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भारतीय मानक मसौदा

उर्वरकों के लिए नमूनाकरण और परीक्षण के तरीके: भाग 2 नाइट्रोजन का निर्धारण

(*आइ एस 6092 (Part 2) का दूसरा पुनरीक्षण*)

Draft Indian Standard

METHODS OF SAMPLING AND TEST FOR FERTILIZERS: PART 2 DETERMINATION OF NITROGEN

(*Second Revision of IS 6092* (*Part 2*))

ICS No. 65.080

Soil Quality and Fertilizers Sectional Committee, FAD 07

Last date of comments: 16 February 2025

FOREWORD

(*Formal clauses would be added later*)

This standard was first published in 1971. 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. Also, the assistance was derived from 'Official methods of analysis, The Association of Official Analytical Chemists, Washington DC, USA. 1978', 'Recommended analytical methods. The National Plant Food Institute, Washington DC, USA' and 'Fertilizer sampling and analytical methods. The Fertilizer Institute Product Quality Committee, Washington DC, USA. 1974'

In the first revision issued in 1985, 'Comprehensive nitrogen method' as a referee method was incorporated. 'Raney powder method', 'Formaldehyde titration method' and 'Dimethyl amine benzaldehyde method' were incorporated as alternate methods. Also, determination of urea and gravimetric method for determination of nitrate nitrogen were included.

In this revision, the test method for determination of cyanamide nitrogen has been incorporated in line with *Fertilizer (Control) Order,* 1985. Also, 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 reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022. 'Rules for rounding off numerical values (*second revision*)'.

1 SCOPE

This standard prescribes the methods for determination of nitrogen in its various forms in fertilizers, including fertilizer mixtures.

2 REFERENCES

The following standards 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 indicated below:

IS No.	*Title*
IS 266 : 2024	Sulphuric acid – Specification (*fourth revision*)
IS 323 : 2009	Rectified spirit for industrial use – Specification (*second revision*)
IS 1070 : 1992	Reagent grade water – Specification (*fourth revision*)
IS 6092 (Part 1) : 1985	Methods of sampling and test for fertilizers: Part 1 Sampling (*first revision*)

3 SAMPLING AND PREPARATION OF SAMPLE FOR ANALYSIS

Representative test sample of fertilizer shall be prepared and drawn as prescribed in IS 6092 (Part 1).

4 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.

5 SELECTION OF TEST METHOD

5.1 General – Methods of determination of total nitrogen, under ammoniacal nitrogen, nitrate nitrogen, urea nitrogen and cyanamide nitrogen have been described under **8** to **20**. These methods can be adapted both for straight and mixed fertilizers. The applicability of each procedure with various combinations has also been described with each method. The relevant methods of analysis which have been described are as follows:

a) Total nitrogen - for nitrate-free sample;

b) Total nitrogen - for nitrate-containing samples whose chloride to nitrate ratio is less than 1 to 3;

c) Total nitrogen - for materials with chloride to nitrate ratio greater than 3.

d) Ammoniacal nitrogen;

e) Ammoniacal and nitrate nitrogen;

f) Nitrate nitrogen;

g) Water Insoluble nitrogen;

h) Urea nitrogen; and

j) Cyanamide nitrogen.

5.2 Detection of Nitrates – For adopting a specified method out of those described under **5.1**, it is necessary to detect the presence of nitrate in the sample before particular procedure is adopted. For this purpose, mix 5 g of the sample with 25 ml of hot water and filter. To one volume of this solution, add 2 volumes of concentrated sulphuric acid free from nitric acid and oxides of nitrogen and let it cool. Add a few drops of concentrated ferrous sulphate solution in such a manner that the fluids do not mix. If nitrates are present, the junction shows that first purple and afterwards brown colour, or if only minute quantity of nitrate is present, then reddish colour is seen.

5.2.1 To another portion of the filtrate, add 1 ml of one percent solution of sodium nitrate and test as before. This checking is necessary only when test under **5.2** gives negative results.

5.2.2 *Alternate Method for Detection of Nitrate* – To about 0.5 g of the dried sample in a small beaker or glass dish, add about 1.5 ml of phenol disulphonic acid (in concentrated H_2SO_4) and triturate well with a glass rod. Dilute with water to about 50 ml and mix well and transfer the supernatant portion to another beaker if necessary. On making alkaline with NH_4OH, the solution will turn intense yellow if nitrates are present. Check with blank without the material. This is also an equally sensitive test (*see* **5.2**) for nitrate.

6 REAGENTS

6.1 The reagents given below are required for carrying out the determinations given under **8** to **19**.

6.1.1 *Mercuric Oxide or Metallic Mercury* – reagent grade.

6.1.2 *Copper Sulphate or Pentahydrate Crystalline* – reagent grade.

