Doc: FAD 07(27329)WC
January 2025

BUREAU OF INDIAN STANDARDS

DRAFT FOR COMMENTS ONLY

भारतीय मानक *मसौदा*

उर्वरकों के नमूने लेने और परीक्षण करने की विधि: भाग 6 नमी और अशुद्धियों का निर्धारण

(*आइ एस 6092 भाग 6 का दूसरा पुनरीक्षण*)

Draft ***Indian Standard***

METHOD OF SAMPLING AND TEST FOR FERTILIZERS: PART 6 DETERMINATION OF MOISTURE AND IMPURITIES

(*Second Revision of IS 6092 (Part 6*))

ICS 65.080

Soil Quality and Fertilizers Sectional Committee, FAD 07

Last date of comments: 15 February 2025

FOREWORD

(*Adoption clauses will be added later*)

This standard was first published in 1971. In the first revision issued in 1985, Silver Diethyldithiocarbamate Method for determination of arsenic was made as a referee method.

In this revision, the standard has been brought out in the latest style and format of the Indian Standards, and references to Indian Standards wherever applicable have been updated.

In the preparation of this standard, consideration has been given to harmonize the test methods with the methods of sampling and test for fertilizers prescribed under the *Fertilizer* (*Control*) *Order*, 1985.

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*)'

CONTENT

1 SCOPE

This standard (Part 6) prescribes the methods for determination of moisture and impurities namely, biuret, free acidity, arsenic, calcium nitrate, fluorine, nickel, chromium and sodium in fertilizers and fertilizer mixtures.

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 listed below:

IS No.	*Title*
IS 323 : 2009	Rectified spirit for industrial use – Specification (*second revision*)
IS 336 : 2021	Ether – Specification (*third revision*)
IS 1070 : 2023	Reagent Grade Water – Specification (*fourth revision*)
IS 6092 (Part 1) : 1985	Methods of sampling and test for fertilizers: Part 1 Sampling (*first revision*)
IS 6092 (Part 5) : 1985	Methods of sampling and test for fertilizers: Part 5 Determination of secondary elements and micronutrients (*first revision*)

3 SAMPLING

Representative test samples of the fertilizers shall be prepared as prescribed in IS 6092 (Part 1).

4 DETERMINATION OF MOISTURE

4.1 Method 1

4.1.1 *Applicability* — This method is not applicable to samples that yield volatile substances other than water at the drying temperature, such as super-phosphate, urea, calcium ammonium nitrate, diammonium phosphate, etc.

4.1.2 *Procedure* — Weigh to the nearest milligram, about 2 g of the prepared sample in a weighed, clean, dry squat form weighing bottle. Heat in an oven for about 5 h at 99 °C to 101 °C (*see* Note) to constant mass. Cool in a desiccator and weigh.

NOTE — In the case of sodium nitrate, ammonium sulphate and potassium salts, heat to constant mass at 129 °C to 131 °C.

4.1.3 *Calculation*

$$\text{Moisture, percent by mass} = \frac{100\,(M_1 - M_2)}{(M_1 - M_3)}$$

Where

M_1 = mass, in g, of the bottle with the material before drying,

M_2 = mass, in g, of the bottle with the material after drying, and

M_3 = mass, in g, of the bottle.

4.1.3.1 Report the temperature used for drying.

4.2 Method 2

4.2.1 *Applicability* — This method shall be used for ammonium chloride and diammonium phosphate

4.2.2 *Procedure* – Weigh accurately about 5 g of the prepared sample in a weighed shallow porcelain dish and dry for 24 h in a vacuum desiccator (40 to 50 mm or less mercury pressure) over sulphuric acid (98 percent minimum) and re-weigh to a constant mass. Preserve the dried material for subsequent tests.

4.2.2 *Calculation*

$$\text{Moisture, percent by mass} = 100 \times \frac{M_1 - M_2}{M_1 - M_3}$$

where

M_1= mass, in g, of the dish with the material before drying,

M_2 = mass, in g, of the dish with the material after drying, and

M_3 = mass, in g, of the porcelain dish.

4.3 Method 3

4.3.1 *Applicability* – For samples like urea and calcium ammonium nitrate which yield volatile substances other than water on drying by heating, the Karl Fischer method (given below) is used for the determination of moisture.

4.3.2 *Reagents*

4.3.2.1 *Karl Fischer reagent* — To a mixture of 650 ml of methanol and 200 ml of pyridine contained in a ground glass stoppered flask, add 125 g of iodine and immediately stopper the flask tightly. Separately, pass dry sulphur dioxide into 100 ml of pyridine contained in a 250 ml graduated cylinder and cool in an ice-bath, until the volume reaches 200 ml. Slowly add iodine solution to the cooled sulphur dioxide solution, stopper immediately and shake well until the iodine is dissolved. Transfer solution to an automatic burette protected from absorption of moisture by a drying agent, and allow to stand for 24 h before standardizing. The reagent deteriorates continuously and it shall be standardized within one hour before use.

NOTE — An alternative method of preparing Karl Fischer reagent consists of adding 30 g of iodine into 1 litre of anhydrous pyridine in a 5 litre flat bottomed flask. Swirl well till dissolution is complete. Then add 2 litres of anhydrous methanol and 140 ml of liquid sulphur dioxide, little by little, swirling after each addition. Stopper the flask with a rubber bung and let stand in dark for 24 h before use.

CAUTION — All operations for the preparation of the Karl Fischer reagent should be carried out in a well ventilated hood. Sulphur dioxide is toxic. If the liquid is handled, suitable protective devices such as goggles and gloves should be worn.

4.3.2.2 *Standard water solution* — Weigh out exactly 2 g of water into a thoroughly dry 1 litre volumetric flask and dilute to volume with dry methanol. Retain sufficient quantity of the same methanol for a blank determination. Keep the solution in tightly closed container.

4.3.3 *Procedure*

4.3.3.1 *Determination of end point in Karl Fischer titration* — With some experience, the end point can be detected visually by the change of colour from a light brownish-yellow to amber. But when the end point is not clearly defined, the electrometric method for determining the end point should be adopted. Adjust the potentiometer so that when a small excess (0.02 ml) of the reagent is present, a current of 50 to 100 micro amperes is recorded. It is necessary that the solution should be continuously and vigorously stirred. At the beginning of the titration, a current of only a few microamperes will flow. After each addition of reagent, the pointer of the micro ammeter is deflected but rapidly returns to the original position. At the end point a deflection is obtained which endures for a longer period.

4.3.3.2 *Standardization of the Karl Fischer reagent*

a) Pipette exactly 10 ml of methanol into a dry titration flask and titrate with the reagent to the end point. Then pipette exactly 10 ml of standard water solution into the flask and again titrate to the end point.
b) Take in a 300 ml beaker 50 ml of methanol and fix in the aquameter. Create dry atmosphere by pumping dry air. Titrate to the Karl Fisher reagent end point (V_1 ml). Take water in a large pipette and weigh up to 0.1 mg. Transfer 1 drop of water to the aquameter beaker and again weigh.

Note the mass of water drop added to the beaker (M mg). Titrate with Karl Fischer reagent till the end point is reached (V_2 ml). Note the volume of Karl Fischer reagent consumed ($V_2 - V_1$) ml. Calculate the Karl Fischer factor as follows:

$$\text{Karl Fischer Factor (F)} = \frac{M}{V_2 - V_1} \text{ mg of water per ml of reagent}$$

where

M = mass of the water drops added to the beaker;

V_1 = volume, in ml, of the reagent used in titration of methanol **4.3.3.2**; and

V_2 = total volume, in ml, of the reagent used.

4.3.3.3 *Titration of the sample* — Transfer 25 ml of methanol to the titration flask and titrate to the end point with the Fischer reagent. The volume consumed may not be recorded. Quickly transfer to the titrated liquid an accurately weighed quantity of the material containing 10 to 50 mg of water, stir vigorously and titrate to the end point.

