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Fertilizers — Determination of different forms of nitrogen in the same sample, containing nitrogen as nitric, ammoniacal, urea and cyanamide nitrogen

Engrais — Détermination des différentes formes d'azote dans un même échantillon contenant l'azote sous forme nitrique, ammoniacale, uréique et cyanamidique

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

ISO 15604 was prepared by CEN/TC 260 as EN 15604:2009 and was adopted (without modification other than those stipulated below) by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners*.

Modifications were made as follows:

a) 5.2: p.a. = pro analysis = analytical grade;

b) 6.2: add "Refer to Figure 1".

Fertilizers — Determination of different forms of nitrogen in the same sample, containing nitrogen as nitric, ammoniacal, urea and cyanamide nitrogen

1 Scope

This International Standard specifies a method for the determination of any one form of nitrogen in the presence of any other form.

The method is applicable to any fertilizer provided for in the Regulation (EC) No 2003/2003, Annex I[2] containing nitrogen in various forms.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 14820-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

ISO 25475, *Fertilizers — Determination of ammoniacal nitrogen*

EN 12944-1, *Fertilizers and liming materials — Vocabulary — Part 1: General terms*

EN 12944-2, *Fertilizers and liming materials — Vocabulary — Part 2: Terms relating to fertilizers*

EN 15562, *Fertilizers — Determination of cyanamide nitrogen*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 apply.

4 Principle

4.1 Total soluble and insoluble nitrogen

According to the list of standard fertilizers given in Regulation (EC) No 2003/2003, Annex I,[2] this determination is applicable to products containing calcium cyanamide.

In the absence of nitrates, the test sample is mineralized by direct Kjeldahl digestion.

In the presence of nitrates, the test sample is mineralized by Kjeldahl digestion after reduction with the aid of metallic iron and stannous chloride.

In both cases, the ammonia is determined according to ISO 25475.

NOTE If analysis shows an insoluble nitrogen content of more than 0,5 %, one concludes that the fertilizer contains other forms of insoluble nitrogen not included in the list in Regulation (EC) No 2003/2003, Annex I.[2]

4.2 Forms of soluble nitrogen

4.2.1 General

The forms of soluble nitrogen referred to in 4.2.2 to 4.2.7 are determined from different aliquots taken from the same solution of the test sample.

4.2.2 Total soluble nitrogen

4.2.2.1 In the absence of nitrates, by direct Kjeldahl digestion. The ammonia is then determined (by the same method as that described in ISO 25475).

4.2.2.2 In the presence of nitrates, by Kjeldahl digestion on an aliquot part taken from the solution after reduction according to Ulsch. The ammonia is then determined (by the same method as that described in ISO 25475).

4.2.3 Total soluble nitrogen with the exception of nitrate nitrogen

By Kjeldahl digestion after elimination in an acid medium of nitrate nitrogen with ferrous sulfate. The ammonia is then determined (by the same method as that described in ISO 25475).

4.2.4 Nitrate nitrogen by difference

4.2.4.1 In the absence of calcium cyanamide, by determining the difference between the nitrogen determined as summarized in 4.2.2.2 and that determined as summarized in 4.2.3 or between total soluble nitrogen (see 4.2.2) and the sum of ammoniacal nitrogen and ureic organic nitrogen (4.2.5 + 4.2.6).

4.2.4.2 In the presence of calcium cyanamide, by determining the difference between the nitrogen determined as summarized in 4.2.2.2 and that determined as summarized in 4.2.3 or between the nitrogen determined as summarized in 4.2.2.2 and the sum of that determined as summarized in 4.2.5, 4.2.6 and 4.2.7.

4.2.5 Ammoniacal nitrogen

4.2.5.1 Solely in the presence of ammoniacal nitrogen and ammoniacal plus nitrate nitrogen, according to ISO 25475.

4.2.5.2 In the presence of urea nitrogen and/or cyanamide nitrogen by cold distillation after making slightly alkaline, the ammonia is absorbed in a standard solution of sulfuric acid and determined according to ISO 25475.