6.1.3 *Potassium Sulphate* (or *Anhydrous Sodium Sulphate*) – reagent grade.

6.1.4 *Sodium Hydroxide* – Pellets or solution, nitrate-free. For making a solution, dissolve approximately 450 g of the solid in water and dilute to one litre (relative density of solution should be 1.36 or higher). The solution is to be tested for nitrate as given under **5.2**.

6.1.5 *Standard Sodium Hydroxide Solution* (*Carbonate Free*) – 0.25 N or 0.1 N.

6.1.6 *Concentrated Sulphuric Acid* – 93 to 98 percent (sp gr 1.83-1.84) nitrogen free. (*see* IS 266).

NOTE - Use freshly opened sulphuric acid, otherwise add dry phosphorus pentoxide to avoid hydrolysis of nitrites and cyanates. If sulphuric acid contains traces of nitrogen in any form, determine a blank estimation and make suitable correction.

6.1.7 *Standard Hydrochloric Acid or Sulphuric Acid Solution* – 0.5 N, (or 0.1 N or 0.02 N when the amount of nitrogen is small).

NOTE – Standardize each standard solution with a primary standard and check one against another.

6.1.8 *Methyl Red Indicator* - Dissolve 0.1 g of methyl red in 100 ml of 95 percent ethyl alcohol.

6.1.9 *Sucrose* (*Crystalline*)

NOTE - Test reagents before using in blank determination with 2 g of sucrose which ensures partial reduction of any nitrates present.

6.1.10 *Salicylic Acid* – reagent grade.

6.1.11 *Sodium Thiosulphate* – crystalline.

6.1.12 *Zinc Dust* – impalpable powder (zinc granules or filings shall not be used).

6.1.13 *Reduced Iron Powder* – electrically reduced.

6.1.14 *Magnesium Oxide* – freshly ignited.

6.1.15 *Devarda Alloy* – Containing 45 parts aluminium, 50 parts copper and 5 parts zinc. Heat the aluminium in a Hessian crucible in a furnace until the content begins to melt. Add copper in small portions and heat until liquified. Then plunge zinc into the molten mass. Cover the crucible and heat the mixture for a few minutes and stir with an iron rod. Allow it to cool slowly with the cover on and then pulverize the crystallized mass. This material is available in lumps or in powdered form.

6.1.16 *Ferrous Sulphate* – crystalline.

6.1.17 *Potassium or Sodium Sulphide Solution* – Dissolve 40 g of potassium or sodium sulphide or 80 g sodium thiosulphate in one litre of water.

6.1.18 *Zinc* – granules, reagent grade, 0.8 mm size (approximately).

6.1.19 *Ethyl Alcohol* – 95 percent (*v*/*v*), rectified spirit (*see* IS 323).

6.1.20 *Neutral Urease Solution* – Shake 1 g of jack bean meal with 100 ml of water for 5 minutes. Transfer 10 ml of the solution to 250 ml conical flask, dilute with 50 ml of water and add 4 drops of methyl purple indicator. Titrate with 0.1 N hydrochloric acid to reddish purple colour, and then back titrate to green colour with 0.1 N sodium hydroxide. From the difference in titres, calculate the amount of 0.1 N hydrochloric acid required to neutralize the remainder of the solution (usually approximately 2.5 ml per 100 ml); add this amount of acid and shake well.

6.1.21 *Barium Hydroxide Solution* – Saturated aqueous solution.

6.1.22 *Sodium Carbonate Solution* – 10 percent.

6.1.23 *Methyl Purple Indicator* – Dissolve 0.1 g of methyl purple in 100 ml of 95 percent ethyl alcohol.

6.1.24 *Dilute Hydrochloric Acid* – 2 N (approximately).

6.1.25 *Sodium Hydroxide-Sodium Thiosulphate Solution* - Dissolve 60 g of sodium hydroxide and 5 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in water and dilute to 100 ml or add 25 ml of 25 percent sodium thiosulphate solution to 100 ml of 50 percent sodium hydroxide solution.

6.1.26 *Boric Acid Solution* – (approximately 4 percent). 40 g of pure boric acid dissolved in about 500 ml of hot water, cooled and made to one litre.

6.1.27 *Methyl Red-Methylene Blue Indicator Solution* – Mix 2 parts of 0.2 percent methyl red solution with 1 part of 0.2 percent methylene blue solution, both dissolved in ethyl alcohol.

6.1.28 *Methyl Red-Bromo Cresol Green Solution* – Mix 1 part of 0.2 percent methyl red solution in ethyl alcohol with 5 parts of 0.2 percent alcoholic solution of bromocresol green.

