

Indian Standard
METHODS OF SAMPLING AND TEST
(PHYSICAL AND CHEMICAL) FOR WATER
AND WASTEWATER
PART 24 SULPHATES
(First Revision)

1. Scope—Prescribes methods for determination of sulphates in water and waste water.

1.1 Three methods as given below are prescribed:

- i) Gravimetric method,
- ii) Thorin method, and
- iii) Turbidity method.

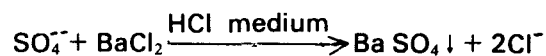
The choice depends upon the concentration range of sulphate and degree of accuracy required. Dilution or concentration of sample will bring most waters into the desired range for any of the methods prescribed in this standard.

2. Gravimetric Method

2.1 Scope and Application—This method is applicable for all the waters having sulphate concentrations above 10 mg/l; however, it is a time consuming method.

2.2 Principle and Theory—Sulphate is precipitated in hydrochloric acid medium as barium sulphate by the addition of barium chloride solution. The precipitation is carried out near boiling temperature and after a period of digestion, the precipitate is filtered, washed with water until free of chlorides, ignited or dried and weighed as barium sulphate (BaSO₄).

The reaction in its simplest form is :



2.3 Interferences—Suspended matter, silica, barium chloride precipitant, nitrate and sulphate are the principal factors in positive error. Alkali metal sulphates and heavy metals, such as chromium and iron, cause low results. To minimize solubility of barium sulphite, the acid concentration while precipitating barium sulphate, should be minimized.

2.4 Sampling and Storage—Sampling and storage shall be done as prescribed in IS : 3025 (Part 1)-1986 'Methods of sampling and test (physical and chemical) for water and wastewater: Part 1 Sampling (first revision)'. Highly polluted or contaminated samples should be stored at low temperature or treated with formaldehyde. Sulphite may be oxidized to sulphate by dissolved oxygen above pH 8.0; samples containing sulphite should have their pH adjusted below this value.

2.5 Apparatus

2.5.1 Steam bath

2.5.2 Drying oven—equipped with thermostatic control.

2.5.3 Muffle furnace—with heat indicator.

2.5.4 Desiccator

2.5.5 Analytical balance—capable of weighing to 0.1 mg.

2.5.6 Filter paper—acid washed, ashless hard finish filter paper sufficiently retentive for fine precipitates (preferably Whatman No. 42).

2.5.7 Crucible—Porous bottom silica or porcelain crucible with a maximum pore size of 5 microns.

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2.5.8 Ion-exchange column — See Fig. 1 for details. The exchange column should be regenerated by passing hydrochloric acid (2.6.2) solution after five or six samples have passed through the column followed by washing with distilled water.

2.6 Reagents

2.6.1 Methyl red indicator — Dissolve 100 mg methyl red sodium salt in distilled water and dilute to 100 ml.

2.6.2 Hydrochloric acid (1 : 4) — Dilute one volume of concentrated hydrochloric acid with four volumes of distilled water.

2.6.3 Barium chloride solution — Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 1 litre distilled water. Filter through a membrane filter or hard finish filter paper (1 ml of this reagent is capable of precipitating approximately 40 mg SO_4^{2-}).

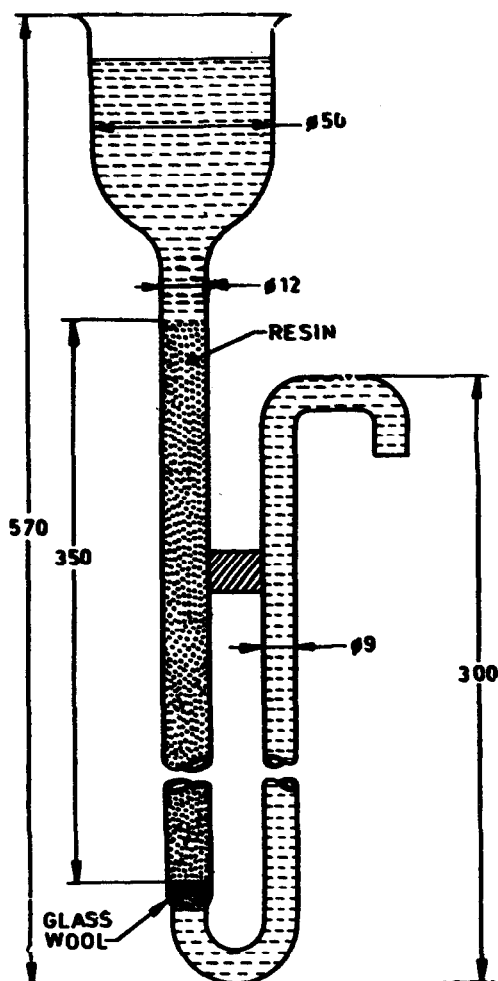
2.6.4 Silver nitrate-nitric acid reagent — Dissolve 8.5 g of silver nitrate and 0.5 ml of nitric acid in 500 ml distilled water.

