution*

**6.5.2.1** Prepare the absorbing solution by adding 5 ml of 1, 10-phenanthroline solution, 0.5 ml of ferric ammonium sulphate solution, 25 ml of distilled water and 5 drop of octyl alcohol to 100 ml of nessler tube, into it insert gas dispersion tube. To gas dispersion tube add 1 ml of sulphamic acid and 100 ml of the sample. Add 10 ml of 1 + 1 HCl and immediately connect gas washing bottle to the train as give in Fig 1.

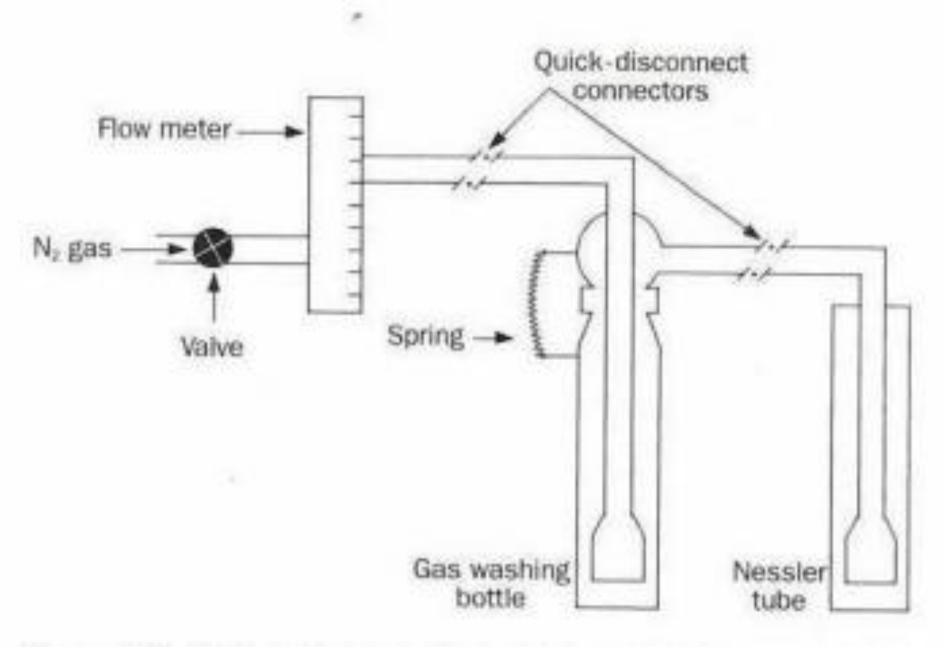

FIG 1. APPARTUS FOR EVOLUTION OF $SO_2$ FROM SAMPLES FOR COLORIMETRIC ANALYSIS

**6.5.2.2** To keep the top of gas washing bottle securely closed during the gas flow by placing spring and rubber band on the gas washing bottle. Adjust the nitrogen flow to 2.0 l/min and purge for 60 min.

**6.5.3** *Colorimetric Measurement*

**6.5.3.1** Turn off the nitrogen flow after 60 min. Disconnect nessler tube, and add 1 ml of ammonium bifluoride solution. Rinse the gas dispersion tube with distilled water. Force the rinse water into the Nessler tube using a rubber bulb. Dilute the contents in the nessler tube to a final volume of 50 ml. Mix the solution by rapidly moving the nessler tube in a circular motion.

**6.5.3.2** Ensure that the rubber stopper or PVC does not come into contact with the absorbing solution. Wait for at least 5 min after adding ammonium fluoride to the solution. Read the absorbance of the solution versus distilled water at a wavelength of 510 nm using either a 5 cm cell for a range of 0 µg to 30 µg of $SO_3^{2-}$ per portion or 1 cm cell for range of 0 µg to 100 µg of $SO_3^{2-}$ per portion.

**6.5.3.3** Take precautions to avoid transferring octyl alcohol into the cell. Let it rise to the surface of the absorbing solution, then transfer the clear lower solution to the cell using a pipette. Prepare a calibration curve by analyzing a procedure blank and at least three standards. For each set of samples, run at least one standard along with them. Maintain the samples and standards at the same temperature for maximum accuracy and keep the time interval constant from the start of purging to the addition of ammonium bifluoride.

$$\text{Sulphite concentration } \mathrm{SO_3^{2-}}, \frac{\mathrm{mg}}{\mathrm{l}}$$

$$= \frac{\text{µg of sulphite from caliberation curve}}{volume\ of\ sample}$$

## ANNEX A

(*Foreword*)

## COMMITTEE COMPOSITION

Water Quality Sectional Committee, CHD 36

| *Organization* | *Representative(s)* |
|---|---|
| Chief Scientist, Environment Protection Training and Research Institute, Hyderabad | Dr N. Raveendhar **(*Chairperson*)** |
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| Bhabha Atomic Research Centre, Mumbai | Shri S. Jayakumar<br>Shri Manoj Mohapatra (*Alternate*) |
| Bharat Heavy Electricals Limited, Haridwar | Shri Shailendra Kumar<br>Shri Sudhir Bhartiya (*Alternate* I)<br>Shri Avinash Kumar (*Alternate* II) |
| CII Triveni Water Institute, New Delhi | Shri Kapil K. Narula<br>Dr Sipika Chauhan (*Alternate*) |
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| Indian Water Works Association, Mumbai | Shri Vijay Carhate |

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| Ministry of Jal Shakti, Department of Drinking Water and Sanitation, New Delhi | Shri Sumit Priyadarshi (*Alternate*) |
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## Amendments Issued Since Publication

| Amend No. | Date of Issue | Text Affected |
|---|---|---|
| | | |
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