4.3.4 *Calculation*

$$\text{Moisture, percent by mass} = \frac{0.1 \times M_1 (V_3 - 2.5\, V_1)}{(V_2 - V_1) M_2}$$

where

M_1 = mass, in mg, of water contained in 10 ml of standard water solution;

V_3 = total volume, in ml, of the reagent used in titration in **4.3.3.3**;

V_1 = volume, in ml, of the reagent used in titration of the methanol in **4.3.3.2**;

V_2 = total volume, in ml, of the reagent used in **4.3.3.2**; and

M_2 = mass, in g, of the material taken for the test in **4.3.3.3**.

5 METHODS OF TESTS FOR IMPURITIES

5.1 Determination of Biuret

5.1.1 *General* — Two procedures for determining biuret content are given below. 'Atomic Absorption Spectrophotometric Method' is the referee method and shall be used in case of any dispute. 'Colorimetric Method' is an alternative one.

5.1.2 *Atomic Absorption Spectrophotometric Method*

5.1.2.1 *Applicability* — This method is intended for determining biuret content in urea and mixed fertilizers.

5.1.2.2 *Apparatus*

a) Atomic absorption spectrophotometer

5.1.2.3 *Reagents*

a) *Copper sulphate solution* — Dissolve 15 g of copper sulphate pentahydrate in water and dilute it to 1 litre, the solution should be capable of hydrolyzing 0.1 g urea per 200 ml solution.
b) *Buffer solution* — Check the *p*H and adjust to 13.4. Dissolve 24.6 g of potassium hydroxide and 30 g of potassium chloride in water and dilute to 1 litre.
c) *Starch solution* — Treat 1 g of starch (soluble) with 10 ml cold water, triturate to a thin paste, and pour gradually into 150 ml boiling water containing 1 g oxalic acid. Boil until solution clears, cool, and dilute it to 200 ml. Prepare fresh solution every week.
d) *Bromocresol purple indicator* — Dissolve 0.1 g bromocresol purple in 19 ml of 0.1 N sodium hydroxide and dilute to 250 ml with water.
e) *Biuret* — Pure biuret with guaranteed composition if not available to recrystallize, weigh approximately 10 g reagent grade biuret, transfer it to 1 litre beaker, add 500 ml of water, and heat on hot plate with occasional stirring until dissolved. Boil slowly until volume decreases to about 250 ml. Remove, and let it cool gradually to room temperature. Filter through fritted-glass funnel, transfer it to evaporating dish, place in an oven at 105 °C to 110 °C and dry for 1 h. Remove it from oven, place it into a desiccator, and cool to room temperature.
f) *Biuret standard solution* (*0.4 mg/ml*) — Dissolve 0.400 0 g re-crystallized biuret in warm water, cool, transfer it to 1 litre flask, and dilute it up to the mark.

g) *Copper stock solution* (*1000 µg Cu/ml*) — Dissolve 1.000 g pure copper metal in minimum amount of concentrated nitric acid and add 5 ml of concentrated hydrochloric acid. Evaporate it almost to dryness and dilute it to 1 litre with 0.1 N hydrochloric acid.

h) *Copper standard solution* — Dilute aliquots of copper stock solution as prepared in [**5.1.2.3** (g)] with water to obtain more than equal to 4 standard solutions within range of determination, 1 to 4 µg, copper/ml in the final solution.

5.1.2.4 *Determination of calibration factor*

Transfer aliquots of biuret standard solution containing 4, 8, and 12 mg biuret separately to 100 ml volumetric flasks; dilute to about 30 ml with water, and add 25 ml of ethanol to each. While stirring with magnetic stirrer, add 20 ml starch solution, 10 ml of copper sulphate solution, and 20 ml of buffer solution. Remove stirring bar, rinse, dilute it to the mark, mix thoroughly and let it stand for 10 min. Filter under vacuum about 50 ml through dry 150 ml medium porosity fritted glass funnel into a dry flask. Transfer 25 ml aliquots of each filtrate to 250 ml volumetric flasks, acidify with 5 ml of 1 N hydrochloric acid, and dilute it to the volume with water. Proceed as given in IS 6092 (Part 5) using copper standard solution to determine complexed copper in solution by atomic absorption spectrophotometer after adding equivalent amounts of ethanol potassium hydroxide solution, buffer solution, and 1 N of hydrochloric acid. Take more than three readings of each solution. From mean value of copper concern, calculate factor relating mg of copper found to mg biuret added. This determination may be done daily or each time when the estimation is taken up.

5.1.2.5 *Procedure*

a) *In urea* — Weigh accurately sample containing less than 10 mg biuret, dissolve in water, transfer it to 100 ml volumetric flask, add 25 ml of ethyl alcohol and proceed as given in **5.1.2.4** beginning 'While stirring with magnetic stirrer.....' from copper found, calculate biuret concentration, using factor.

b) *In mix fertilizers* — Transfer accurately weighed sample not exceeding 5 g, containing less than 40 mg biuret to 250 ml beaker and add 1 ml of water for each g of sample. Warm, add 65 ml alcohol and 7 drops bromocresol purple, and adjust *p*H to first blue colour (*p*H 6 to 7) with 10 percent of potassium hydroxide. Place on hot plate, heat it to boiling, cool, and if *p*H has changed, make final adjustment to first blue with vacuum, filter through paper pulp pad which has been washed with alcohol, into 100 ml volumetric flask (if filtrate is not clear, improper *p*H adjustment has been made. Add hydrochloric acid and readjust to *p*H 6 to 7). Wash pad and precipitate with ethanol and further dilute it to volume. Transfer 25 ml aliquot to 100 ml volumetric flask and proceed as given in **5.1.2.4**, beginning: 'While stirring with magnetic stirrer….'.

5.1.2.6 *Calculation* — From copper found, calculate biuret concentration using factor and appropriate dilution factors. (Final aliquot may be varied to give copper concentration between 1 and 4 µg/ml.)

5.1.3 *Colorimetric Method*

5.1.3.1 *Applicability* — This method is applicable to urea samples only, and not for complex/mixed fertilizers.

5.1.3.2 *Reagents*

a) *Alkaline tartrate solution* — Dissolve 40 g of sodium hydroxide in 50 ml of water, cool, add 50 g of sodium potassium tartrate and dilute to 1 litre. Let it stand for at least one day before use.
b) *Copper sulphate solution* — Dissolve 15 g of copper sulphate pentahydrate in double glass distilled water and dilute to 1 litre.
c) *Standard biuret solution (1 mg/ml)* — Dissolve 100 mg of reagent grade biuret in carbon dioxide-free water and make up to 100 ml.

5.1.3.3 *Preparation of standard curve* — Pipette out a series of aliquots, 2 to 50 ml, of standard biuret solution in 100 ml volumetric flasks. Bring the volume to approximately 50 ml with carbon dioxide free water. Add one drop of methyl red and neutralize with 0.1 N sulphuric acid to pink colour. Add with swirling 20 ml of alkaline tartrate solution and then 20 ml of copper sulphate solution. Dilute to mark. Shake for 10 seconds and place in a water-bath for 15 min at (30 ± 5) °C.

a) *Prepare the reagent blank simultaneously* — Determine absorbance of each solution against blank at 555 nm (an instrument with 500 to 570 nm filter is also satisfactory) with 2 to 4 cm cell and plot the standard curve.

5.1.3.4 *Procedure*

a) *In urea* – Dissolve (with stirring) 2 to 5 mg of the sample in a 100 ml of water at temperature approximately 50 °C for 30 min. Filter and wash into 250 ml volumetric flask and dilute to volume. Transfer 25 ml aliquot to a 100 ml volumetric flask and proceed as given under **5.1.2.5** (a).

5.1.3.5 *Calculation* — From the standard curve, determine the concentration of biuret in final dilution. Then calculate as given below:

$$\text{Biuret, percent by mass} = \frac{C_1 \times 100}{C_2}$$

where

C_1 = concentration, in mg/ml, of biuret in final dilution obtained from standard curve; and

C_2 = concentration of original sample in final dilution expressed as mg/ml.

5.2 Determination of Free Acidity

5.2.1 *Applicability* — This method is intended for determining free acidity in ammonium sulphate and ammonium sulphate nitrate.

