SCHEDULE 2

METHODS OF ANALYSIS

PART I

8a.

DETERMINATION OF DIFFERENT FORMS OF NITROGEN IN THE SAME SAMPLE—IN THE PRESENCE OF CYANAMIDE NITROGEN

SCOPE

1. This method is for the determination of any one form of nitrogen in the presence of any other form.

FIELD OF APPLICATION

2. Any fertiliser in Group 1(a) of Section A, and Groups 1, 2 and 3 of Section B of the Table in Schedule 1 of the Fertilisers Regulations 1990(**1**) containing nitrogen in various forms.

PRINCIPLE

Total soluble and insoluble nitrogen

Total soluble and insoluble nitrogen

3.—(3.1) According to the list of standard fertilisers, this method is applicable to products containing calcium cyanamide.

(3.1.1) *In the absence of fertilisers*, the sample is subjected to direct Kjeldahl digestion.

(3.1.2) *In the presence of nitrates*, the sample is subjected to Kjeldahl digestion after reduction with the aid of metallic iron and stannous chloride.

In both cases, the ammonia is determined according to Method 2.

Note: If analysis shows an insoluble nitrogen content of more than 0.5%, it is presumed that the fertiliser contains other forms of insoluble nitrogen not specified for fertilisers covered by the list in paragraph 2.

Forms of soluble nitrogen

(3.2) The following are determined from different aliquot parts taken from the same solution of the sample:

(3.2.1) *Total soluble nitrogen*

(3.2.1.1) *In the absence of nitrates*, by direct Kjeldahl digestion.

(3.2.1.2) *In the presence of nitrates*, by Kjeldahl digestion on an aliquot part taken from the solution after reduction according to Ulsch, the ammonia being determined in both cases as described in Method 2.

(**1**) S.I. 1990/887.

(3.2.2) *Total soluble nitrogen with the exception of nitric nitrogen*, by Kjeldahl digestion after elimination in an acid medium of nitric nitrogen with ferrous sulphate, the ammonia being determined as described in Method 2.

(3.2.3) *Nitric nitrogen by difference*

(3.2.3.1) *In the absence of calcium cyanamide*, between (3.2.1.2) and (3.2.2) or between total soluble nitrogen (3.2.1.2) and the sum of ammoniacal nitrogen and ureic nitrogen (3.2.4 + 3.2.5).

(3.2.3.2) *In the presence of calcium cyanamide*, between (3.2.1.2) and (3.2.2) and between (3.2.1.2) and the sum of (3.2.4 + 3.2.5 + 3.2.6).

(3.2.4) *Ammoniacal nitrogen*

(3.2.4.1) *Solely in the presence of ammoniacal nitrogen and ammonical + nitric nitrogen*, by applying Method 2.

(3.2.4.2) *In the presence of ureic nitrogen and/or cyanamide nitrogen*, by cold distillation after making slightly alkaline, the ammonia being absorbed in a standard solution of sulphuric acid and determined as described in Method 2.

(3.2.5) *Urea nitrogen*

Either

3.2.5.1 *By conversion using urease*, into ammonia which is titrated with a standard solution of hydrochloric acid,

or:

3.2.5.2 *By gravimetry with xanthydrol*, although biuret will also be precipitated by xanthydrol, this should not give rise to a significant error in the determination since its level is generally low in absolute value in compound fertilisers,

or:

3.2.5.3 *By difference*, according to the following table:

Case	*Nitric Nitrogen*	*Ammoniacal Nitrogen*	*Cyanamide Nitrogen*	*Difference*
1	Absent	Present	Present	(3.2.1.1)-(3.2.4.2 + 3.2.6)
2	Present	Present	Present	(3.2.2)-(3.2.4.2 + 3.2.6)
3	Absent	Present	Absent	(3.2.1.1)-(3.2.4.2)
4	Present	Present	Absent	(3.2.2)-(3.2.4.2)

(3.2.6) *Cyanamide nitrogen*, by precipitation as a silver compound, the nitrogen being estimated in the precipitate by the Kjeldahl method.

