

BUREAU OF INDIAN STANDARDS

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भारतीय मानक मसौदा
मृदा में कुल सल्फर एवं सल्फर यौगिक — परीक्षण पद्धतियाँ
(आइ एस 14685 का पहला पुनरीक्षण)

Draft Indian Standard

TOTAL SULPHUR AND SULPHUR COMPOUNDS IN SOILS — TEST METHODS

(First revision of IS 14685)

ICS 65.080

Soil Quality and Fertilizers Sectional Committee, **Last date of comments:** 10 February 2025
FAD 07

FOREWORD

(Formal clauses would be added later)

Fertility of Indian soils varies with geographical existence. Various types of Indian soils are enriched with few major and/or minor nutrients responsible for successful crop production. Sulphur is one of them and responsible for successful crop production.

A need was felt to formulate standard procedure for determination of sulphur and sulphur compounds for the benefit of research organisations and those engaged in organised farming including plantation crops.

This standard was first published in 1999. In this revision, the test method used for determination of sulphate and extractable sulphur by lithium chloride has been replaced by determination of sulphate and extractable sulphur by calcium chloride.

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

1 SCOPE

This standard prescribes the method for determination of total sulphur and sulphur compounds in soils.

2 DETERMINATION OF TOTAL SULPHUR BY DIGESTION WITH NITRIC/PERCHLORIC/PHOSPHORIC ACIDS

2.1 Apparatus

2.1.1 *Beaker* — 150 ml

2.1.2 *Water Bath*

2.1.3 *Hot Plate*

2.1.4 *Volumetric Flask* — 100 ml

2.2 Reagents

2.2.1 *Nitric Acid* — 69 percent (v/v)

2.2.2 *Perchloric Acid* — 60 percent (v/v)

2.2.3 *Phosphoric Acid* — 85 percent (v/v)

2.2.4 *Mixture of Perchloric Acid and Phosphoric Acid* — Take 3.0 ml of perchloric acid (*see 2.2.2*) and 7.0 ml phosphoric acid (*see 2.2.3*) solutions in a measuring cylinder and mix well.

2.2.5 *Hydrochloric Acid* — 37 percent (v/v).

2.2.6 *Dilute Hydrochloric Acid*

2.3 Procedure

Weigh 2 g soil sample into a 150 ml beaker, add 3 ml nitric acid (*see 2.2.1*), cover the beaker with a watch glass, mix by swirling and heat on a water bath for 1 h. Remove the beaker after heating from water bath, uncover, and add perchloric acid and phosphoric acid mixture (*see 2.2.4*). Heat on a hot plate at 190 °C to 210 °C until heavy white fumes of perchloric acid are visible. Replace the watch glass and continue heating for 30 min. Cool, uncover, add 2 ml hydrochloric acid (*see 2.2.5*) and heat again until perchloric acid fumes are again visible. Transfer to a 100 ml volumetric flask and make up to volume with dilute hydrochloric acid. The total acidity of the diluted sample should be at least one molar.

The siliceous residue may be removed by filtration or allowed to settle in the volumetric flask. Take a 1 to 5 ml aliquot for sulphur analysis by the Johnson Nishita method.

NOTE — Aliquots more than 2 ml should be reduced in volume by evaporation or addition of reducing agent. Also, soils with very high iron content may require the addition of extra reducing agent. When the reducing agent is added to the sample aliquot in the boiling flask, the need for extra amounts may easily be judged.

3 DETERMINATION OF TOTAL SULPHUR BY POTASSIUM NITRATE/NITRIC ACID DIGESTION

3.1 Apparatus

3.1.1 *Muffle Furnace*

3.1.2 *Water Bath*

3.1.3 *Beaker* — 50 ml

3.2 Reagents

3.2.1 *Nitric Acid* — 25 percent (v/v) prepared from nitric acid analytical reagent grade

3.2.2 *Digesting Solution* — Dissolve 100 g potassium nitrate, analytical reagent grade in 600 ml distilled water. Add 350 ml concentrated nitric acid and dilute to one litre.

3.2.3 *Filter Paper* — Whatman no. 42

3.3 Procedure

Weigh 1 g of the grounded and air-dried soil into a 50 ml beaker. Add 10 ml of the digesting solution (*see 3.2.2*) and evaporate to dryness on a water bath. Place the beaker in a muffle furnace, heat at 500 °C for 3 h. After cooling add 5 ml of 25 percent nitric acid (*see 3.2.1*) and again digest the contents for 1 h on a water bath. Extract the soluble salts with distilled water and filter the solution through a Whatman No. 42 or equivalent filter paper. Dilute to a known volume and take a suitable aliquot of the filtrate for the turbidimetric determination of sulphate. A blank shall also be carried out with each sample.

4 DETERMINATION OF SULPHATE AND EXTRACTABLE SULPHUR BY CALCIUM PHOSPHATE

4.1 Apparatus

4.1.1 *Hot Plate*

4.1.2 *Air Oven*

4.1.3 *Beaker* — 200 ml.