5.2.2 *Reagents*

a) *Standard sodium hydroxide solution* — 0.02 N.
b) *Methyl red indicator* – Dissolve 0.2 g of methyl red indicator in 100 ml rectified spirit or in 85 percent ethyl alcohol.
c) *Methyl red — methylene blue mixed indicator solution* – Prepare by mixing equal volumes of 0.2 percent solution of methyl red and 0.1 percent solution of methylene blue both dissolved in rectified spirit.

5.2.3 *Procedure*

Dissolve about 20 g of the prepared sample, accurately weighed, in about 50 ml of freshly distilled and cooled water. Filter (*see* Note), if necessary, make up the volume to about 200 ml. Titrate with standard sodium hydroxide solution taken in a microburette using one or two drops of methyl red as indicator, if satisfactory end point with methyl red is not obtained, methyl red-methylene blue mixed indicator may be used.

NOTE — The filtering medium shall be neutral preferably sintered glass funnel and shall not contain any alkaline or acidic material which would affect the titration.

5.2.4 *Calculation*

5.2.4.1 *For ammonium sulphate*

$$\text{Free acidity (as } H_2SO_4\text{), percent by mass} = \frac{4.904\,VN}{M}$$

where

V = volume, in ml, of standard alkali solution;

N = normality of standard alkali solution; and

M = mass, in g, of prepared sample taken for the test.

5.2.4.2 *For ammonium sulphate nitrate* — Calculate free acidity in terms of nitric acid, using factor 6.3 in place of 4.904 in the above formula.

5.3 Determination of Arsenic

Two methods for determination of arsenic are given here. Silver diethyldithiocarbamate method shall be the referee method and shall be used in case of any dispute. Modified Gutziet method will be an alternative one.

5.3.1 Silver diethyldithiocarbamate procedure is to be followed when actual arsenic content is to be determined. The method is applicable to quantities of arsenic (as As) greater than 5 mg. Modified Gutzeit method of test for arsenic shall be employed in cases where arsenic content is not needed and only a knowledge of the limit is desired. While the methods are of general applicability, these are prescribed below with ammonium sulphate fertilizer in view, particularly the bye product material.

5.3.2 *Apparatus*

5.3.2.1 For silver diethyldithiocarbamate method, the apparatus shall consist of the following:

a) *Evolution and absorption apparatus* — It consists of a conical flask A of 100 ml capacity for evolution of arsine, a connecting tube B to trap hydrogen sulphide, and absorption tube C with a spherical or conical ground-glass joint. A spring clip may be used to ensure firm joint between the connecting tube B and absorption tube C when a spherical joint is used. Suitable forms of apparatus using spherical joint and conical joint are shown in Fig. 2 and 3.
b) *Spectrophotometer* — with 10 mm cells.

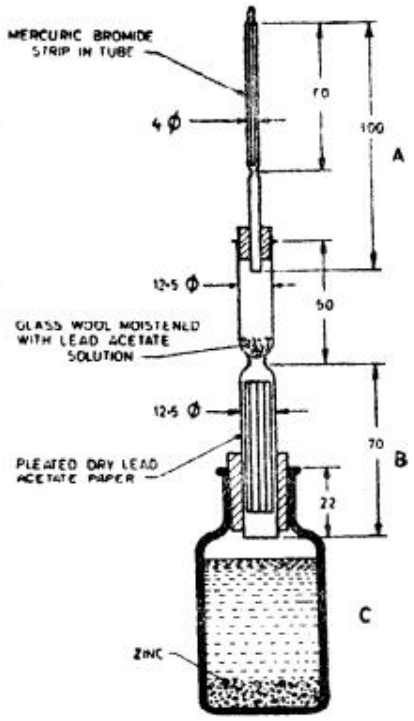
5.3.2.2 For modified Gutzeit method, the apparatus shall be as given in Fig. 1.

5.3.3 *Reagents* – All the reagents used shall be free from arsenic.

5.3.3.1 *Lead acetate solution* — Prepare 10 percent solution of lead acetate with sufficient acetic acid added to clear the solution.

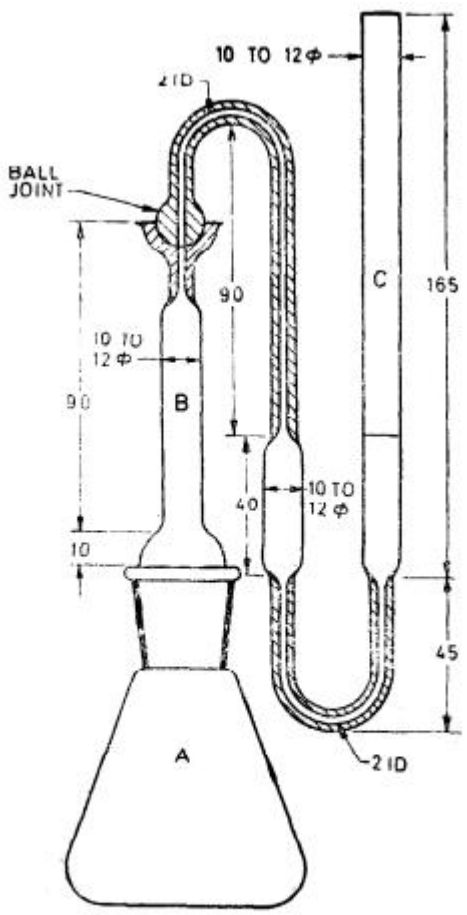
5.3.3.2 *Dry lead acetate paper* — Cut filter paper (Whatman No. 1 or equivalent) into strips 70 x 50 mm and keep them permanently suspended in lead acetate solution in a glass-stoppered bottle. Before use, take out the strips and dry them in an atmosphere free from hydrogen sulphide.

a) *Absorbent cotton wool saturated with lead acetate* — Dissolve 50 g of lead acetate trihydrate [$Pb(C_2H_3O_2)_2.3H_2O$] in 250 ml of water. Saturate the absorbent cotton wool with this solution remove excess solution by allowing it to drain and dry the cotton wool under vacuum at room temperature. Store in an air-tight container.



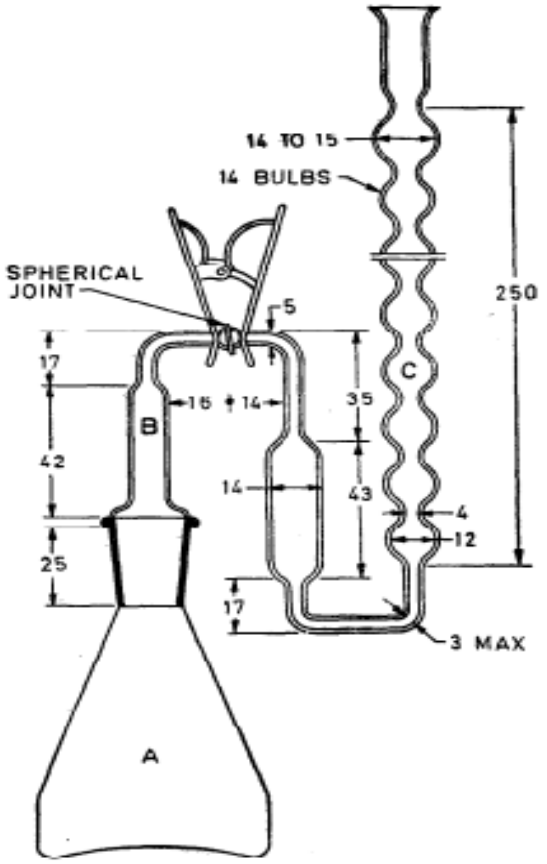
All dimensions in millimetres.

FIG. 1 APPARATUS FOR DETERMINATION OF ARSENIC
(MODIFIED GUTZEIT METHOD)



All dimensions in millimetres.

FIG. 2 APPARATUS FOR DETERMINATION OF ARSENIC
(WITH JOINT CONICAL)



All dimensions in millimetres.

FIG. 3 APPARATUS FOR DETERMINATION OF ARSENIC (SILVER DIETHYLDITHIOCARBAMATE METHOD)

5.3.3.3 *Mercuric bromide solution* — Dissolve 5 g of mercuric bromide in 100 ml of rectified spirit.