7 APPARATUS

7.1 For Digestion – Use Kjeldahl flask of hard, moderately thick, well-annealed glass, with total capacity approximately 500 to 800 ml. Conduct digestion over a heating device, adjusted to bring 250 ml of water at 25 °C to rolling boil in approximately 5 min. Add 3 to 4 boiling chips to prevent superheating, if necessary.

7.1.1 For very small samples, 50 ml capacity Kjeldahl flasks can be used. Use rack with either gas or electric heaters which will supply enough heat to 50 ml flask to cause 35 ml of water to come to boiling within 2 or 3 min.

7.2 For Distillation – Use Kjeldahl or other flask 800 to 1 000 ml capacity fitted with ground glass joint or rubber stopper through which passes the lower end of efficient scrubber bulb or trap to prevent any carry-over of sodium hydroxide during distillation, and a dropping funnel. Connect the upper end of the bulb tube to a condenser by ground glass joint or rubber tubing. Trap the outlet of the condenser in such a way as to ensure complete absorption of ammonia distilled over into the acid contained in a receiver.

7.3 For micro-Kjeldahl distillation, the apparatus requirements are as given in **8.3**.

8 TOTAL NITROGEN IN NITRATE-FREE SAMPLE (KJELDAHL METHOD)

8.1 General - Two procedures namely, macro and micro-Kjeldahl methods are given here.

8.2 Macro-Kjeldahl Method

8.2.1 *Procedure*

8.2.1.1 Place 0.5 to 2.0 g of the prepared sample accurately weighed, in the digestion flask. Add 0.7 g of mercuric oxide or 0.65 g metallic mercury or 0.7 g of crystalline copper sulphate, 15 g of powdered potassium sulphate or anhydrous sodium sulphate and 40 ml of concentrated sulphuric acid. If more than 2.0 g of the sample is used, increase sulphuric acid by 10 ml for each gram of sample. Allow to react with occasional shaking. Place the flask in an inclined position and heat gently until frothing ceases (if necessary, add a small amount of paraffin to reduce frothing). Boil briskly until solution clears and then for at least 30 min longer (at least for an hour for samples containing organic materials).

NOTE - Ratio of salt to acid (*m*/*v*) should be approximately (1:1) at the end of the digestion for proper temperature control. Digestion may be incomplete at the end of digestion for lack of proper temperature control. Digestion may be incomplete at lower ratio and nitrogen may be lost at higher ratio.

8.2.1.2 Cool, add about 200 ml of water and cool to 25 °C or below. In case HgO or metallic Hg has been used as catalyst, add 25 ml of potassium sulphate or sodium thiosulphate solution and mix to precipitate the mercury. Add a few zinc granules to prevent bumping. Add sodium hydroxide solution down the side without agitation (for each 10 ml of concentrated sulphuric acid used, 15 g of sodium hydroxide is required). Immediately connect the flask to distilling bulb on condenser and with tip of condenser immersed in a measured volume of standard acid and add 5 to 7 drops of methyl red indicator in the receiver, rotate flask to mix contents thoroughly. Then heat and boil steadily until1 all ammonia has distilled (150 ml distillate).

In case the colour of the acid turns yellow, repeat the determination using either a small sample weight or a larger volume of standard acid. Remove receiver, wash tip of condenser and titrate excess acid with standard sodium hydroxide solution.

Alternatively, the ammonia evolved can be collected in 25 ml of boric acid solution (4 percent) in the receiver with 8-10 drops of mixed indicator (bromo cresol green-methyl red). In this case, the ammonia collected in the receiver is directly titrated with standard acid, the colour changing from blue to light purple violet.

8.2.1.3 Carry out a blank determination on all reagents, using 2 g of pure sucrose in place of the sample and apply the necessary correction in the calculation.

8.2.2 Calculation

Total nitrogen, percent by mass = $\frac{(V_1N_1 - V_2N_2) \times 1.4}{M}$

where,

V_1 = volume, in ml, of standard acid used;

N_1 = normality of standard acid;

V_2 = volume, in ml, of standard alkali solution used;

N_2 = normality of standard alkali solution; and

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

When the ammonia is distilled into boric acid solution, the calculation = $\frac{V_1N_1 \times 1.4}{M}$

8.3 Micro-Kjeldahl Method

8.3.1 *Procedure*

8.3.1.1 Weigh sample requiring 3 to 10 ml of 0.01 N or 0.02 N for titration hydrochloric acid and transfer to 30 ml or 50 ml digestion flask. If sample mass is less than 10 mg, use micro balance (mass should be less than or equal to 100 mg dry organic matter). Use changing tube for dry solids, porcelain boat for sticky solids or non-volatile liquids, and capillary or capsule for volatile liquids. Add about 2 g of potassium sulphate, 40 mg of mercuric oxide or 50 mg of copper sulphate and 2 mg of sulphuric acid. If sample mass is greater than 15 mg, add additional 0.1 ml of sulphuric acid for each 10 mg dry organic matter greater than 15 mg. Make certain that acid has specific gravity of 1.84. Add boiling chips. If boiling time required for digestion rack heaters is 2 to 3 min, digest to one and a half hours after acid comes to boiling.