2.6.5 Ion exchange resin — Strong cation exchange resin, Amberlite IR-120 or equivalent.

2.7 Sample Preparation

2.7.1 The sample used for analysis should either be free from turbidity or filtered through 0.45 μm filter.

2.7.2 If the total cation concentration in the sample is more than 250 mg/l or if the total heavy metal ion concentration is more than 10 mg/l, pass the sample through a cation removing ion exchange column.



All dimensions in millimetres.

FIG. 1 ION EXCHANGE COLUMN

2.7.3 If the silica concentration exceeds 25 mg/l, evaporate the sample nearly to dryness in a platinum dish on a steam bath. Add 2 ml hydrochloric acid (2.6.2), tilt the dish and rotate it until the acid comes in contact with the residue; continue the evaporation to dryness. Complete the drying in an oven at 180°C and if organic matter is present, char over the flame of a burner. Moisten the residue with 2 ml distilled water and 2 ml hydrochloric acid (2.6.2) and evaporate to dryness on steam bath. Add 5 ml hydrochloric acid (2.6.2), take up the soluble residue in hot water and filter. Wash the insoluble silica with several small portions of hot distilled water. Combine the filtrate and washings.

2.8 Procedure

2.8.1 Adjust the clarified sample, treated if necessary to remove interfering agents, to contain approximately 100 mg of sulphate ion in 500 ml volume.

2.8.2 Add 2 to 3 drops of methyl red indicator solution (2.6.1). Add hydrochloric acid (2.6.2) drop by drop till an orange red colour appears. Lower concentrations of sulphate ion may be tolerated if it is impracticable to concentrate the sample to the optimum level, but in such cases it is better to fix the total volume at 150 ml after concentration on hot plate.

2.8.3 Heat the solution to boiling, while stirring gently, add warm barium chloride solution (2.6.3) slowly until precipitation appears to be complete, then add about 2 ml in excess. Digest the precipitate at 80-90°C for at least 2 hours.

2.8.4 Filtration — Filter the precipitate through filter paper (2.5.6) and wash the precipitate with small portion of warm distilled water until the washings are free of chloride ions as indicated by testing with silver nitrate-nitric acid reagent (2.6.4).

2.8.5 Dry the precipitate in crucible and ignite at 800°C for 1 hour.

Note — Do not allow the filter paper to flame.

2.8.6 Cool in a desiccator and weigh.

2.9 Calculation — Calculate the sulphate concentration in the sample from the equation:

$$\text{Sulphate concentration as mg/l BaSO}_4 = \frac{\text{mg BaSO}_4 \times 411.5}{\text{ml of sample}}$$

3. Thorin Method

3.1 Scope and Application — This method is applicable to surface and groundwaters with sulphate concentration in the range 5 to 150 mg/l. Samples having higher concentrations can be measured by appropriate dilution of sample.

3.2 Principle and Theory — Sulphate ion is titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution, using thorin as the indicator.

3.3 Interferences — There are no interferences in normal waters; however, chloride ions in concentrations greater than 1 000 mg/l cause an indistinct end point when the sulphate present is low (less than 10 mg/l SO₄²⁻). To overcome this interference, a known amount of sulphate present is added to sample to increase the sulphate concentration.

3.4 Sampling and Storage — Sampling and storage shall be done as prescribed in IS : 3025 (Part 1)-1986. The sample container shall be tightly capped as soon as the sample has been collected

3.5 Apparatus

3.5.1 White porcelain basin — 100 to 125-ml capacity.

3.5.2 Burette — along with titration assembly.

3.5.3 Ion exchange column — See 2.5.8 and Fig. 1.

3.6 Reagents

3.6.1 Ethyl alcohol — 95%.

3.6.2 Ammonium hydroxide solution (1 + 99) — Mix one volume of concentrated ammonia with 99 volumes of distilled water.

3.6.3 Hydrochloric acid solution (1 + 99) — Mix one volume of concentrated hydrochloric acid with 99 volumes of distilled water.

3.6.4 Hydrochloric acid solution (1 + 4) — Dilute one volume of concentrated hydrochloric acid with 4 volumes of distilled water.

3.6.5 Thorin solution — Dissolve 0.2 g thorin (2, 2-Hydroxy-3, 6-disulpho-1-naphthylazo benzene arsenic acid) in 100 ml of distilled water.

3.6.6 Ion exchange resin — Strong cation-exchange resin, Aberlite IR-120 or equivalent.

3.6.7 Stock sulphate solution (100 mg/l SO_4^{2-})— Dissolve 1.479 g anhydrous sodium sulphate (Na_2SO_4) (dried at 110°C for 1 hour) in distilled water and make up to 1 litre in volumetric flask.

3.6.8 Standard sulphate solution— Prepare a series of standard solutions by diluting stock solution of sulphate with distilled water. The concentrations of standard solutions are 0 (blank), 10, 20, 30, 40, 50, 80, 100 and 150 mg/l SO_4^{2-} .

3.6.9 Standard barium chloride solution— Dissolve 0.4 g barium chloride ($BaCl_2 \cdot 2H_2O$) in 800 ml of distilled water and adjust the pH to 3.5 to 4.0 with dilute hydrochloric acid (3.6.3) or ammonia solution (3.6.2) and finally make up to one litre.