5.3.3.4 *Sensitized mercuric bromide paper strips* — Cut filter paper (Whatman no 1 or equivalent) into strips 120 x 2.5 mm. Keep the strips permanently suspended in dark in a glass-stoppered cylinder or amber bottle having mercuric bromide solution. Before use take out a strip, press it between sheets of filter paper and dry it in an atmosphere free from hydrogen sulphide.

5.3.3.5 *Dilute sulphuric acid* — approximately 5 N.

5.3.3.6 *Concentrated hydrochloric acid*

5.3.3.7 *Potassium iodide solution 15 percent*

5.3.3.8 *Stannous chloride solution* — Dissolve 40 g of stannous chloride dihydrate in 100 ml of concentrated hydrochloric acid. Boil if necessary to dissolve. Add some metallic tin to the solution to check oxidation.

5.3.3.9 *Zinc* — It is recommended that zinc rods prepared as described below should be used. For routine work, however, pellets prepared as described below may be used.

a) *Preparation of zinc rods* — Take a clean and dry hard glass test tube of 10 mm internal diameter and 20 cm length. Heat the test tube over a flame of Bunsen or blowpipe burner and add slowly pure granulated zinc in small portions (1 to 2 g at a time) the next portion being added after the first one has completely melted. Continue heating and adding zinc until the melt is about 10 cm high. Heat the clear melt for half an hour and then cool to room temperature. Break the tube to obtain the rod of zinc. Cut the rod into pieces 20 mm long. Coat the plane ends of the pieces with a paste of magnesium carbonate and gum arabic solution and dry. Then coat the pieces all over with 1.5 mm thick layer of paraffin wax. When required for use, scrape off the wax from the plane ends with a knife, protecting the wax collar round the rods. Remove the paste coat from the plane ends by soaking in water and activate the exposed surface by dipping in a solution containing one part of stannous chloride solution and seven parts of concentrated hydrochloric acid.

b) *Preparation of zine pellets* — Treat zinc shots passing through 5.6 mm IS Sieve and retained on 2.8 mm IS Sieve with concentrated hydrochloric acid until the surface of zinc becomes clean and dull. Wash and keep under water, preventing contamination with dust.

5.3.3.10 *Sodium hydroxide solution* — approximately 20 percent

5.3.3.11 *Standard arsenic trioxide solution* — Dissolve 1.000 g of resublimed arsenic trioxide (As_2O_3) in 25 ml of sodium hydroxide solution and neutralize with dilute sulphuric acid. Dilute with freshly distilled water containing 10 ml of concentrated sulphuric acid per litre and make up the volume to 1 litre. Again dilute 10 ml of this solution to 1 litre and finally dilute 100 ml of the latter solution to 1 litre with water containing sulphuric acid. One millilitre of this solution contains 0.001 mg of arsenic trioxide (As_2O_3). The dilute solution shall be prepared afresh as and when required.

5.3.3.12 *Silver diethyldithiocarbamate Solution* — Dissolve 1 g of silver diethyldithiocarbamate in colourless pyridine and dilute to 200 ml with pyridine. Store the solution in glass stoppered bottles protected from light.

Silver diethyldithiocarbamate, if commercially not available, may be prepared from sodium diethyldithiocarbamate as follows:

> Dissolve 10 g of sodium diethyldithiocarbamate [$(C_2H_5)_2N.CS.SNa.3H_2O$] in 35 ml of rectified spirit (*see* IS 323) and filter. Add to the solution with stirring, 100 ml of ether (*see* IS 336). Filter by using suction, wash the precipitate with ether and dry in air. Dissolve separately 2.2 g of the material in 100 ml of water, and 1.7 g silver nitrate in 100 ml of water. Slowly mix these two solutions with constant stirring. Keep the mixture below 10 °C. Decant the supernatant liquid, wash the precipitate 3 or 4 times with water, at a temperature below 10 °C. Filter and dry the product in vacuum at room temperature. Preserve the material protected from light in a cool place.

5.3.4 *Procedure*

5.3.4.1 *Silver diethyldithiocarbamate method*

a) *Preparation of calibration curve* — The curve shall be confirmed every time when a new solution of silver diethyldithiocarbamate is prepared.

b) *Evolution of arsine* — Transfer to a series to 100 ml conical flasks, aliquots of standard arsenic solution corresponding to 0, 5, 10, 15, 20 and 25 µg of arsenic and proceed as below.

Add 10 ml of concentrated hydrochloric acid and dilute to 50 ± 5 ml with water. Run down 2 ml of potassium iodide and 0.4 ml of stannous chloride solution respectively. Mix well and let it stand. Pack lightly the top third of the connecting tube with impregnated absorbent cotton wool and assemble the absorption tube. Transfer 50 ml of silver diethyldithiocarbamate solution to absorption tube C. After 15 to 20 min, introduce 5 g of zinc granules into the conical flask A and quickly reassemble the apparatus. Allow the reaction to proceed for 45 to 60 min at room temperature.

c) *Spectrophotometric measurements* — Disconnect the absorption tube and tilt the absorber so that the reagent solution flows back and forth between the absorber and bulb to dissolve the solid contents, if any, and to mix in the solution well. Transfer the solution to a photometric cell and measure its absorbance at the wavelength of maximum absorption, 540 nm, using water as reference liquid.

NOTE — The colour of the complex is not very stable for long time and hence spectrophotometric measurement should be made within 2 h of the development of colour. Care should also be taken to prevent the evaporation of solution as its volume is small.

d) *Plotting of calibration curve* — Calculate corrected absorbance by subtracting the reading obtained for the solution containing no standard arsenic solution from the observed reading. Plot a graph of corrected absorbance of solutions against their arsenic contents.

The test solutions shall be prepared as prescribed in relevant individual material specifications so as to contain 1 to 10 g of arsenic in a solution of 5.0 + 0.5 ml volume. Transfer the solution to the conical flask, cool to room temperature if necessary and proceed as prescribed in (b).

e) *Blank test* — Carry out a blank test, as prescribed in (b) omitting the sample.

f) *Calculation* — Calculate the corrected absorbance by subtracting the value obtained for the blank solution from that recorded for the test solution and read from the calibration curve the corresponding mass of arsenic.

Arsenic content, parts per million by mass = $\frac{M_1}{M_2}$

where

M_1 = mass, in µg, of arsenic found, and

M_2 = mass, in g, of sample in the solution tested.

5.3.4.2 *Modified Gutzeit Method*

a) Dissolve 10 g of the prepared sample in 20 ml of water.

b) Place dry lead acetate paper in the lower portion of the tube B (*see* Fig. 3) and glass wool moistened with lead acetate solution in the upper part. Place the sensitized strip of mercuric bromide paper in tube A and connect the tube together with a rubber stopper.

c) Introduce the solution of the material prepared in (a) into the bottle C (120 ml) and then add 10 ml of dilute sulphuric acid. Add 0.5 ml of stannous chloride solution, 5 ml of potassium iodide solution and make up the volume with water to about 50 ml. Mix the contents and add about 10 ml of zinc piece by piece. Immediately fit in position the rubber stopper and carrying the tube B. Place the bottle at a temperature about 40 °C. At the end of two hours remove the test strip by means of tweezers.

d) Carry out the test as prescribed above using a volume of standard arsenic trioxide solution containing 0.1 mg of arsenic trioxide, in place of the solution of the material and compare the stain produced with the material with that produced with arsenic trioxide solution.

e) The limit of 0.01 percent shall be taken as not having been exceeded if the length of the stain as well as the intensity of its colour produced in the test with the material is not greater than those produced with the standard arsenic solution.

5.4 Determination of Calcium Nitrate

Two methods for determination of calcium nitrate are given below. The method given in **5.4.1** is the referee method and shall be used in case of any dispute. The method given in **5.4.2** is an alternative one. This test is applicable for calcium ammonium nitrate nitrophosphate.

5.4.1 *Method A*

5.4.1.1 *Reagents*

a) *Ammoniacal methyl alcohol* — containing 97 ml of methyl alcohol and 3 ml of aqueous ammonia (8 N approx).
b) *Dilute hydrochloric acid* — approximately 4 N.
c) *Methyl red indicator* — 0.1 percent solution in rectified spirit.
d) *Ammonium oxalate solution* — Dissolve 50 g of ammonium oxalate [$(NH_4)_2C_2O_4.H_2O$] in 1 litre of water. Also prepare a dilute solution containing 1 g of the salt per litre.