REAGENTS

4.—(4.1) Potassium sulphate.

(4.2) Iron power, reduced with hydrogen (the presribed quantity of iron must be able to reduce at least 50 mg of nitric nitrogen).

(4.3) Potassium thiocyanate.

(4.4) Potassium nitrate.

(4.5) Ammonium sulphate.

(4.6) Urea.

(4.7) Sulphuric acid solution: dilute an appropriate volume of sulphuric acid (d = 1.84 g/ml) with an equal volume of water.

(4.8) Sulphuric acid, 0.2 N solution.

(4.9) Sodium hydroxide solution, 30 g per 100 ml, ammonia free.

(4.10) Sodium or potassium hydroxide, 0.2 N solution, free from carbonates.

(4.11) Stannous chloride solution:

dissolve 120 g of stannous chloride ($SnCl_2.2H_2O$) in 400 ml of conentrated hydrochloric acid (d = 1.18 g/ml) and make up to 1 litre with water. The solution must be perfectly clear and prepared immediately before use.

It is essential to check the reducing power of stannous chloride: dissolve 0.5 g of stannous chloride in 2 ml of concentrated hydrochloric acid (d = 1.18 g/ml) and make up to 50 ml with water. Then add 5 g of Rochelle salt (potassium sodium tartrate) and a sufficient quantity of sodium bicarbonate for the solution to be alkaline to litmus paper.

Titrate with 0.1 N iodine solution in the presence of a starch solution as an indicator.

1 ml of 0.1 N iodine solution corresponds to 0.01128 g of $SnCl_2.2H_2O$.

At least 80% of the total tin present in the solution thus prepared must be in bivalent form. For the titration, at least 35 ml of 0.1 N iodine solution must therefore be used.

(4.12) Sulphuric acid, concentrated (d = 1.84 g/ml).

(4.13) Hydrochloric acid solution, approximately 30% (W/V) H_2SO_4.

(4.14) Glacial acetic acid.

(4.15) Sulphuric acid solution, approximately 30% (W/V) H_2SO_4.

(4.16) Ferrous sulphate, crystalline $FeSO_4.7H_2O$.

(4.17) Sulphuric acid, 0.1 N solution.

(4.18) Octan-1-ol.

(4.19) Potassium carbonate, saturated solution.

(4.20) Sodium or potassium hydroxide, 0.1 N solution, free from carbonate.

(4.21) Barium hydroxide, saturated solution.

(4.22) Sodium carbonate solution, 10 g per 100 ml.

(4.23) Hydrochloric acid, 2 N solution.

(4.24) Hydrochloric acid, 0.1 N solution.

Urease solution:

(4.25) suspend 0.5 g of active urease in 100 ml of distilled water.

Using 0.1 N hydrochloric acid (4.24), adjust the pH to 5.4, measured by a pH meter.

(4.26) Xanthydrol solution, 5 g per 100 ml in ethanol or methanol (4.31) (do not use products giving a high proportion of insoluble matter). The solution may be kept for three months in a well-stoppered bottle, away from the light.

(4.27) Copper oxide (CuO): 0.3 to 0.4 g per determination or an equivalent quantity of copper sulphate pentahydrate of 0.95 to 1.25 g per determination.

(4.28) Anti-bump granules washed in hydrochloric acid and ignited.

(4.29) Indicator solutions:

Mixed indicator solution:

(4.29.1) Solution A: dissolve 1 g of methyl red in 37 ml of 0.1 N sodium hydroxide solution and make up to one litre with water.

Solution B: dissolve 1 g of methylene blue in water and make up to one litre.

Mix one volume of solution A and 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution.

Use 0.5 ml (10 drops) of this indicator solution.