4.1.4 *Flask*

4.2 Reagents

4.2.1 *Monocalcium Phosphate Solution* — prepared by dissolving 20.2 g monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O})$] in one litre water.

4.2.2 *Nitric Acid and Perchloric Acid Mixture* — 2:1 (v/v)

4.2.3 *Filter Paper* — Whatman No. 42

4.3 Procedure

Take 20 g of soil in a beaker and add 100 ml of monocalcium phosphate solution (*see* 4.2.1). Mix thoroughly by shaking. Filter through Whatman no. 42 or equivalent filter paper.

Transfer an aliquot to a flask, and place in drying oven overnight or until evaporation is complete. After cooling, add 2 ml nitric acid and perchloric acid mixture (*see* 4.2.2) and digest on a hot plate, beginning at low heat but increasing temperature gradually until the white fuming stage is reached. Continue digestion at slightly reduced temperature, to minimize loss of perchloric acid, for 15-20 min. After cooling, dilute with water and determine sulphate turbidimetrically.

5 DETERMINATION OF SULPHATE AND EXTRACTABLE SULPHUR BY CALCIUM CHLORIDE

5.1 Apparatus

5.1.1 *Colorimeter or Spectrophotometer*

5.1.2 *Mechanical shaker*

5.2 Reagents

5.2.1 *Calcium Chloride Solution (0.15 Percent)* — Dissolve 1.5 g of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in about 500 ml of distilled water and make the volume to 1 litre.

5.2.2 *Barium Chloride Crystals* — Grind BaCl_2 , (AR grade) crystals to pass through a 30-mesh sieve and retain on a 60 mesh sieve, and store in a clean bottle.

5.2.3 *Standard S Solution* — Dissolve 0.5434 g of oven-dried AR grade K_2SO_4 in distilled water and dilute to 1 L. This contains 100 micro g S ml^{-1} .

5.2.4 *Gum Acacia Solution* — Dissolve 0.25 g of gum acacia in distilled water and dilute to 100 ml.

5.3 Preparation of Standard Curve

5.3.1 Take 0.25, 0.50, 1.0, 2.5 and 5.0 ml of standard S solution in 25 ml volumetric flasks, and add 10 ml of extracting solution (*i.e.* 0.15 % CaCl_2 solution) to each flask. For blank take 10 ml of extracting solution in a 25 ml volumetric flask.

5.3.2 Add 1 g of BaCl_2 crystals to each flask and swirl to dissolve the crystals.

5.3.3 Add 1 ml of 0.25 percent gum acacia solution, make up the volume with distilled water and shake well manually.

5.3.4 Within 5-30 min of development of turbidity (white colour), read the absorbance at 340 nm on a spectrophotometer, or on a colorimeter using blue filter.

5.3.5 Draw a curve taking S concentrations on X-axis and absorbance readings on Y-axis.

5.4 Procedure

Weigh 10 g of air-dry soil in a 150 ml conical flask and add 50 ml of 0.15 percent CaCl₂ solution (see 5.2.1). Shake for 30 min on a rotary shaker and filter through Whatman no. 42 filter paper. Take 10 ml of the clean filtrate in a 25 ml volumetric flask, follow the steps given for standard curve to develop the turbidity and record the absorbance.

5.5 Calculation

$$\text{Available S in soil, in mg/kg} = R \times \frac{50}{10} \times \frac{1}{10}$$

where,

R = S content in µg as read on X-axis

Note — In case, the available S content of the soil is very low, a 20 ml aliquot (instead of 10 ml) should be taken to develop the turbidity.

6 PREPARATION OF COLLOID FREE SOIL EXTRACT

6.1 Apparatus

6.1.1 *Suitable Bacteriological Filter*

6.1.2 *Pressure Filtration Funnels* — fitted with metrical filters.

6.1.3 *Centrifuge with Centrifuge Bottles*

6.2 Reagent

6.2.1 *Sulphur Free Distilled Water*

6.3 Procedure

Take 20 g of soil sample in a 200 ml centrifuge bottle, add 100 ml of sulphur free distilled water and shake for 30 min. Centrifuge the suspension at 2000 rpm for 15 min. Filter the supernatant liquid through a suitable bacteriological filter which has previously been washed several times with sulphur free distilled water to remove any soluble sulphur compounds. Pressure filtration funnels fitted with metrical filters shall then be used to obtain soil water extracts free of clay colloids.