5.4.1.2 *Procedure* — Weigh 5 g of sample in a 500 ml conical flask and add 50 ml of ammoniacal methyl alcohol to extract calcium nitrate. Stir thoroughly the contents on a magnetic stirrer for 20 min. Filter through a filter paper (Whatman no. 42 or equivalent) and wash with ammoniacal methyl alcohol (4 x 25 ml) and add the washings to the original filtrate. Remove methyl alcohol from the filtrate by evaporation and dissolve the solid residue in water. Acidify the filtrate with 5 ml of dilute hydrochloric acid, dilute to 200 ml, add a few drops of methyl red indicator and 10 ml of warm ammonium oxalate solution. Heat the solution to 70° C to 80 °C and add ammonium hydroxide (1 : 1) drop-wise, while stirring, until the colour just change from red to yellow. Allow the calcium oxalate precipitate to stand for one hour with occasional stirring during the first 30 min; filter and wash 3 or 4 times with cold 0.1 percent ammonium oxalate solution.

Dry the precipitate in a weighed, covered platinum crucible, char the paper without inflaming, burn the carbon at as low a temperature as possible and finally heat the crucible tightly covered in an electric furnace or over a blast lamp at a temperature of 1100 °C to 1200 °C. Cool in a desiccator (to guard against absorption of moisture by ignited calcium oxide) and weigh as calcium oxide. Repeat the ignition to constant mass.

5.4.1.3 *Calculation*

$$\text{Calcium nitrate, percent by pass} = \frac{M_1 \times 2.93 \times 100}{M_2}$$

Where,

M_1 = mass, in g, of calcium oxide, and

M_2 = mass, in g, of the material taken for test.

Alternately, wash the calcium oxalate precipitate with cold water till free from chloride. Pierce a hole in the filter with a pointed glass rod and wash the bulk of the precipitate through the funnel into a conical flask with hot water. Treat the filter with small quantities of dilute sulphuric acid (1 : 8) and again wash into the flask. Finally wash the filter-paper thoroughly with hot water, when the precipitate has completely dissolved (add more dilute sulphuric acid, if necessary), dilute the solution to about 200 ml and titrate with standard 0.1 N potassium permanganate as described below:

a) Add 90-95 percent of the required quantity of permanganate solution from a burette at a rate of 25-35 ml per minute while stirring slowly.
b) Heat to 55-60 °C (use a thermometer as stirring rod) and complete the titration by adding permanganate solution until a faint pink colour persists for 30 seconds.

5.4.2 *Method B*

The method is based on the solubility of calcium nitrate in amyl alcohol. Calcium carbonate is insoluble in this solvent.

5.4.2.1 *Reagents*

a) *n-Amy1 alcohol*
b) *Dilute hydrochloric acid* — approximately 4 N.
c) *Standard calcium solution* — Weigh 1.000 g of calcium carbonate (analytical reagent grade) dried at (120 ± 5) °C and dissolve in the minimum quantity of dilute hydrochloric acid. Dilute the solution to 1 litre in a volumetric flask.
d) *Ammonium chloride ammonium hydroxide buffer solution* – Dissolve 67.5 g of ammonium chloride in a mixture of 570 ml of ammonium hydroxide (relative density 0.92) and 250 ml of water. Also dissolve separately a mixture of 0.931 g of disodium ethylenediamine tetraacetate dihydrate and 0.616 g of magnesium sulphate ($MgSO_4.7H_2O$) in about 50 ml of water. Mix the two solution and dilute to 1 litre.
e) *Eriochrome Black T indicator solution* — Dissolve 0.1 g in 20 ml of rectified spirit. The solution shall be used for not more than a week.
f) *Standard disodium ethylenediamine tetra-acetate (EDTA) solution* — Weigh 3.72 g of disodium ethylenediamine tetraacetate dihydrate in water and dilute in a graduated flask to

1 litre. The solution shall be standardized frequently against standard calcium solution following the procedure given in **5.4.2.2**.

5.4.2.2 *Procedure* — Grind quickly about 5 g of the material, accurately weighed, with about 50 ml of amyl alcohol in a pestle and mortar and transfer the contents to a conical flask. Wash the pestle and mortar with a few ml of amyl alcohol and add the washings to the flask. Shake the contents of the flask manually or in a mechanical shaker for about half an hour and then filter. Transfer the filtrate to a separating funnel and extract the calcium nitrate completely with water in five to six instalments. A few drops of dilute hydrochloric acid may be added during the extraction with water to avoid the formation of an emulsion of amyl alcohol with water. Concentrate the water extract at a low temperature to nearly half its volume.

Transfer the concentrated solution to a conical flask, add 5 ml of ammonium chloride-ammonium hydroxide buffer solution, 5 drops of Eriochrome black T indicator solution and titrate against standard EDTA solution to a pure blue end point.

5.4.2.3 *Calculation*

$$\text{Calcium nitrate, percent by mass} = \frac{8.2\ NV}{M}$$

Where,

N = normality of standard EDTA solution,

V = volume, in ml, of standard EDTA solution used in the titration, and

M = mass, in g, material taken for the test.

5.5 Determination of Fluorine

5.5.1 *Range* — Applicable for fluorine contents between 2 and 100 micrograms in the final aliquot. With larger quantities, thorium fluoride comes out of solution and affects the colour matching. The titratable range can be increased, however, by the use of a protective colloid to keep thorium fluoride in solution. Relatively large amounts of phosphates interfere, as traces of phosphoric acid may distil over and calculated as fluoride; a modification of the procedure is given to overcome this interference.

5.5.2 *Outline of the Method* — In this method, after destruction of the organic matter, followed by distillation, the fluoride solution is buffered to *p*H 3.0, and titrated with thorium nitrate in the presence of chrome azure 1 S until the colour matches a blank consisting of trace of thorium nitrate added to a buffered solution of the dyestuff. The fluorine content is obtained from a calibration curve prepared from a standard fluoride solution treated similarly.

5.5.2.1 By a modification of this technique (*see* Note), the fluorine content can be measured absorptiometrically, but this technique requires very careful control, as the colour intensity is dependent on the concentration of all substances in solution.

NOTE — The principle of the method may be applied to a colorimetric technique. In this case a lake formed by thorium nitrate with the dye is produced, and the test solution is then added, the colour of the solution being diminished proportionately to the formation of the thorium fluoride complex. This reduction in colour intensity may then be measured in an absorptiometer, add the fluorine content obtained from a calibration curve prepared at the same time. As in the titrimetric method, rigid adherence to the conditions is necessary.

5.5.3 *Apparatus*

5.5.3.1 *Distillation apparatus* —The distillation apparatus shown in Fig. 4 shall consist of a Claisen flask of 200 ml capacity, a large flask for generating shown steam and an efficient condenser. The main neck of the Claisen flask shall be fitted with a 2-hole stopper through which shall pass a thermometer and a glass tube for connecting with the steam supply, both the thermometer and the tube extending almost to the bottom of the flask. The side neck of the flask shall be connected with the condenser. Steam shall be generated from water made alkaline with sodium hydroxide. Local overheating of the Claisen flask be avoided by use of an asbestos board with a hole which shall fit closely to the lower surface of the flask.