Methyl red indicator solution:

(4.29.2) dissolve 0.1 g of methyl red in 50 ml of 95% ethanol, make up to 100 ml with water and filter if necessary. This indicator (4 to 5 drops) can be used instead of the previous one.

Indicator papers:

(4.30) Litmus, bromothymol blue (or other papers sensitive to pH 6 to 8).

(4.31) Ethanol or methanol: solution 95%.

APPARATUS

5.—(5.1) Distillation apparatus. See Method 2.

(5.2) Apparatus for the determination of ammoniacal nitrogen according to analytical technique 7.2.5.3. An example of recommended apparatus is reproduced in Figure 6 in the Appendix.

The apparatus is made up of a specially shaped receptacle with a ground glass neck, a side neck, a connecting tube with a splash head and a perpendicular tube for the introduction of air. The tubes can be connected to the receptacle by means of a simple perforated rubber bung. It is important to give a suitable shape to the end of the tubes introducing air, since the bubbles of gas must be evenly distributed throughout the solutions contained in the receptacle and the absorber. The best arrangement consists of small mushroom-shaped pieces with an external diameter of 20 mm and six openings of 1 mm around the periphery.

(5.3) Apparatus for the estimation of urea nitrogen according to the urease technique (7.2.6.1).

It consists of a 300 ml Erlenmeyer flask, with a seperating funnel and a small absorber. An example of recommended apparatus is reproduced in Figure 7 in the Appendix.

(5.4) Rotary shaker, 35-40 turns per minute.

(5.5) pH meter.

(5.6) Laboratory oven.

(5.7) Sintered glass crucibles, diameter of pores 5 to 15 microns.

PREPARATION OF THE SAMPLE

6. See Method 1.

PROCEDURE

7.—(7.1) *Total soluble and insoluble nitrogen*

(7.1.1) *In the absence of nitrate*

(7.1.1.1) *Digestion*

Weigh to the nearest 0.001 g, a quantity of the prepared sample containing 100 mg of nitrogen at the most. Place it in the flask of the distillation apparatus (5. 1). Add 10 to 1 5 g of potassium sulphate (4. 1), the prescribed quantity of catalyst (4.27), and a few anti-bump granules (4.28). Then add 50 ml of dilute sulphuric acid (4.7), and mix thoroughly. First heat gently, mixing from time to time, until foaming ceases. Then heat so that the liquid boils steadily and keep it boiling for one hour after the solution has become clear, preventing any organic matter from sticking to the sides of the flask. Allow to cool. Carefully add about 350 ml of water, with mixing. Ensure than the dissolution is as complete as possible. Allow to cool and connect the flask to the distillation apparatus (5.1).

(7.1.1.2) *Distillation of ammonia*

Transfer with a pipette, into the receiver of the apparatus, 50 ml standard 0.2 N sulphuric acid (4.8). Add the indicator (4.29.1 or 4.29.2). Ensure that the tip of the condenser is at least 1 cm below the level of the solution.

Taking the necessary precautions to avoid any loss of ammonia, carefully add to the distillation flask enough of the concentrated sodium hydroxide solution (4.9) to make the liquid stongly alkaline (120 ml is generally sufficient: check by adding a few drops of phenolphthalein. At the end of the distillation the solution in the flask must still be clearly alkaline). Adjust the heating of the flask so as to distil 150 ml in half an hour. Test with indicator paper (4.30) that the distillation has been completed. If it has not, distil a further 50 ml and repeat the test until the supplementary distillate reacts neutrally to the indicator paper (4.30). Then lower the receiver, distil a few ml more and rinse the tip of the condenser. Titrate the excess acid with a standard solution of potassium or sodium hydroxide 0.2 N (4.10) to the end point of the indicator.

(7.1.1.3) *Blank test*

Make a blank test under the same conditions (omitting only the sample) and use this value in the calculation of the final result.

(7.1.1.4) Expression of the result

$$\% N = \frac{(a - A) \times (1,28}{M}$$

where:

a= ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50.0 ml of standard solution of sulphuric acid (0.2 N) (4.8).

A= ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the analysis.

M=weight of the sample in grams.

(7.1.2) In the presence of nitrate

(7.1.2.1) *Test sample*

Weigh to the nearest 0.001 g, a quantity of the sample containing not more than 40 mg of nitric nitrogen.

(7.1.2.2) *Reduction of the nitrate*

Mix the sample in a small mortar with 50 ml of water. Transfer with the minimum amount of distilled water into a 500 ml Kjeldahl flask. Add 5 g of reduced iron (4.2) and 50 ml of stannous chloride solution (4.11). Shake and leave it to stand for half an hour. During this time shake again after 10 and 20 minutes.

(7.1.2.3) *Kjeldahl digestion*

Add 30 ml of sulphuric acid (4.12), 5 g of potassium sulphate (4.1), the prescribed quantity of catalyst (4.27) and some anti-bump granules (4.28). Heat gently with the flask slightly tilted. Increase the heat slowly and shake the solution frequently to keep the mixture suspended; the liquid darkens and then clears with the formation of a yellow-green anhydrous iron sulphate suspension. Continue heating for one hour after obtaining a clear solution, maintaining it at simmering point. Leave to cool. Cautiously take up the contents of the flask in a little water and add little by little 100 ml of water. Mix and transfer the contents of the flask into a 500 ml graduated flask. Rinse the flask several times with distilled water. Make up the volume with water and mix. Filter through a dry filter into a dry receiver.

(7.1.2.4) *Distillation of ammonia*

Transfer by pipette, into the flask of the distillation apparatus (5.1), an aliquot part containing 100 mg of nitrogen at the most. Dilute to about 350 ml with distilled water, add a few anti-bump granules (4.28), connect the flask to the distillation apparatus and continue the estimation as described in paragraph 7.1.1.2.

(7.1.2.5) *Blank test*

See 7.1.1.3.

(7.1.2.6) *Expression of the result*

$$\% \text{ N} = \frac{(a - A) \times 0.28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50.0 ml of standard solution of sulphuric acid (0.2 N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0.2N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

(7.2) *Forms of soluble nitrogen*

Preparation of the solution to be analysed

(7.2.1) Weigh to the nearest 0.001 g, 10 g of the sample and place it in a 500 ml graduated flask,

(7.2.1.1) *In the case of fertilisers not containing cyanamide nitrogen*

Add to the flask 50 ml of water and then 20 ml of dilute hydrochloric acid (4.13). Shake and leave it to stand until the evolution of carbon dioxide ceases. Then add 400 ml of water and shake for half an hour on the rotary shaker (5.4).

Make up to the volume with water, mix and filter through a dry filter into a dry receiver.

(7.2.1.2) *In the case of fertilisers containing cyanamide nitrogen*

Add to the flask 400 ml of water and a few drops of methyl red (4.29.2). If necessary make the solution acid by using acetic acid (4.14). Add 15 ml of acetic acid (4.14). Shake on the rotary shaker (5.4) for 2 hours. If necessary, re-acidify the solution during the operation, using acetic acid (4.14). Make up to the volume with water, mix, filter immediately through a dry filter into a dry receiver and immediately determine the cyanamide nitrogen.

In both cases, determine the various soluble forms of nitrogen the same day the solution is made up, starting with the cyanamide nitrogen and urea nitrogen, if they are present.

(7.2.2) *Total soluble nitrogen*

(7.2.2.1) *In the absence of nitrate*

Transfer by pipette into a 300 ml Kjeldahl flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2), containing 100 mg of nitrogen at the most. Add 15 ml of concentrated sulphuric acid (4.12), 0.4 g of copper oxide or 1.25 g of copper sulphate (4.27) and a few anti-bump granules (4.28). First heat gently to begin the digestion and then at a higher temperature until the liquid becomes colourless or slightly greenish and white fumes are clearly apparent. After cooling, quantitatively transfer the solution into the distillation flask, dilute to about 500 ml with water and add a few anti-bump granules (4.28). Connect the flask to the distillaton apparatus (5. 1) and continue the distillation as determination in paragraph 7.1.1.2.