8.3.1.2 Cool, add minimum quantity of water to dissolve solids and place a thin film of vaseline on rim of flask. Transfer digest and boiling chips to distillation apparatus and rinse flask 5 or 6 times with 1 to 2 ml portions of water. Place 125 ml Erlenmeyer flask containing 5 ml of 14 percent boric acid solution and 2 to 4 drops of MR-BCG indicator solution under condenser with the tip extending below surface of solution. Add 8 to 10 ml of sodium hydroxide-sodium thiosulphate solution (sodium hydroxide only if copper sulphate is used in place of mercury solution) to still, collect about 15 ml distillate, and dilute to about 15 ml (use 2.5 ml boric acid solution and 1 to 2 drops indicator solution, and dilute to about 25 ml if 0.01 N hydrochloric

acid is to be used. Titrate to get first appearance of violet. Make blank determination and calculate the percentage of nitrogen as given in **8.3.2**.

8.3.2 *Calculation*

$$\text{Total nitrogen, percent by mass} = \frac{(V_1 - V_2) \times N \times 14.0 \times 100}{M}$$

where

V_1 = volume, in ml, of hydrochloric acid used for sample;

V_2 = volume, in ml, of hydrochloric acid used for blanks;

N = normality of the hydrochloric acid; and

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

9 TOTAL NITROGEN IN NITRATE CONTAINING SAMPLES (SALICYLIC ACID METHOD)

9.1 Applicability - This method is applicable to liquid or to samples whose chloride to nitrate ratio is less than 1:3.

9.2 Procedure – Place an accurately weighed quantity of the prepared sample, about 0.5 to 2.0 g, in the digestion flask. Add 40 ml of concentrated sulphuric acid containing 2 g of salicylic acid. Shake until thoroughly mixed and let it stand, with occasional shaking, for 30 min or more. Then add 5 g of crystalline sodium thiosulphate or 2 g of zinc dust (impalpable powder); shake the flask and let it stand for 15 to 30 min then heat over low flame until frothing ceases. Turn off the heat, add 0.7 g of copper sulphate or mercuric oxide, 15 g of powdered potassium sulphate (or anhydrous sodium sulphate) and boil briskly until solution clears and then for at least 30 min more (at least one hour for samples containing organic material). Proceed further as in **8.2.1.2**. Carry out a blank determination as in **8.2.1.3**.

9.3 Calculation – Calculate as given in **8.2.2**.

10 TOTAL NITROGEN (COMPREHENSIVE METHOD)

10.1 Applicability – This method is applicable for determining total nitrogen in all nitrogen carrying fertilizers, and those where chloride to nitrate ratio is higher than 1 : 3.

10.2 Reagents

10.2.1 *Chromium Metal* - 100 micron, low nitrogen.

10.2.2 *Alundum Boiling Stones* – Norton 14 X.

10.2.3 *Dilute Sulphuric Acid* – Slowly add 625 ml of concentrated sulphuric acid to 300 ml of water. Dilute to approximately one litre and mix. After cooling, dilute to one litre with water and mix. Avoid absorption of Ammonia from air during preparation, particularly, if stream of air is used for mixing.

10.2.4 *Sodium Thiosulphate* – 160 g of sodium thiosulphate per litre.

10.2.5 For other reagents (*see* **6**).

10.3 Procedure

Place 0.2 to 2.0 g of the prepared sample (not containing more than 50 mg nitrate nitrogen) in 500 ml Kjeldahl flask and add 1.2 g chromium powder. Add 35 ml of hater, or with liquids, lesser amount to make total volume of liquid 35 ml. Let it stand for 10 minutes with occasional gentle swirling to dissolve all nitrate salts. Add 7 ml of concentrated hydrochloric acid and let it stand for at least 30 seconds and not more than 10 minutes. Place flask on preheated burner with heat input set at 7 to 8 min boil test (*see* **7.1**). After heating for 3 min, remove it from heat and allow to cool.

Add 15 to 20 g of potassium sulphate, 0.7 g of mercuric oxide, or copper sulphate and few granules of alundum. Add 40 ml of dilute sulphuric acid (if adequate ventilation is available, 25 ml of concentrated sulphuric acid may be added instead of dilute sulphuric acid. If organic matter which consumes large amount of acid exceeds 1.0 g, add additional 1.0 ml of concentrated sulphuric acid for each 0.1 g organic matter in excess of 1.0 g.