7 DETERMINATION OF ELEMENTAL SULPHUR

7.1 Apparatus

7.1.1 *Glass Bottle with Stopper*

7.1.2 *Centrifuge with Tubes*

7.1.3 *Rotary Film Evaporator*

7.1.4 *Distillation Apparatus*

7.1.5 Round Bottom Flask

7.1.6 Test Tubes

7.2 Reagents

7.2.1 Chloroform — Re-distilled analytical reagent grade.

7.2.2 Iron Powder — Analytical reagent grade.

7.2.3 Hydrochloric Acid — Mix equal volumes of concentrated hydrochloric acid and water.

7.2.4 Sodium Hydroxide Solution — Dissolve 40 g sodium hydroxide in one litre of water.

7.2.5 Acetone : Dithizone Solution — Dissolve about 0.01 g of dithizone in one litre of glass distilled acetone freshly prepared.

7.2.6 Mercuric Chloride Solution — Dissolve 0.271 g in one litre of distilled water to give a 0.001 M solution.

7.2.7 Standard Sulphur Solution — Dissolve 0.1 g of sulphur in chloroform and adjust to 100 ml. This solution contains 1 mg of sulphur per millilitre and may be diluted with chloroform.

7.2.8 Sulphur Free Nitrogen Gas

7.3 Procedure

7.3.1 Weigh about 50 g of soil into a glass bottle and add 100 ml chloroform. Stopper with a rubber blunge protected by a small piece of thin polyethylene. Shake intermittently by hand for about 30 min. Centrifuge, if necessary, to separate the extract from the soil. Take with a pipette an aliquot of the supernatant liquid containing 10-400 µg of sulphur into a 50 ml round bottom flask and evaporate to dryness on a rotary film evaporator. Unused chloroform may be recovered from the soil by distillation.

7.3.2 Add 2 ml acetone and about 0.2 ml chloroform to the 50 ml round bottom flask containing the evaporate sample as described in **7.3.1**. Place about 0.2 g iron powder in the flask and attach the flask to the distillation apparatus. Sweep the apparatus free of air by passing nitrogen for a few minutes. Place 10 ml sodium hydroxide solution in a 2.5 cm diameter test tube and attach it to the side arm so that the test tube dips below the surface. Fill the graduated receptacle with the hydrochloric acid and run 10 ml into the apparatus. Apply a low flame with a microburner and allow 10 to 15 minutes for transfer of sulphide. Detach the glass tube from the apparatus and leave it in the test tube. Add 10 ml of the acetone: dithizone solution (*see 7.2.5*) to the test tube washing the inside of the glass tube with it. Titrate against the mercuric chloride to a pink end point. It is convenient to stir the solution during titration by bubbling nitrogen through it. Standardize the mercuric chloride solution against standard solutions of sulphur reduced in the same way.

NOTE — One advantage of this procedure is that wet soils can be extracted without preliminary drying.

8 DETERMINATION OF ORGANIC SULPHUR

8.1 Apparatus

8.1.1 Muffle Furnace

8.1.2 Gooch Crucible

8.1.3 Porcelain Crucible

8.1.4 Sieve 20 Mesh

8.1.5 Erlenmeyer Flask

8.2 Reagents

8.2.1 Hydrochloric Acid — 1 N and 6 N.

8.2.2 Calcium Acetate Solution [$\text{Ca}(\text{CH}_3\text{COO})_2$] — 1 N

8.2.3 Acetic Acid — 2N.

8.2.4 Extracting Solution — Dissolve 4.6 g of sodium phosphate ($\text{NaH}_2\text{PO}_4\text{H}_2\text{O}$) in one litre of 2 N acetic acid.

8.2.5 Filter Paper Whatman No. 1

8.3 Procedure

Take 10 g dried soil in a gooch crucible. Add 50 ml of 1 N hydrochloric acid (*see* **8.2.1**) and shake well. Transfer the contents in a porcelain crucible through Whatman no. 1 filter paper. Wash the residue with 100 ml calcium acetate solution (*see* **8.2.2**) followed by distilled water alone to remove the excess calcium acetate. Dry the crucible and contents at 105 °C to permit final calculations made on the basis of the original mass of soil sample.

Pass the soil sample through a 20 mesh sieve. Weigh and place 2.5 g soil in a suitable porcelain crucible. Thoroughly mix 0.5 g sodium bicarbonate with the soil, and then add an additional 0.5 g uniformly as a surface layer. Ignite the mixture at 500 °C in muffle furnace for 3 h. Allow the sample to cool, and then transfer the contents of the crucible to a 50 ml Erlenmeyer flask. By means of a pipette, add 25 ml extracting solution, using the first 10 ml to rinse the crucible and adding the rest slowly to avoid loss by spattering. After the reaction subsides, shake the contents of the flask for 30 minutes. Filter the soil suspension through a dry Whatman no. 1 or equivalent filter paper.

The determination of sulphate in an aliquot of the filtrate can be carried out by turbidimetry.

NOTE — The initial extraction with 1N hydrochloric acid to remove sulphides may not remove certain sulphides for example, Cu, As, Sb, etc. Also, it may be preferable to substitute a calcium phosphate solution for calcium acetate to ensure removal of adsorbed sulphate.