4.2.6 Urea nitrogen

4.2.6.1 By conversion using urease into ammonia which is titrated with a standard solution of hydrochloric acid.

or

4.2.6.2 By gravimetry with xanthydrol: the co-precipitated biuret can be counted with urea nitrogen without great error, its content remaining generally low in absolute value in compound fertilizers.

or

4.2.6.3 By difference according to Table 1.

Table 1 — Determination of urea nitrogen by difference

Case	Nitrate nitrogen	Ammoniacal nitrogen	Cyanamidic nitrogen	Difference
1	Absent	Present	Present	(4.2.2.1) - (4.2.5.2 + 4.2.7)
2	Present	Present	Present	(4.2.3) - (4.2.5.2 + 4.2.7)
3	Absent	Present	Absent	(4.2.2.1) - (4.2.5.2)
4	Present	Present	Absent	(4.2.3) - (4.2.5.2)

4.2.7 Cyanamide nitrogen

By precipitation as a silver compound, the nitrogen being determined in the precipitate by the Kjeldahl method.

5 Reagents

5.1 General.

Use only reagents of recognized analytical grade and distilled or de-mineralized water of grade 3 according to ISO 3696.

5.2 Potassium sulfate, p.a. (p.a. = pro analysis = analytical grade).

5.3 Iron powder, reduced with hydrogen.

The prescribed quantity of iron shall be able to reduce at least 50 mg of nitrate nitrogen.

5.4 Potassium thiocyanate, p.a.

5.5 Potassium nitrate, p.a.

5.6 Ammonium sulfate, p.a.

5.7 Urea, p.a.

5.8 Sulfuric acid diluted.

Dilute one volume of sulfuric acid (ρ_{20} = 1,84 g/ml) in one volume of water.

5.9 Sulfuric acid, standard solution, c = 0,1 mol/l.

5.10 Sodium hydroxide solution, aqueous solution of about 30 % (mass concentration), free from ammonia.

5.11 Sodium or potassium hydroxide, standard solution, c = 0,2 mol/l, free from carbonates.

5.12 Stannous chloride solution.

Dissolve 120 g of $SnCl_2 \cdot 2H_2O$ in 400 ml of concentrated hydrochloric acid (ρ_{20} = 1,18 g/ml) and make up to 1 l with water. The solution shall be perfectly clear and prepared immediately before use.

It is essential to check the reducing power of stannous chloride: dissolve 0,5 g of $SnCl_2 \cdot 2H_2O$ in 2 ml of concentrated hydrochloric acid (ρ_{20} = 1,18 g/ml) and make up to 50 ml with water. Then, add 5 g

of Rochelle salt (potassium sodium tartrate), then a sufficient quantity of sodium bicarbonate for the solution to be alkaline to litmus paper.

Titrate with an iodine solution (I_2) of c = 0,05 mol/l in the presence of a starch solution as an indicator.

1 ml of iodine solution (I_2) of c = 0,05 mol/l corresponds to 0,011 28 g of $SnCl_2 \cdot 2H_2O$.

At least 80 % of the total tin present in the solution thus prepared shall be in bivalent form. For the titration, at least 35 ml of the c = 0,05 mol/l iodine solution (I_2) should be used.

5.13 Sulfuric acid, ρ_{20} = 1,84 g/ml.

5.14 Hydrochloric acid diluted.

Mix one volume of hydrochloric acid (ρ_{20} = 1,18 g/ml) with one volume of water.

5.15 Acetic acid, 96 % to 100 %.

5.16 Sulfuric acid solution, containing about 30 % of H_2SO_4 (mass concentration).

5.17 Ferrous sulfate, crystalline, $FeSO_4 \cdot 7H_2O$.

5.18 Sulfuric acid standard solution, c = 0,05 mol/l.

5.19 Octyl alcohol.

5.20 Potassium carbonate, saturated solution..

5.21 Sodium or potassium hydroxide standard solution, c = 0,1 mol/l (free from carbonates).

5.22 Barium hydroxide saturated solution.

5.23 Sodium carbonate solution, at 10 % (mass concentration).

5.24 Hydrochloric acid, c = 2 mol/l.

5.25 Hydrochloric acid standard solution, c = 0,1 mol/l.

5.26 Urease solution.

Suspend 0,5 g of active urease in 100 ml of water. Using hydrochloric acid 0,1 mol/l (5.25), adjust the pH to 5,4, measured by a pH-meter.