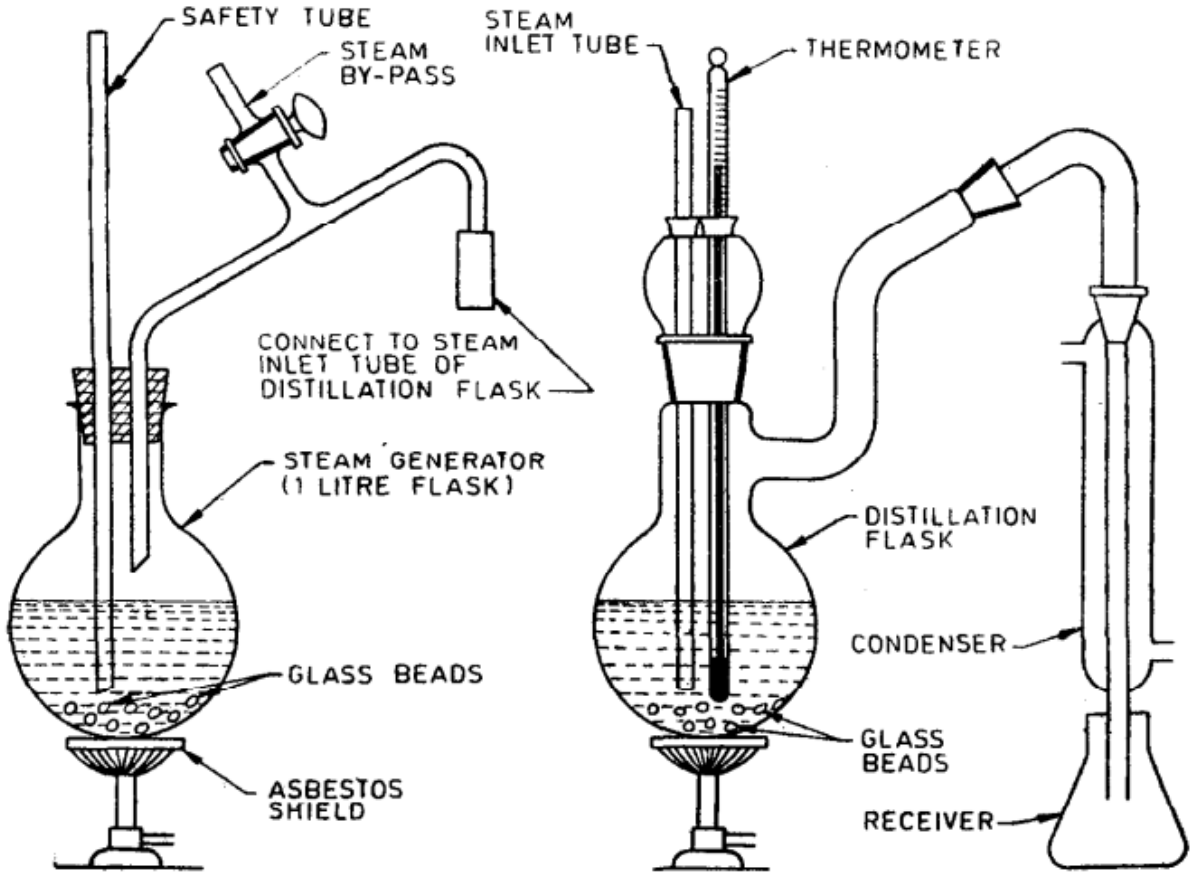


FIG. 4 STEAM DISTILLATION APPARATUS FOR FLUORIDE DETERMINATION

5.5.4 *Reagents*

5.5.4.1 *Calcium oxide* (*Fluoride free*) — Prepare an ammonium carbonate, reagent by dissolving 110 g of ammonium carbonate (analytical reagent grade) and 55 ml of concentrated ammonia solution (20 percent *m*/*m*) in water and diluting to 600 ml. Dissolve 200 g of dry calcium chloride (analytical reagent grade) in about 600 ml of warm water. Stir into this solution 20 ml of the ammonium carbonates reagent, bring the mixture to just the boiling point, allow the precipitate to settle for a few minutes, filter through a Buchner funnel using suction, and discard the precipitate. Repeat the precipitation and filtration three times, using 20 ml of ammonium carbonate reagent each time.

Finally, treat the clear filtrate from the last precipitation with the remainder of the ammonium carbonate reagent, stir the mixture well, bring just to the boiling point, allow the precipitate to settle, filter, and wash several times with hot water until the washings are free from chloride. Dry the residue at 100 °C, and ignite to oxide in a platinum dish in small quantities of 1 to 2 g as required.

5.5.4.2 *Silver perchlorate*

5.5.4.3 *Perchloric acid* — 60 percent, redistilled.

5.5.4.4 *Glass wool* — fluoride free.

5.5.4.5 *Phenolphthalein indicator solution* — 0.1 percent in 60 percent rectified spirit.

5.5.4.6 *Sodium hydroxide solution* — approximately 1 N.

5.5.4.7 *Dilute perchloric acid* — 5 percent (*m*/*v*).

5.5.4.8 *Chrome azurol S solution* — a 0.02 percent (*m*/*v*) solution of chrome azurol S in water.

5.5.4.9 *Mono chloroacetate buffer solution* — Dissolve 22.7 g of mono chloracetic acid in 100 ml of water. Titrate 50 ml of this solution with 6 N sodium hydroxide solution to neutrality; combine the neutralized and un-neutralized portions, and dilute to 1 litre with water.

5.5.4.10 *Standard thorium nitrate solution* — 0.004 N. Dissolve 0.552 g of thorium nitrate [$Th(NO_3)_{4.4}H_2O$)] in water, and dilute to 1 litre at 20 °C with water.

5.5.4.11 *Standard fluoride solution* — Dissolve 0.221 g of dry sodium fluoride analytical reagent grade in water, and dilute to 100 ml at 20 °C with water. Dilute 10.0 ml of this solution to 1 litre at 20 °C with water; one millilitre of the solution contains 10 micrograms of fluorine.

5.5.5 *Procedure*

5.5.5.1 *Preparation of sample* — Into a platinum basin, weigh a suitable quantity of sample (containing not more than 200 micrograms of fluorine), add 1 g of calcium oxide and 50 ml of water, evaporate the contents to dryness on a water-bath, and thoroughly char the residue at a temperature below visible red heat. Transfer the basin and contents to a muffle furnace maintained at approximately 600 °C, ignite for 1½ to 2 h, and cool.

5.5.5.2 *Setting up of apparatus* - Into the Claisen flask measure a quantity of silver perchlorate sufficient to precipitate any chloride that may be present in the sample and add 7 ml of water and 15 ml of perchloric acid. Place about 0.1 g of glass wool or 2 to 3 glass beads in the flask, and proceed to steam-distil the contents with the heating suitably adjusted, the distillation temperature is maintained between 135 °C and 145 °C. Distil about 200 ml of the liquid (*see* Note), steam out the condenser, and discard the distillate.

> NOTE — To ensure complete distillation of all the fluorine, about 200 ml of distillate shall be collected, although about 80 percent of the fluorine comes over with the first 50 ml. If the temperature of distillation falls below 135 °C, the removal of fluorine becomes incomplete even with 200 ml of distillate. A distillation temperature above, 145°C result in the distillation of excessive amounts of perchloric acid, which may interfere in the subsequent titration.

5.5.5.3 *Determination of blank* — Proceed to steam-distil a further 200 ml, and determine the fluoride in the distillate by the method described below. The titration figure for the blank should

not exceed the equivalent of 4 micrograms of fluorine (*see* Note), and should remain approximately constant for further 200 ml fractions.

NOTE — Blank distillations show that a titration figure is always obtained, equivalent to about 4 micrograms of fluorine. This is said to be derived from the glass of the distillation apparatus. Higher blanks then this are usually due to impurity in the perchloric acid, which should be heated to 140 °C and then redistilled before use.

5.5.5.4 *Distillation of sample* — Cool the contents of the flask. Transfer the ash of the sample (*see* **5.5.5.1**) to the flask with the aid of the minimum quantity of water, and proceed to steam-distil further 200 ml, collecting the distillate. Proceed to the fluoride titration. If the sample contains appreciable amounts of phosphates, that is, if the amount of P_2O_5, in the flask exceeds 0.5 g, collect a further 200 ml of distillate, and if this last fraction shows an appreciable apparent fluorine content, the first test distillate should be evaporated to dryness in the presence of 1 g of calcium oxide, and redistilled to give 200 ml of distillate. The titration of this distillate will give the fluorine content of the sample.