3.7 Sample Preparation— The sample should be free from turbidity or filtered through a 0.45 μm filter.

3.8 Procedure

3.8.1 Pass the sample through ion exchange column (50 ml at a time), discard the first 10 ml effluent and then collect in a 100-ml beaker. Pipette 10 ml of this sample into a porcelain basin (3.5.1).

3.8.2 Add 40 ml alcohol and 2 drops of thorin indicator. Adjust the pH to 3.8 to 4.0 by carefully adding, drop by drop ammonia solution (3.6.2) until the solution just turns pink. Then add hydrochloric acid (3.6.3) solution drop by drop until the pink colour disappears; a drop is usually sufficient.

Note— If the ammonia is added too fast, it is possible to overrun the colour change from yellow to pink and the sample continues to be yellow. It is then impossible to develop the pink colour by addition of ammonia solution.

3.8.3 Titrate with standard barium chloride solution (3.6.9) until sample just turns pink.

3.9 Calculation— Prepare a calibration curve, ml of standard barium chloride solution needed to titrate standard sulphate solution (3.6.8) vs mg/l SO_4^{2-} , and read the sulphate concentration of sample directly from the graph.

4. Turbidity Method

4.1 Scope and Application— This method is applicable to surface and ground water in the range of 1 to 40 mg/l SO_4^{2-} . Samples having higher concentrations than this can be measured by appropriate dilution of sample.

4.2 Principle and Theory— Sulphate ion is precipitated in hydrochloric acid medium with barium chloride in such a manner as to form barium sulphate crystals of uniform size. The absorbance of barium sulphate suspension is measured by a nephelometer or transmission photometer (turbidity meter) and the sulphate ion concentration is determined by comparison of the reading with a standard curve.

4.3 Interference

4.3.1 Colour or suspended matter in large amounts will interfere.

4.3.2 In waters containing large quantities of organic material, it may not be possible to precipitate barium sulphate satisfactorily.

4.4 Sampling and Storage— Sampling and storage shall be done as prescribed in IS : 3025 (Part 1)-1986. The bottles shall be capped tightly as soon as the sample is collected.

4.5 Apparatus

4.5.1 Turbidity meter or spectrophotometer— for use at 420 nm.

4.5.2 Usual laboratory glass apparatus

4.6 Reagents

4.6.1 Barium chloride

4.6.2 Gelatin powder

4.6.3

a) Conditioning reagent (1)— Add 0.3 g gelatin in 100 ml distilled water and warm it on hot plate till it is dissolved. The gelatin solution is kept for about 12 hours, or overnight preferably, at 4°C. After bringing the solution to room temperature, 3.0 g of barium chloride is added to gelatin solution and dissolved by mixing. The turbid solution is kept standing for 2 hours and mixed before use.

Note— The reagent can be used for a week, if stored in a refrigerator.

b) Conditioning reagent (2)— Mix 50 ml glycerol with a solution containing 30 ml concentrated hydrochloric acid, 300 ml distilled water, 100 ml 95 percent ethyl or isopropyl alcohol and 75 g sodium chloride.

4.6.4 Stock sulphate solution (100 mg/l)— Dissolve 0.1479 g of anhydrous sodium sulphate (Na_2SO_4) in distilled water and dilute to one litre.

4.6.5 Standard sulphate solution— Prepare a series of standards by diluting stock solution of sulphate to cover the desired range in between 1 to 40 mg/l.

4.6.6 Hydrochloric acid (1 + 9)— Dissolve one volume of concentrated hydrochloric acid with 9 volumes of distilled water.

4.7 Sample Preparation

4.7.1 Filter the sample through 0.45 μm , filter, if there is any turbidity.

4.8 Procedure

4.8.1 Take 20 ml of clear aliquot of the water sample or suitable amount diluted to 20 ml in 100-ml conical flask.

4.8.2 Add 1.0 ml hydrochloric acid solution (4.6.6) and 1.0 ml conditioning reagent and mix well for 30 seconds.

4.8.3 Read the absorbance on spectrophotometer after 10 minutes if glycerol conditioning reagent is used or 30 minutes if gelatin is used, at 420 nm, or read the turbidity occurred on turbidity meter following the manufacturer's instructions to operate.

4.8.3.1 If water sample is turbid, take 20 ml sample or suitable amount dilute to 20 ml with distilled water. Do not add conditioning reagent. Read the absorbance of this sample and subtract this value from the absorbance in 4.8.3.

4.8.4 Calibration curve— Prepare a series of standards taking at least 4 standards and run a blank and follow the steps 4.8.2 and 4.8.3. Prepare a calibration curve of standards mg/l vs absorbance.

4.9 Calculation— Read the sulphate concentration of sample directly from the calibration curve.

EXPLANATORY NOTE

This standard offers choice of three methods for determination of sulphate. The choice depends upon the concentration range of sulphate and the degree of accuracy required. Dilution or concentration of the sample will bring most waters into the desired range of any one of the methods given in this standard.

This method supersedes 6 of IS : 2488 (Part 3)-1968 'Methods of sampling and test for industrial effluents: Part 3' and 20 of IS : 3025-1964 'Methods of sampling and test (physical and chemical) for water used in industry'.