Place flask on burners set at 5 min boil test (preheated burners reduce foaming with most samples). Cut back heat input if foam fills more than two-thirds of bulb of flask. (Use variable heat input until this phase is past). Heat at 5 min boil test until dense white fumes of concentrated sulphuric acid clear bulb of flask. Digestion is now complete for samples containing ammoniacal nitrate and urea nitrogen. For other samples, swirl flask gently and continue digestion for one hour more.

Proceed as prescribed in **8.2.1.2** substituting sodium thiosulphate by sodium hydroxide - Sodium thiosulphate solution.

11 RANEY POWDER METHOD

11.1 Applicability – The method is applicable to all fertilizer samples except those containing non-sulphate sulphur.

11.2 Reagents

11.2.1 *Raney Catalyst Powder* – containing 50 percent nickel and 50 percent aluminium.

> CAUTION - Raney catalyst powders react slowly in water on moist air to form alumina; avoid prolonged contact with air or moisture during storage or use.

11.2.2 *Sulphuric Acid – Potassium Sulphate Solution* – Slowly add 200 ml of concentrated sulphuric acid to 625 ml of water and mix without cooling, add 106.7 g of potassium sulphate and continue stirring until all salt dissolves. Dilute to approximately one litre and mix. Cool, make up to one litre with water, and mix. Avoid absorption of ammonia from air during preparation particularly if stream of air is used for mixing.

11.2.3 For other reagents (*see* **6**).

11.3 Procedure

11.3.1 Place 0.2 to 2.0 g of prepared sample containing less than or equivalent to 42 mg nitrate nitrogen in 500 ml Kjeldahl flask (800 ml flask is preferred with samples which foam considerably, especially for samples containing organic matter).

11.3.2 Add 1.7 g Raney catalyst powder, 3 drops of tributylcitrate, and 150 ml of concentrated sulphuric acid-potassium sulphate solution.

If organic matter exceeds 0.6 g, add additional 2.5 ml the solution for each 0.1 g organic matter in excess of 0.6 g.

11.3.3 Swirl to mix sample with acid and place flask on cold burner. When flask as on burner, set heat input to 5 min boil test. As the sample starts boiling, reduce heat to pass 10 min boil test. After 10 min, raise flask to vertical position and add 0.7 g mercuric oxide or copper sulphate and 15 g of potassium sulphate. Replace flask in inclined position and increase heat to 4 to 5 min boil test until dense white fumes of concentrated sulphuric acid clear bulb of flask. Digestion is now complete for samples containing only ammoniacal, nitrate and urea nitrogen. For other samples, swirl flask and continue digestion for additional 30 min.

11.3.4 Proceed as prescribed in **8.2.1.2**. If 800 ml Kjeldahl flask has been used, add 300 ml of water instead of 200 ml.

12 AMMONIACAL NITROGEN (MAGNESIUM OXIDE DISTILLATION METHOD)

12.1 Applicability – This method is for the determination of ammoniacal nitrogen present in the sample. This method is not applicable in presence of urea.

12.2 Procedure - Place 0.7 to 3.5 g of the prepared sample, accurately weighed according to its ammoniacal nitrogen content, in the distillation flask, add approximately 300 ml of water and 2 g of freshly ignited, carbonate-free magnesium oxide. Connect the flask to the condenser by the connecting bulb. Distil 200 ml of the liquid into a measured quantity of standard acid and back titrate with standard sodium hydroxide solution, using methyl red as an indicator or distil into boric acid solution acid, titrate with standard acid as given under **8.2.1.2**. Carry out a blank determination and apply the necessary correction in the calculation.

12.2 Calculation - Calculate as given in **8.2.2**.

13 COMBINED AMMONIACAL NITROGEN (FORMALDEHYDE TITRATION METHOD)

13.1 Applicability – This method is applicable for determination of ammoniacal nitrogen present in ammonium nitrate; ammonium sulphate, calcium ammonium nitrate and ammonium chloride. This method is not applicable for samples containing ammonium carbonate, or ammonium phosphates or also for compound fertilizers.

13.2 Reagents

13.2.1 *Neutral Formaldehyde Solution* – Neutralize 37 percent formaldehyde solution (formation) with 0.25 N sodium hydroxide to phenolphthalein end point. In case some precipitates have been formed the formation should be filtered.

13.2.2 *Standard Sodium Hydroxide* – 0.25 N.

13.2.3 *Phenolphthalein Indicator* - (0.5 percent solution in 80 percent ethyl alcohol).

13.3 Procedure

Weigh the sample (containing not more than 2.0 g ammoniacal nitrogen) into a 250 ml volumetric flask, dissolve in water and make up to the mark. Pipette 25 ml formaldehyde solution into an Erlenmeyer flask containing 100 ml distilled water and titrate with 0.25 N sodium hydroxide to phenolphthalein end point (V_1 ml). Pipette 25 ml of aliquot into an Erlenmeyer flask, add 25 ml neutral formaldehyde solution (1 ml for each 0.1 g sample), add 5 drops of phenolphthalein indicator and titrate with 0.25 N sodium hydroxide till proper shade of pink colour persists (V_2 ml).