(7.2.2.2) *In the Presence of nitrate*

Transfer by pipette into a 500 ml Erlenmeyer flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 40 mg of nitric nitrogen. At this stage of the analysis the total quantity of nitrogen is not important. Add 10 ml of 30% sulphuric acid (4.15), 5 g of reduced iron (4.2) and immediately cover the Erlenmeyer flask with a watch glass. Heat gently until the reaction is steady but not vigorous. At this juncture stop the heating and allow the flask to stand for at least three hours at ambient temperature. With water, quantitatively transfer the liquid into a 250 ml graduated flask, leaving behind the undissolved iron and make up to the mark with water. Mix thoroughly, and transfer by pipette into a 300 ml Kjeldahl flask, an aliquot part containing 100 mg of nitrogen at the most. Add 15 ml of concentrated sulphuric acid (4.12), 0.4 g of copper oxide or 1.25 g of copper sulphate (4.27) and some anti-bump granules (4.28). First heat gently to begin the digestion and then at a higher temperature until the liquid becomes colourless or slightly greenish and white fumes are clearly apparent. After cooling, quantitatively transfer the solution into the distillation flask, dilute to approximately 500 ml with water and add some anti-bump granules (4.28). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in paragraph 7.1.1.2.

(7.2.2.3) *Blank test*

See 7.1.1.3.

(7.2.2.4) *Expression of the result*

$$\% \text{ N} = \frac{(a - A) \times 0.28}{M}$$

where:

a= ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50.0 ml of standard solution of sulphuric acid (0.2 N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0. 2 N) used for analysis.

M=weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

Total soluble nitrogen with the exception of nitric nitrogen

(7.2.3) Transfer by pipette into a 300 mi Kjeldahl flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 50 mg of nitrogen to be determined. Dilute to 100 ml with water, add 5 g of ferrous sulphate (4.16), 20 ml of concentrated sulphuric acid (4.1) and some anti-bump granules (4.28). First heat gently and then increase the heat until white fumes appear. Continue the digestion for 15 minutes. Stop the heating, introduce the copper oxide (4.27) as a catalyst and keep it at a temperature such that white fumes are emitted for a further 10 to 15 minutes. After cooling, quantitatively transfer the contents of the Kjeldahl flask into the distillation flask of the apparatus (5. 1). Dilute to approximately 500 ml with water and add a few anti-bump granules (4.28). Connect the flask to the distillaton apparatus and continue the determinaton as described in paragraph 7.1.1.2.

(7.2.3.1) *Blank test*

See 7.1.1.3.

(7.2.3.2) *Expression of result*

$$\% \, N = \frac{(a - A) \times 0.28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50 ml of the standard sulphuric acid solution (0.2N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

(7.2.4) *Nitric nitrogen is obtained:*

(7.2.4.1) *In the absence of calcium cyanamide*

By the difference between the results obtained in paragraphs 7.2.2.4 and 7.2.3.2 and/ or the result obtained in paragraph 7.2.2.4 and the sum of the results obtained in paragraphs 7.2.5.2 or 7.2.5.5 and 7.2.6.3 or 7.2.6.5 or 7.2.6.6.

(7.2.4.2) *In the presence of calcium cyanamide*

By the difference between the results obtained in paragraphs 7.2.2.4 and 7.2.3.2 and between the result obtained in paragraph 7.2.2.4 and the sum of the results obtained in paragraphs 7.2.5.5 and 7.2.6.3 or 7.2.6.5 or 7.2.6.6 and 7.2.7.