5.27 Xanthydrol.

Use a solution at 5 % in ethanol or methanol (5.32) (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.

5.28 Catalyst.

Use 0,3 g to 0,4 g of copper oxide per determination or an equivalent quantity of copper sulfate pentahydrate of 0,95 g to 1,25 g per determination.

5.29 Anti-bump granules, washed in hydrochloric acid and calcined.

5.30 Indicator solutions.

5.30.1 Solution A.

Dissolve 1 g of methyl red in 37 ml of sodium hydroxide solution 0,1 mol/l and make up to 1 l with water.

5.30.2 Solution B.

Dissolve 1 g of methylene blue in water and make up to 1 l.

5.30.3 Combined indicator solution.

Mix one volume of solution A with two 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.

5.30.4 Methyl red indicator solution.

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 (four or five drops) may be used instead of that described in 5.30.3.

5.31 Indicator papers, litmus bromothymol blue (or other papers sensitive to pH = 6 to pH = 8).

5.32 Ethanol or methanol, solution 95 %.

6 Apparatus

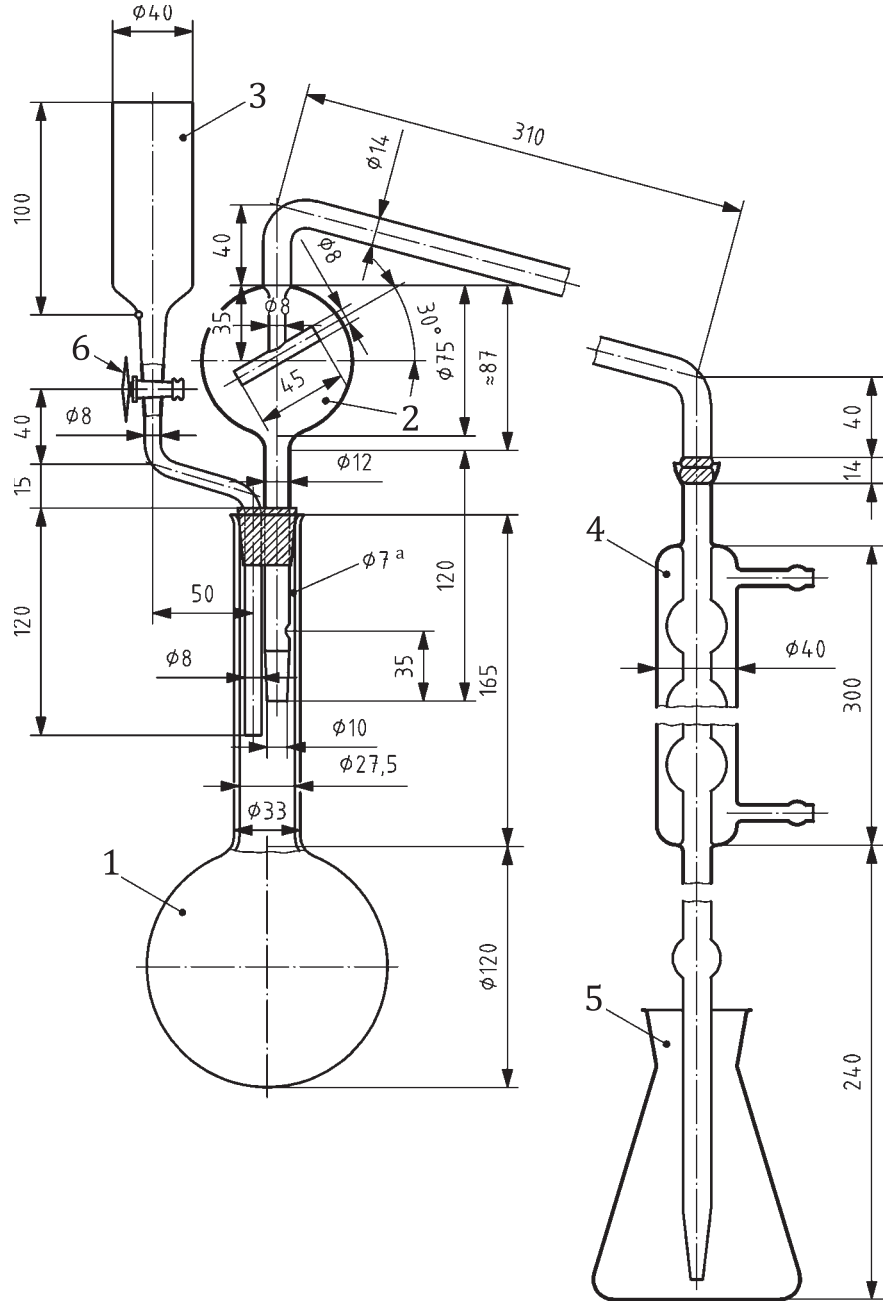
6.1 Distillation apparatus.