5.5.5.5 *Titration of fluoride* — Dilute 200 ml of distillate to a known volume with water, transfer an aliquot containing less than 100 micrograms of fluoride to a Nessler cylinder standing on a white tile, and neutralize to phenolphthalein with sodium hydroxide solution. Just discharge the pink colour with dilute perchloric acid, and add 1 ml of chrome azurol S solution, followed by dilute perchloric acid until the yellow colour of the dye just changes to pink, and then 0.5 ml of chloroacetate buffer solution. Into a similar Nessler cylinder place a volume of water equal to that of test aliquot, followed by 1 ml of chrome azurol S solution and 0.5 ml of chloroacetate buffer solution, and add, from a micro-burette, 0.10 ml of standard thorium nitrate solution; the colour changes from pink to bluish purple. Then titrate the test solution in the first Nessler cylinder with standard thorium nitrate solution until it exactly matches the liquid in the second Nessler cylinder in colour.

From this titration figure subtract 0.1 ml, and refer the result to a calibration curve to obtain the concentration of fluoride in the sample.

5.5.5.6 *Calibration of curve* — Although the above procedure is capable of giving reproducible results without difficulty, slight modifications in the conditions may influence the end-point owing to the variable composition of the lake formed between thorium salts and the dye. Therefore, a calibration curve shall be prepared each time a change in the conditions is encountered. Into matched Nessler cylinders measure aliquots of dilute standard fluoride solution, covering the range 2 to 100 micrograms of fluorine titration as described in **5.5.5.5** Construct a graph relating titration figure to the fluoride content.

5.6 Determination of Nickel

5.6.1 *Range* — For nickel contents up to 100 micrograms in the final aliquot.

5.6.2 *Outline of the Method* — After destruction of organic matter, nickel is extracted from an ammoniacal solution as its dimethylglyoxime complex, and determined absorptiometrically as the nickel complex.

5.6.3 *Reagents*

5.6.3.1 *Sodium citrate solution* — 25 percent.

5.6.3.2 *Sodium dimethyl glyoxime solution* — 0.2 percent (*m*/*v*) solution in diluted ammonia solution (1 : 19 *v*/*v*).
5.6.3.3 *Chloroform* — Shake 500 ml of chloroform with 50 ml of 10 percent (*m*/*v*) hydrochloric acid, allow to separate, run off the lower chloroform layer into another separating funnel, and wash it in similar manner with water until it is free from acid.
5.6.3.4 *Dilute hydrochloric acid* — 1 : 19 (*see* IS 263)
5.6.3.5 *Bromine water* — saturated.
5.6.3.6 *Standard nickel solution* - Dissolve 0.673 g of nickel ammonium sulphate [$NiSO_3.(NH_4)_2SO_4.6H_2O$] in water, add 5 ml of nitric acid and dilute the solution to 1000 ml at 20 °C with water. Further dilute 100 ml of the solution to 1000 ml with water. One millilitre of this solution contains 10 micrograms of nickel.

5.6.4 *Procedure*

5.6.4.1 Into a beaker, measure a suitable aliquot of the acid solution of the sample containing not more than 100 micrograms of nickel, dilute to 100 ml with water, and add 10 ml of sodium citrate solution. Place a small piece of litmus paper in the solution, add ammonium hydroxide with mixing until the solution is just ammoniacal, and then add 10 drops in excess. Transfer the solution to a 250 ml separating funnel, add 10 ml of sodium dimethylglyoxime solution, shake for 1 min, and allow to separate for 10 min. Add 10 ml of chloroform, shake for 1 min, and allow to separate. Run the lower chloroform layer into another separating funnel, and rinse the stem of the first separating funnel with about 3 ml of chloroform, adding the rinsing to the first chloroform extract. Repeat the extraction of the aqueous layer with rinsing the stem of the funnel as before. To the combined chloroform extracts add 13 ml of dilute hydrochloric acid, shake vigorously for 1 min, allow to separate, and run the lower chloroform layer into another separating funnel. Repeat the washing of the chloroform layer with 5 ml of dilute hydrochloric acid, and discard the chloroform layer. Transfer the two acid extracts to a 100 ml beaker, rinsing the two separating funnels that contain the acid extracts with a few millilitres of water and adding the rinsings to the combined acid extracts in the beaker. Heat the solution very carefully over a low Bunsen flame to approximately 25 ml. Cool the solution, transfer to a 50 ml calibrated flask, rinsing the beaker with two successive 5 ml portions of water, and add the rinsing to the calibrated flask. Add, in order, mixing after each addition, 2 ml of sodium citrate solution; 2 ml of bromine water; just enough ammonium hydroxide to destroy the bromine colour and to give 1 ml in excess; and 4 ml of sodium dimethylglyoxime solution; dilute the solution to the mark with water, and mix well.

5.6.4.2 Carry out a blank determination on all the reagents used.

5.6.4.3 Measure the optical densities of the test and blank solution in a spectrophotometer at a wavelength of 400 nm, or in an absorptiometer using a suitable blue filter; use 4 cm cells, with water in the comparison cell. Read the number of micrograms of nickel equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of nickel in the sample.

5.6.4.4 For establishing the calibration graph, measure appropriate amounts of standard nickel solution, covering the range 0 to 100 micrograms of nickel into a series of 50 ml calibrated flasks. To each add 20 ml of dilute hydrochloric acid and add, in order, mixing after each addition, 2 ml of sodium citrate solution; 2 ml of bromine water; just enough ammonium hydroxide to destroy the bromine colour and to give 1 ml in excess; and 4 ml of sodium dimethylglyoxime solution;

dilute the solution to the mark with water, and mix well. Measure the optical densities of the solution, and construct a graph relating the optical densities to the number of micrograms of nickel.

5.6.4.5 If an instrument is not available, the colours may be matched visually against a series of standards.

5.7 Determination of Chromium

5.7.1 *Range* — For chromium contents up to 20 micrograms in the final aliquot.

5.7.2 *Outline of the Method* — In this method, after destruction of any organic matter, the chromium present is oxidised to chromate, which is determined absorptiometrically as the violet-coloured complex that is formed on the addition of diphenylcarbazide.

5.7.3 *Reagents*

5.7.3.1 *Distilled water* — This should be specially prepared by distilling tap water to which sulphuric acid and a few crystals of potassium permanganate have been added. This specially prepared water shall be used for preparing the reagents and for the procedure.

a) *Calcium oxide*
b) *Concentrated hydrochloric acid*
c) *Orthophosphoric acid* - 60 percent.
d) *Potatsium permanganate solution* - 1 percent.
e) *Sodium hydroxide solution* - 15 percent.
f) *Sodium azide solution* - 5 percent.
g) *Dilute sulphuric acid* - 1 : 20.
h) Diphenylcarbaeide solution — Dissolve 0.374 g of diphenylcarbazide in 25 ml of 95 percent ethanol and dilute to 100 ml with distilled water.
j) *Standard chromium solution* — Dissolve 0.374 0 g of reagent grade potassium chromate in distilled water and dilute to 1 litre at 20 °C with distilled water. Dilute 10.0 ml of this solution to 500 ml at 20 °C with distilled water, freshly as required. One millilitre of this solution contains 2 micrograms of chromium (as Cr).

5.7.4 *Procedure*

5.7.4.1 *Preparation of sample* — Ignite at not more than 600 °C a suitable quantity of sample (containing not more than a few milligrams of chromium) mixed with twice its weight of calcium oxide moistened with an equal quantity of distilled water, continue the ashing until all the organic matter has been destroyed. Treat the cooled residue with the minimum quantity of concentrated hydrochloric acid necessary to bring the calcium and chromate ions into solution, filter off any insoluble matter, dilute the filtrate to 100 ml with distilled water in a calibrated flask and mix well.

NOTE — In the case of mineral fertilizers, place it in a nickel crucible, mix with about 10 time the quantity of a mixture of 2 parts of sodium peroxide and 1 part of sodium carbonate and fuse completely. Cool the melt, transfer the nickel crucible with contents to a beaker and dissolve then in about 200 ml of hot water; remove the crucible and then boil the contents for 15 min. Add slowly a small quantity of sulphuric acid (1 + 1) to dissolve the residue, add 10 ml in excess, and then 2 ml of hydrochloric acid (1 + 1) and boil for a while. Cool and dilute to a known volume with water.