(7.2.5) *Ammoniacal nitrogen*

(7.2.5.1) *Solely in the presence of ammoniacal nitrogen and ammoniacal+nitric nitrogen*

Transfer by pipette into the flask of the distillation apparatus (5.1) an aliquot part of the filtrate (7.2.1.1) containing 100 mg of ammoniacal nitrogen at the most. Add water to obtain a total volume of about 350 ml and some anti-bump granules (4.28) to facilitate boiling. Connect the flask to the distillation apparatus, add 20 ml of sodium hydroxide solution (4.9) and distil as described in paragraph 7.1.1.2.

(7.2.5.2) *Expression of result*

$$\% \text{ N (ammoniacal)} - \frac{(a-A)\times 0.28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50 ml of the standard sulphuric acid solution (0.2 N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0.2 N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

(7.2.5.3) *In the presence of urea and/or cyanamide nitrogen*

Transfer by pipette into the dry flask of the apparatus (5.2), an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing 20 mg of ammoniacal nitrogen at the most. Then assemble the apparatus. Transfer by pipette into the 300 ml Erlenmeyer flask 50 ml of the standard sulphuric acid solution 0.1 N (4.17) and enough distilled water for the level of the liquid to be approximately 5 cm above the opening of the delivery tube; add the indicator (4.29.1). Introduce, through the side neck of the reaction flask, distilled water to make up the volume to about 50 ml and mix. To avoid foaming during aeration, add a few drops of octan-1-o1 (4.18). Make the solution alkaline by adding 50 ml of saturated potassium carbonate solution (4.19) and immediately begin to expel the ammonia thus liberated from the cold suspension. A strong current of air is necessary (flow of approximately 3 litres per minute) and should be purified beforehand by passing it through washing flasks containing dilute sulphuric acid and dilute sodium hydroxide. Instead of using pressurised air, it is also possible to use a vacuum (water pump) provided that the inflow tube is connected in a sufficiently airtight manner to the receiver used to collect the ammonia. The liberation of the ammonia is generally complete after three hours. It is nevertheless advisable to verify this by changing the receiving flask. When the operation is finished, disconnect the flask from the apparatus, rinse the tip of the tube and the sides of the flask with a little distilled water. Titrate the excess acid with standard sodium hydroxide solution (0.1 N) (4.20) to the end point of the indicator (4.29.1).

(7.2.5.4) *Blank test*

See 7.1.1.3.

(7.2.5.5) *Expression of the result*

$$\% \text{ N (ammoniacal)} = \frac{(a-A)\times 0.14}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0.1 N) used for the blank, carried out by placing in the 300 ml Erlenmeyer flask of the apparatus (5.2), 50 ml of the standard solution of sulphuric acid (0.1 N) (4.17).

A = ml of standard solution of sodium or potassium hydroxide (0.1 N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

(7.2.6) *Urea nitrogen*

(7.2.6.1) *Urease method*

Transfer by pipette into a 500 ml graduated flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 250 mg of urea nitrogen. To remove phosphates add saturated barium hydroxide solution (4.21) until no further precipitaton occurs. Eliminate the excess of barium ions and any dissolved calcium ions by adding 10% sodium carbonate solution (4.22). Allow the precipitate to settle and check whether total Precipitation has occurred. Make up to the mark, mix and filter through a pleated filter. Transfer by pipette 50 ml of the filtrate into the 300 ml Erlenmeyer flask of the apparatus (5.3). Acidify the filtrate with 2 N hydrochloric acid (4.23), until pH of 3.0 measured by the pH meter (5.5) is obtained. Then raise the pH to 5.4 with 0.1 N sodium hydroxide (4.20).

To avoid losses of ammonia during decomposition by the urease, close the Erlenmeyer flask with a stopper provided with a separating funnel and a small bubble trap containing exactly 2 ml of standard 0.1 N hydrochloric acid (4.24). Introduce through the separating funnel 20 ml of urease solution (4.25), and allow to stand for one hour at 20-25°c.Transfer by pipette 25 ml of standard 0.1 N hydrochloric acid (4.24) into the separating funnel, allow it to run through into the solution and then rinse with a little water. In the same way quantitatively transfer the contents of the bubble trap into the solution contained in the Erlenmeyer flask. Titrate the excess acid with the standard solution of sodium hydroxide (0.1 N) (4.20), until a pH of 5.4 is obtained, measured by the pH meter.