Consisting of a round-bottomed flask of suitable capacity connected to a condenser by means of a splash head. The equipment is made of borosilicate glass.

NOTE The different types of equipment recommended for this determination are reproduced, showing all the features of construction, in Figures 1, 2, 3 and 4.

An automatic distillation apparatus may also be used, provided that the results are statistically equivalent.

Dimensions in millimetres



Key

1 round-bottomed, long-necked flask of 1 000 ml capacity

2 distillation tube with a splash head, connected to the condenser by means of a spherical joint (No 18) (the spherical joint for the connection to the condenser may be replaced by an appropriate rubber connection)

3 funnel with a polytetrafluoroethylene (PTFE) tap (6) for the addition of sodium hydroxide (the tap may likewise be replaced by a rubber connection with a clip)

4 six-bulb condenser with spherical joint (No 18) at the entrance and joined at the issue to a glass extension tube by means of a small rubber connection (when the connection to the distillation tube is effected by means of a rubber tube, the spherical joint may be replaced by a suitable rubber bung)

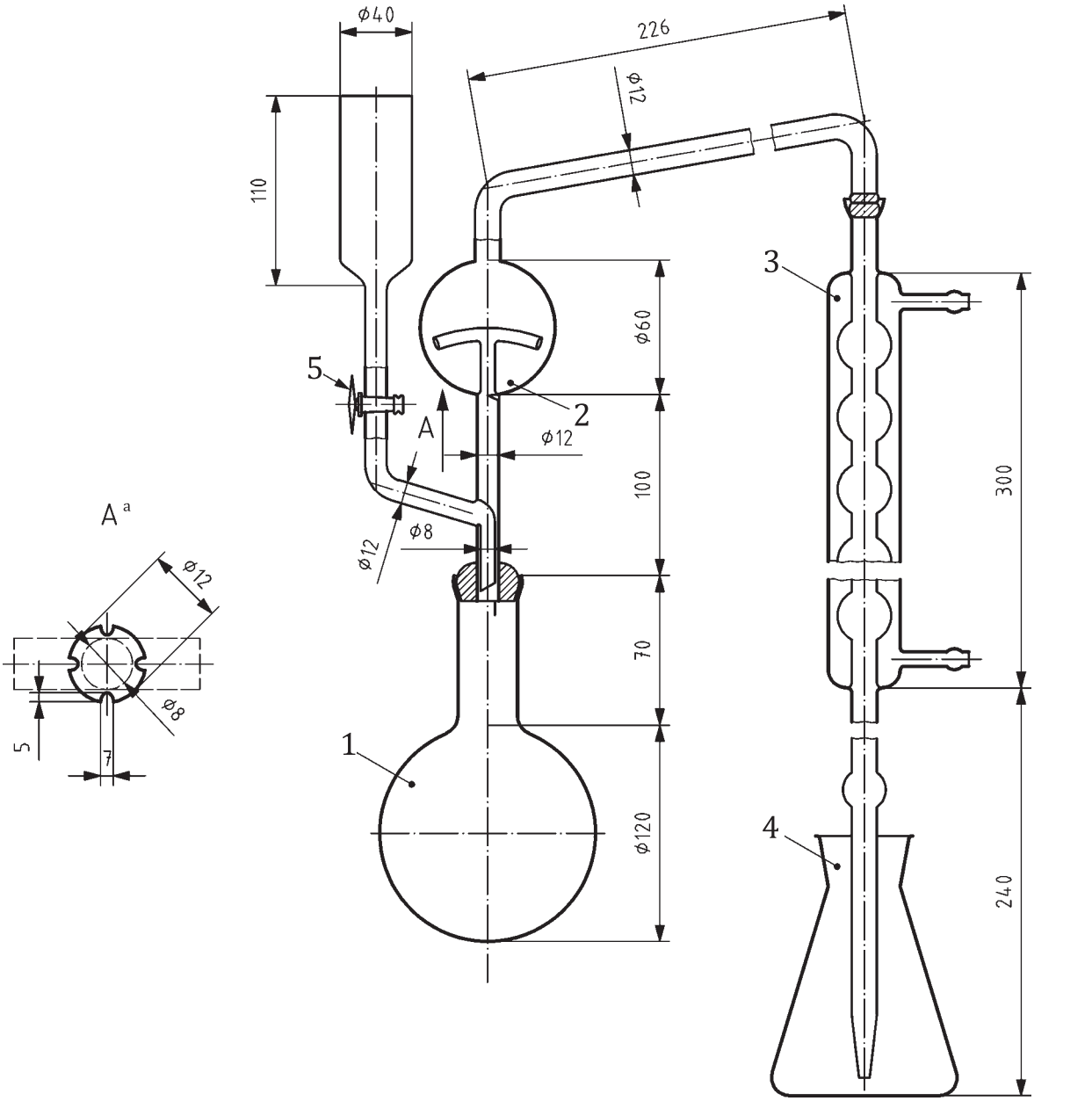
5 500 ml flask in which the distillate is collected