5.7.4.2 Place 5.0 ml (or a larger aliquot, if necessary) of the solution prepared in **5.7.4.1,** in a small beaker, add 5 drops of orthophosphoric acid and evaporate until white fumes are evolved. Cool

the solution, add 1 ml of potassium permanganate solution, cover the beaker with a watch-glass, and heat on a water-bath for 20 min. Neutralize the solution to litmus paper with sodium hydroxide solution, and 1 ml in excess Add sodium oxide solution, drop by drop, so as to decolourize the permanganate, and allow the solution to simmer gently on a hot plate for 10 min. Cool the solution, dilute to 20 ml with distilled water in a calibrated flask, and filter. Measure accurately a suitable volume of the filtrate (5 to 10 ml) into a 25 ml calibrated flask, add 5 ml of dilute sulphuric acid, and dilute the solution to about 20 ml with distilled water. Add 2.5 ml of diphenylcarbazide solution, dilute the solution to the mark with distilled water, and allow to stand for 5 min before the colour measurement; this timing is important as the colour fades on standing.

5.7.4.3 Carry out a blank determination on all reagents used.

5.7.4.4 Measure the optical densities of the test and blank solutions in a spectrophotometer at a wavelength of 540 nm, or in an absorptiometer using a suitable green filter; use water in the comparison cell. Read the number of micrograms of chromium equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph, and obtain the net measure of chromium in the sample.

Establish the calibration graph as follows:

Measure appropriate amounts of standard chromium solution, covering the range 0 to 20 micrograms of chromium, into a series of 25 ml calibrated flasks. To each, add 5 ml of dilute sulphuric acid and dilute the solutions to about 20 ml with distilled water. Add 2.5 ml of diphenylcarbazide solution, dilute the solution to the mark with distilled water, and allow to stand for 5 min before the colour measurement; this timing is important as the colour fades on standing. Measure the optical densities of the solution, and construct a graph relating the optical densities to the number of micrograms of chromium.

5.7.4.5 If an instrument is not available, the colours may be matched visually against a series of standards.

5.8 Determination of Sodium and Sodium Salts

5.8.1 *General* — Two methods are given below. The method given in **5.8.2** is for determination of sodium by flame photometer which shall be used as referee method in case of any dispute. Gravimetric method given in **5.8.3** shall be used as an alternative one. This method is applicable for determination of sodium salts in potassium chloride and potassium sulphate.

NOTE — If the sodium content is substantial in the potassic fertilizer under test, it is preferable to remove potassium in the first instance by perchloric acid method before proceeding for the determination of sodium and sodium salts in the fertilizers.

5.8.2 *Determination of Sodium by Flame Photometer*

5.8.2.1 *Apparatus*

a) *A flame photometer*

5.8.2.2 *Reagents*

a) *Ammonium oxalate solution* — Dissolve 40 g ammonium oxalate in 1 litre of water.
b) *Methyl red indicator* — Dissolve 0.2 g of methyl red in 100 ml of rectified spirit.

c) *Dilute nitric acid* — 5 percent; 1 : 10 (*v*/*v*).
d) *Sodium chloride* — Dry for 2 h at 105 °C.

5.8.2.3 *Preparation of solution*

a) *Mixed fertilizers and potassium magnesium sulphate* — Weigh 2.5 g sample (for less than 4 percent sodium) or 1.25 g (for 4 to 20 percent sodium) into 250 ml volumetric flask (500 ml flask if sample contains more than 30 percent potassium), add 125 ml of water and 50 ml of ammonium oxalate solution, make just alkaline with NH_4OH to methyl red and boil for 30 min, cool, dilute to volume, mix and pass through dry filter (Whatman no. 42) rejecting the first few ml of filtrate.

5.8.2.4 *Preparation of standard curve*

a) *For samples containing 1 percent or more sodium* — Dissolve 1.2716 g of sodium chloride in 500 ml of water to have 1000 ppm sodium solution, range of dilution 0 to 40 ppm sodium, of intervals not less than or equal to 2 ppm, and full scale for 10 ppm sodium solution. Atomize portions of standard solutions until readings for series are reproducible.
b) *For samples containing less than I percent sodium* — Proceed as given in **5.8.2.4**, (a) using 1.2716 g of sodium chlorides range of dilution 0 to 10 ppm sodium, intervals 2 ppm, and full scale for 10 ppm sodium.

5.8.2.5 *Procedure* — Transfer 25 ml (for less than 4 percent sodium) or 10 ml (for 4 to 20 percent sodium) a sample solution (**5.8.2.3**) to 250 ml volumetric flask, dilute to volume with water and mix. Atomize portions of sample several times to obtain reliable average readings for each solution. Determine ppm sodium from standard curve as given in **5.8.2.4** (a) and (b).

5.8.2.6 *Calculation*

a) For 0 to 4 percent sodium, calculate the percentage of sodium as follows:

Sodium (as Na), percent by mass = $\frac{ppm\ of\ Sodium}{10}$

b) For 0 to 20 percent sodium, calculate the percentage of sodium as follows:

Sodium (as Na), percent by mass = $\frac{ppm\ of\ Sodium}{2}$

5.8.3 *Determination of Sodium Salts*

5.8.3.1 *Reagents*

a) *Concentrated hydrochloric acid* — (*see* IS 265).
b) *Barium chloride solution* — 12 percent.
c) *Ammonium carbonate solution* — 2 N.
d) *Perchloric acid* — 60 percent.
e) *Ethanol* — 96 percent.
f) *Washing alcohol* — Prepared by mixing ethanol with 0.2 percent (*v*/*v*) of perchloric acid.
g) *Ammonium hydroxide* — 2 N.
h) *Magnesium uranyl acetate solution* — Dissolve 90.0 g of crystallized uranyl acetate in 60 ml of glacial acetic acid and sufficient water by stirring and warning to 70 °C. Dilute the solution to 1000 ml.

Dissolve 600 g of crystallized magnesium acetate in 60 ml of glacial acetic acid and sufficient water by stirring and warming to 70 °C. Dilute the solution to 1000 ml.

Mix the two solutions prepared above and allow to stand for several hours. Filter off any residue. The final solution should be kept at 20 °C in flasks made of resistant glass with very low sodium content. The solution should also be used at 20 °C.

5.8.3.2 *Procedure* — Weigh accurately about 10 g of the prepared sample, add a few millilitres of concentrated hydrochloric acid and 100 ml of water and heat to boiling in a beaker. To the boiling solution, add slowly in small quantities barium chloride solution. Heat for some time and then cool. Transfer to a 250 ml volumetric flask and dilute to the mark with water. Stir the solution thoroughly and filter through Whatman no. 42. Reject the first few millilitres of the filtrate. Take exactly 10 ml of the filtrate and add a few millilitres of ammonium carbonate solution. Filter off the precipitated carbonates and wash the precipitate with water, the washings being added to the filtrate. Evaporate the filtrate and washings to dryness in a porcelain dish of 10 cm diameter and calcine gently. Add to the residue a small quantity of water and 6 ml of perchloric acid and evaporate almost to dryness in a water-bath. Dilute with 5 ml of water and repeat evaporation with perchloric acid about 1 ml, two or three times.

Cool the residue, add a few millilitres of ethanol and crush the moist mass to a fine state by using a glass pestle. Decant the liquid. Repeat the crushing of the residue and decantation with further additions of washing alcohol, collecting all the decanted liquid. Transfer the precipitate to a small filter and wash thoroughly with ethanol adding these washings also to the decanted liquid. Neutralize the filtrate and washings with ammonium hydroxide and heat to dryness. Transfer the residue to a beaker with about 5 ml of water and an excess of magnesium uranyl acetate solution maintaining the temperature at 20 °C. Decant off the clear solution through a sintered glass crucible Grade 3 which has been previously washed with methanol dried at (120 ± 5) °C and weighed. Again add a small quantity of ethanol and repeat the decantation twice. Finally, wash the precipitate with ethanol on the filter. Dry the crucible with the precipitate for half an hour at (120 ± 5) ^{o}C, cool in a desiccator and weigh.

5.8.3.3 *Calculation*

Sodium (as NaCl), percent by mass (on dry basis) = $\frac{97.05\ M_1}{M_2}$

where

M_1= mass, in g, of the precipitate, and

M_2 = mass, in g, of the prepared sample taken for the test.

6 QUALITY OF REAGENTS

Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070) shall be used in tests.

NOTE — ''Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.