13.4 Calculation

Ammoniacal nitrogen, percent by mass = $\frac{(V_2 - V_1) \times N \times 1.400}{M}$

where

V_1 = volume, in ml, of sodium hydroxide used in blank titration;

V_2 = volume, in ml, of sodium hydroxide used in formaldehyde added titration;

N = normality of the sodium hydroxide; and

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

14 AMMONIACAL AND NITRATE NITROGEN (DEVARDA'S ALLOY METHOD)

14.1 Applicability – This method is suitable for the determination of total nitrogen when only nitrate or a mixture of nitrate and ammoniacal form is present. It is not applicable in presence of urea, calcium cyanamide and organic matter in the sample.

14.2 Procedure – Place 0.35 to 2.0 g of the prepared sample, accurately weighed, in a 500 to 800 ml distillation flask and add 300 ml of water, 3 g of Devarda's alloy and 5 ml of sodium hydroxide solution (42 percent by mass), pouring the latter down the side of the flask so that it does not mix at once with contents. Care should be taken against heavy frothing. Allow the flask to stand for 15 min. Connect the apparatus as described in **8.2.1.2** and mix the contents of the distilling flask by rotating. Heat slowly at first and then at a rate to yield 250 ml distillate in one hour. Collect the distillate in a measured quantity of standard acid and titrate with standard sodium hydroxide solution, using methyl red as an indicator. Alternatively, the distillate can be collected in boric acid solution and titrated with standard acid. Carry out a blank determination and apply the necessary correction in calculation.

14.3 Calculation - Calculate as given in **8.2.2**.

15 NITRATE NITROGEN (ROBERTSON METHOD)

15.1 Applicability – The method is recommended for adoption in the presence of calcium cyanamide and urea in the sample.

15.2 Procedure

15.2.1 Determine total nitrogen as given under **9**.

15.2.2 Determine water insoluble nitrogen as given under **17** but use 2.5 g of the prepared sample and dilute the filtrate to 250 ml.

15.2.3 Transfer 50 ml portion of the filtrate in 500 ml Kjeldahl flask and 5 g of ferrous sulphate heptahydrate and 20 ml of concentrated sulphuric acid. Digest over hot flame until all water is evaporated and white fumes appear, and continue digestion for at least ten minutes more to drive off nitrate nitrogen. If there is severe bumping, add 10 to 15 glass beads. Add 0.7 g of mercuric oxide or copper sulphate and, 10 g of potassium sulphate and digest till all organic matter is oxidized. Cool, dilute, and complete the determination as in **8.2.1.2**. Before distillation, add a pinch of a mixture of zinc dust and granular zinc to each flask to prevent bumping. Carry out a blank determination and apply the necessary correction.

15.3 Calculation - From total nitrogen (*see* **15.2.1**) subtract water insoluble nitrogen (*see* **15.2.2**) to obtain water soluble nitrogen. From that, further subtract (ammoniacal urea) nitrogen as obtained in **15.2.3** to get the nitrate nitrogen content.

16 NITRATE NITROGEN (GRAVIMETRIC METHOD)

16.1 General – Gravimetric estimations of nitrate can be done by using a specific reagent nitron, a yellow crystalline solid ($C_{20}H_{16}N_4$) an organic base insoluble in water. It yields sparingly soluble crystalline nitrate ($C_{20}H_{16}N_4.HNO_3$) in solutions acidified with sulphuric acid or acetic acid. Bromide, iodide, chlorate, chromate nitrite interferes and should be removed by a preliminary treatment.

16.2 Reagents – Dissolve 5 g of nitron in 50 ml of 5 percent acetic acid. Store in an amber bottle.

16.3 Procedure – Take 75 to 100 ml of solution in 250 ml beaker. The solution should be neutral containing about 1 g of nitrate. In case of acid or alkaline extracts, this solution should be neutralized first. Add 1 ml of glacial acetic acid and 0.5 ml of 2N H_2SO_4. Heat nearly to boiling point. Add 10 to 12 ml of nitron reagent with constant stirring and cool in ice-cool water for about 2 hours. Filter through a previously weighed sintered glass or gooch crucible. Wash with 10 to 12 ml portion of cold saturated solution of nitron nitrate 5 to 7 times allowing to drain out completely after each washing. Finally wash with 2 to 3 ml portion of ice-cool water. Dry at 100 °C to 105 °C for about an hour and weigh as $C_{20}H_{16}N_4.HNO_3$.