6 PTFE tap

a Hole.

Figure 1 — Distillation apparatus 1

Dimensions in millimetres



Key

1 round-bottomed, short-necked flask of 1 000 ml capacity with a spherical joint (No 35)

2 distillation tube with a splash head, equipped with a spherical joint (No 35) at the entrance and a spherical joint (No 18) at the issue, connected at the side to a funnel with a polytetrafluoroethylene (PTFE) tap (5) for the addition of sodium hydroxide

3 six-bulb condenser with a spherical joint (No 18) at the entrance and joined at the issue to a glass extension tube by means of a small rubber connection

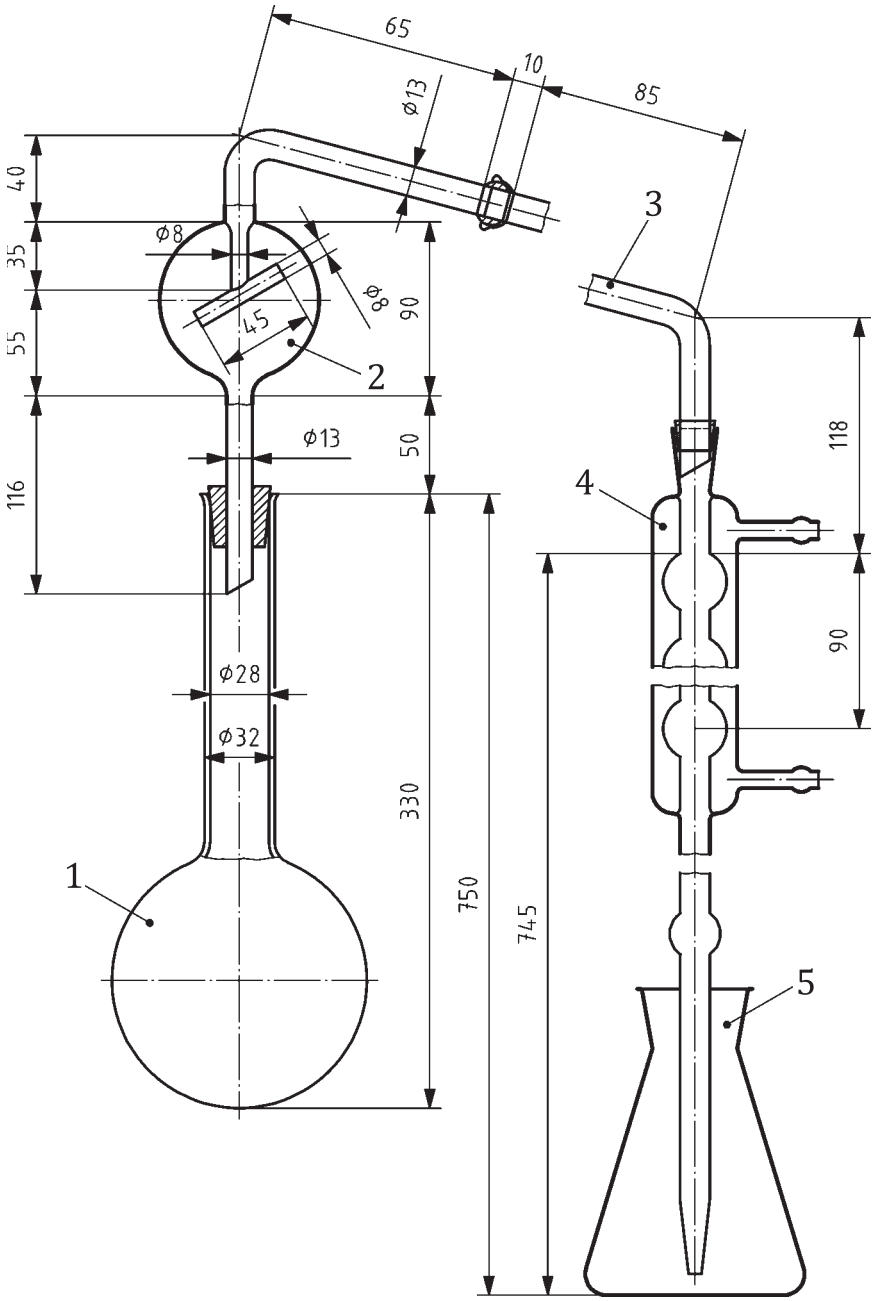
4 500 ml flask in which the distillate is collected

5 PTFE tap

[a] Enlarged cross-section.

Figure 2 — Distillation apparatus 2

Dimensions in millimetres



Key

1 round-bottomed, long-necked flask of 750 ml or 1 000 ml capacity with a bell mouth

2 distillation tube with a splash head and a spherical joint (No 18) at the issue