(7.2.6.2) *Blank test*

See 7.1.1.3.

(7.2.6.3) *Expression of result*

$$\% \text{ N (urcic)} = \frac{(a \cdot \cdot A) \times (0.1 \text{ 4}}{M}$$

where:

a = ml of standard solution of sodium of potassium hydroxide (0.1 N) used for the blank, carried out exactly under the same conditions as the analysis.

A = ml of standard solution of sodium of potassium hydroxide (0. I N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

(1) *Remarks*

After precipitation by the solutions or barium hydroxide and sodium carbonate, make up to the mark, filter and neutralise as rapidly as possible.

(2) The titration may also be carried out with the indicator (4.29.2), but the end point is then more difficult to observe.

(7.2.6.4) *Gravimetric method with xanthydrol*

Transfer by pipette into a 250 ml beaker, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 20 mg of urea. Add 40 ml of acetic acid (4.14). Stir with a glass rod for one minute, allow any precipitate to settle for five minutes. Filter into a 100 ml beaker, wash with several ml of acetic acid (4.14), then add to the filtrate drop by drop, 10 ml of xanthydrol solution (4.26), stirring continuously with a glass rod. Allow to stand until the precipitate appears, then stir again for one or two minutes. Allow to stand for one and a half hours. Filter through a sintered glass crucible (5.7) which has been previously dried and weighed, using a slight reduction

in pressure. Wash three times with 5 ml ethanol (4.31) without trying to remove all the acetic acid. Place it in the oven (5.6) at a temperature of 130°C for one hour (do not exceed 145°C). Allow to cool in a desiccator and weigh.

(7.2.6.5) *Expression of result*

$$\% \text{ urea N} + \text{biuret} - \frac{6,67 \times m}{M}$$

where:

m=weight of the precipitate obtained, in grams.

M=weight of the sample, in grams, present in the aliquot part taken for analysis. Correct for the blank.

Note: although biuret will also be precipitated by xanthydrol, this should not give rise to a significant error in the determination since its level is generally low.

(7.2.6.6) *Method by difference*

Urea nitrogen may also be calculated according to the following table:—

Case	Nitric Nitrogen	Ammoniacal Nitrogen	Cyanamide Nitrogen	Ureic Nitrogen
1	Absent	Present	Present	(7.2.2.4)-(7.2.5.5+7.2.7)
2	Present	Present	Present	(7.2.3.2)-(7.2.5.5+7.2.7)
3	Absent	Present	Absent	(7.2.2.4)-(7.2.5.5)
4	Present	Present	Absent	(7.2.3.2)-(7.2.5.5)

Cyanamide Nitrogen

(7.2.7) Take an aliquot part of the filtrate (7.2.1.2), containing 10 to 30 mg of cyanamide nitrogen and place it in a 250 ml beaker. Continue the analysis according to Method 6.

VERIFICATION OF THE RESULTS

8.—(8.1) In certain cases, a difference may be found between the total nitrogen obtained directly from a weighed out sample (paragraph 7.1) and total soluble nitrogen (paragraph 7.2.2). Nevertheless, the difference should not be greater than 0.5%. If this is not the case, the fertiliser contains forms of insoluble nitrogen not specified for fertilisers covered by the list in paragraph 2.

(8.2) Before each analysis, check that the apparatus is working properly and that the correct application of the method is used, with a standard solution including the various forms of nitrogen in proportions similar to those of the test sample. This standard solution is prepared from solutions of potassium thiocyanate (4.3), potassium nitrate (4.4), ammonium sulphate (4.5) and urea (4.6).