16.4 Calculation

Nitrate nitrogen = Weight of precipitate × 0.165 3

17 WATER INSOLUBLE NITROGEN

17.1 General – Two techniques for dissolving out the water soluble nitrogen are given below. The one given in **17.2.1** is the reference method and that given in **17.2.2** is an alternative one.

17.2 Procedure

17.2.1 place 1 to 1.5 g of prepared sample, accurately weighed, in a 50 ml beaker and moisten well with 95 percent ethyl alcohol. Add 20 ml of water and allow to stand for 15 min, stirring occasionally. Transfer the supernatant liquid to 11 cm filter paper (Whatman No. 42 or equivalent) in a 6 cm diameter long stem funnel, and wash the residue 4 or 5 times by decanting with water at room temperature. Finally transfer all residue to the filter paper and complete washing until filtrate measures exactly 250 ml.

17.2.2 *Alternate Technique* – Place 1.0 to 1.5 g of the prepared sample, accurately weighed, in a 500 ml conical flask, wet with 25 ml of rectified spirit (better to avoid denatured spirit which may contain some tar base), and add 225 ml of water maintained at a temperature of 20 °C to 25 °C. Total volume should be exactly 250 ml. Stopper the flask and fix it to a wrist action shaker. Shake for exactly 1 hour and filter through a dry filter paper (Whatman No. 41 or equivalent). If the filtrate is turbid, add a little filter paper pulp to the solution and then filter. Reject the first few portions of the filtrate before using it for any determination.

17.1.3 Determine total nitrogen in the insoluble residue (along with filter paper by the methods prescribed under **8**).

18 DETERMINATION OF UREA NITROGEN

18.1 Applicability – This procedure is prescribed for determination of urea content of any fertilizer.

18.2 Procedure

18.2.1 Weigh accurately 10 g of the prepared sample, and transfer to a 15 cm fluted filter paper (Whatman No. 1 or equivalent). Leach with approximately 300 ml of water in 20-25 ml portions into a 500 ml volumetric flask. Add 75 to 100 ml of saturated barium hydroxide solution to precipitate phosphate. Let it settle and test for complete precipitation with a few drops of saturated barium hydroxide solution. Add 20 ml of 10 percent sodium carbonate solution to precipitate excess barium and any soluble calcium salts. Test for complete precipitation. A slight excess of sodium carbonate must be present. Dilute to volume, mix and filter through a 15 cm fluted paper (Whatman No. 1 or equivalent).

18.2.2 Transfer 50 ml aliquot (equivalent to 1 g of prepared sample) to a 250 ml conical flask and add 1 to 2 drops of methyl purple indicator. Acidify the solution with 2 N hydrochloric acid and add drop-wise until indicator turns purple and add 2 to 3 drops in excess. Neutralize with 0.1 N sodium hydroxide solution to first change in colour of the indicator. Then add 20 ml of one percent suspended urease solution, close the flask with rubber stopper and let it stand for one hour at 20 °C to 25 °C. Cool the flask in ice water and titrate at once with 0.1 N hydrochloric acid to purple colour, then add 5 ml in excess. Record the total volume of acid added, and back titrate excess acid with 0.1 N sodium hydroxide to neutral end point. Carry out a blank determination and apply the necessary correction in the calculation.

18.3 Calculation

Urea content (as urea), percent by mass = $\frac{0.300\ (\ V_1N_1 - V_2N_2\ )}{M}$

where

V_1 = total volume, in ml, of 0.1 N acid added;

N_1 = normality of the acid added;

V_2 – volume, in ml, of 0.1 N alkali required;

N_2 = normality of the alkali used; and

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

19 DETERMINATION OF CYANAMIDE NITROGEN

19.1 Principle

Cyanamide nitrogen is precipitated as a silver complex and estimated in the precipitate by Kjeldahl's method.

19.2 Reagents

19.2.1 *Ammonical Silver Nitrate Solution* — Mix 500 ml of 10% silver nitrate ($AgNO_3$) solution in water with 500 ml of 10% ammonia solution.

19.2.2 *Glacial Acetic Acid*

19.2.3 *Sulphuric Acid* — 93-98 per cent H_2SO_4, N free.

19.2.4 *Copper sulphate* — $CuSO_4.5H_2O$ reagent grade, N free.

19.2.5 *Potassium sulphate* (*or anhydrous sodium sulphate*) — reagent grade.

19.2.6 *Salicylic acid* — reagent grade, N free.

19.2.7 *Sulphide or thiosulphate solution* — Dissolve 40 g commercial K_2S in 1 litre distilled water. (Solution — of 40 g Na_2S or 80 g $Na_2S_2O_3.5H_2O$ in 1 litre may be used).

19.2.8 *Sodium hydroxide* — Pellets or solution, nitrate free. For solution dissolve approximately 450 g solid NaOH in distilled water and dilute to 1 litre (Sp. gr. of solution should be 1.36 or higher).