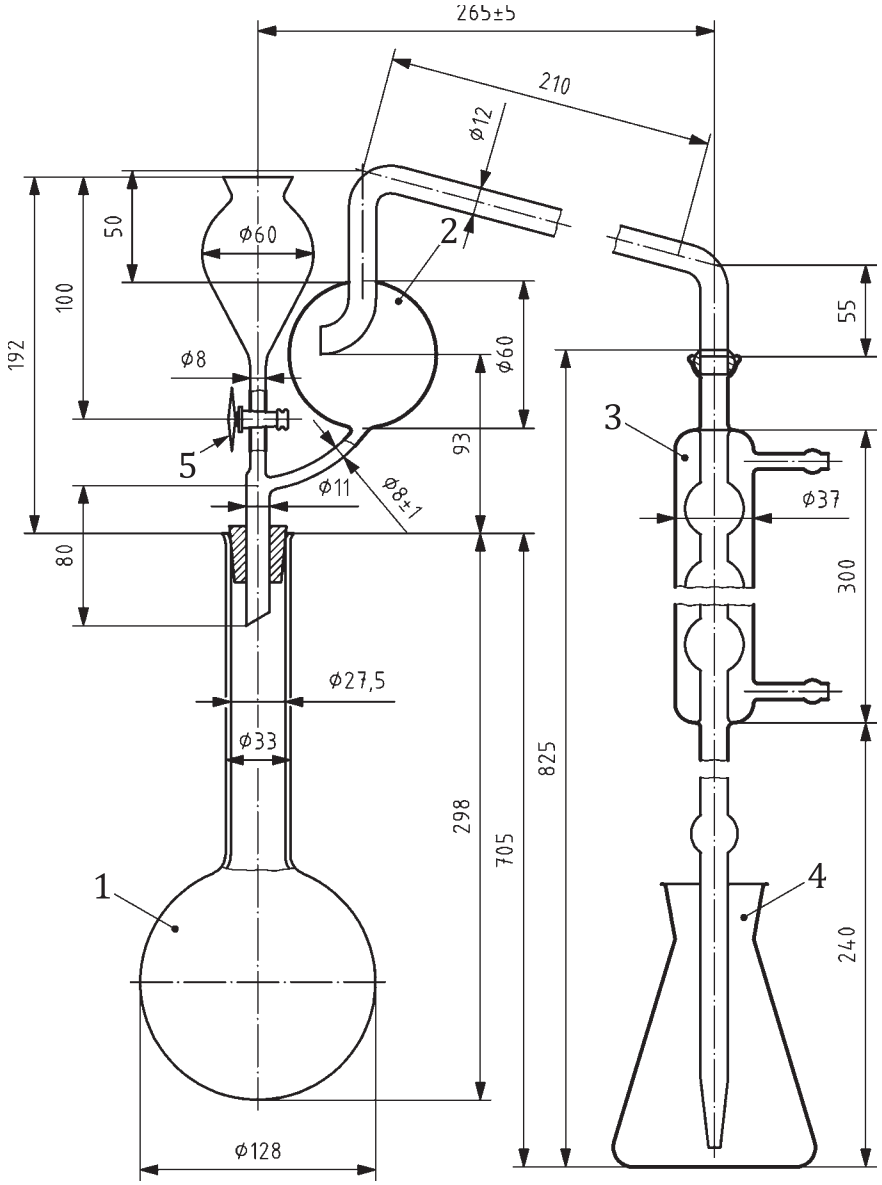
3 elbow tube with a spherical joint (No 18) at the entrance, and a drip cone (the connection to the distillation tube may be effected by means of a rubber tube instead of a spherical joint)

4 six-bulb condenser joined at the issue to a glass extension tube by means of a small rubber connection

5 500 ml flask in which the distillate is collected

Figure 3 — Distillation apparatus 3

Dimensions in millimetres



Key

1 round-bottomed, long-necked flask of 1 000 ml capacity with a bell mouth

2 distillation tube with a splash head and a spherical joint (No 18), at the issue, connected at the side to a funnel with a polytetrafluoroethylene (PTFE) tap (5) for the addition of sodium hydroxide (a suitable rubber bung may be used instead of the spherical joint; the tap may be replaced by a rubber connection with an appropriate clip)

3 six-bulb condenser with a spherical joint (No 18) at the entrance, joined at the issue by a rubber connection, to a glass extension tube (when the connection to the distillation tube is effected by means of a rubber tube, the spherical joint may be replaced by a suitable rubber bung)

4 500 ml flask for the collection of the distillate

5 PTFE tap

Figure 4 — Distillation apparatus 4