19.2.9 *Zinc granule* — reagent grade.

19.2.10 *Zinc dust* – impalpable powder.

19.2.11 *Methyl red indicator* — Dissolve 1 g methyl red in 200 ml alcohol.

19.2.12 *Hydrochloric or sulphuric acid standard solution* — 0.5 N or 0.1 N when amount of N is small.

19.2.13 *Sodium hydroxide standard solution* — 0.1 N (or other specified concentration).

19.3 Procedure

19.3.1 Weigh 2.5 g (*M*) sample and place it in a small glass mortar. Grind the sample 3 times with water, pouring off the water after each grinding into a 500 ml volumetric flask. Transfer quantitatively the sample into 500 ml volumetric flask, washing the mortar, pestle and funnel with water. Make up volume to approximately 400 ml. Add 15 ml of glacial acetic acid. Shake on rotary shaker for 2 hours. Make up the volume to 500 ml with water, mix and filter. Transfer 25 ml of filterate into 250 ml beaker. Add ammonia solution until slightly alkaline and add 20 ml of warm ammoniacal silver nitrate. Yellow precipitate will form. Leave overnight. Filter using Whatman No.40 filter paper and wash the precipitate with cold water until it is completely free of ammonia. Place the filter and precipitate in a Kjeldahl flask. Add 0.7 g copper sulphate, 15 g Potassium sulphate and 30 ml of H_2SO_4. Place flask in inclined position and heat gently. Boil bristly until solution becomes clear or pale green. Continue digestion for

30 min more. Remove from burner and cool. Transfer the contents of Kjeldahl flask to 1 litre capacity, distillation flask, make volume to about 350 ml with water and a pinch of zinc dust. Mix and cool. Distil ammonia by adding 10 ml of NaOH (40%) and collect the distillate in receiver conical flask containing 25 ml of 0.1 N HCl or H_2SO_4 containing 5 drops of Methyl red indicator. Titrate the contents in receiver conical flask with 0.1 N NaOH & calculate the volume of 0.1 N HCl consumed (*V*).

19.3.2 Determine blank on reagents using same quantity of standard acid in receiver conical flask.

19.4 Calculation

$$\text{Cyanamide Nitrogen \% (by weight)} = \frac{(Blank - V)}{M} \times 2.8$$

20 DETERMINATION OF UREA

20.1 Outline of the Method – Urea reacts with *p*-dimethyl amino benzaldehyde (PDAB) to give a yellowish green colour with a maximum absorbance at 425 nm. If the reagent is made in *iso*-propyl alcohol medium, and care is taken to exclude water from the reaction, the colour developed obeys Beer's Law in the concentration range 0 to 40 ppm urea.

20.2 Reagents

20.2.1 *p-Dimethyl Amino Benzaldelyde (PDAB)* **–** Dissolve 2 g of PDAB in 100 ml of *iso*-propylalcohol, add 0.6 ml of concentrated sulphuric acid and mix well.

20.2.2 *Standard Urea Solution* **–** Dissolve 0.05 g of pure urea in 250 ml of *iso*-propyl alcohol. One millilitre of this solution contains 0.2 mg of urea.

20.2.3 *Standard Urea Solution* **–** The solution will be used in determination of urea in diammonium phosphate. Dissolve 0.05 g of urea and a similar quantity of diammonium phosphate as is present in sample under examination, in 250 ml of *iso*-propyl alcohol. Prepare a calibration curve using this standard solution instead of that mentioned in **20.2.2.**

20.2.4 *Sample Solution* **–** Dissolve suitable quantity of sample containing not more than 0.05 g urea in 250 ml of *iso*-propyl alcohol.

20.3 Procedure

20.3.1 *Preparation of Calibration Curve* **–** Take 0, 1, 2,3, 4 ml of standard urea solution into five 25 ml dry volumetric flask. Add 10 ml of PDAB reagent to each flask and make up to the mark with *iso*-propyl alcohol. Mix it well. Allow it to stand for 15 min for colour development. Determine the absorbance reading in a colorimeter with 420 nm filter using 12.5 mm diameter tubes after setting the instrument to read zero with reagent blank (using 0 ml of urea solution in the above standard).

20.3.2 Draw a calibration curve showing milligrams of urea versus calorimeter scale reading.

20.3.3 *Determination of Urea in Sample* **–** Take an aliquot of sample solution (to contain less than 0.8 mg urea) into a 25 ml dry volumetric flask. Add 10 ml of PDAB reagent and make up to mark with *iso*-propyl alcohol. Mix it well. Keep it for 15 min. Determine the absorbance in calorimeter using 12.5 mm diameter.

20.3.4 From the calibration curve read the milligram urea present in sample aliquot, corresponding to calorimeter scale reading. Calculate the percentage of urea present in sample.