6.2 Apparatus for the determination of ammoniacal nitrogen.

According to analytical technique (8.2.5.3). (Refer to Figure 1.)

The apparatus is made up of a specially shaped receptacle with a ground glass neck, with 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 should 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.

6.3 Apparatus for the determination of urea nitrogen.

According to the urease technique (8.2.6.1).

It consists of a 300 ml Erlenmeyer flask, with a separating funnel and a small absorber.

6.4 Rotary shaker, 35 r/min to 40 r/min.

6.5 pH meter.

6.6 Oven, capable of being maintained at a temperature of 130 °C.

6.7 Glassware:

a) pipettes of 2 ml, 5 ml, 10 ml, 20 ml, 25 ml, 50 ml and 100 ml capacity;

b) long-necked Kjeldahl flasks of 300 ml and 500 ml capacity;

c) graduated flasks of 100 ml, 250 ml, 500 ml and 1 000 ml capacity;

d) crucibles of sintered glass, pore diameter, 5 µm to 15 µm;

e) mortars.

7 Sampling and sample preparation

Sampling is not part of the method specified in this International Standard. A recommended sampling method is given in ISO 14820-1.[1]

Sample preparation shall be carried out in accordance with ISO 14820-2.

8 Procedure

8.1 Total soluble and insoluble nitrogen

8.1.1 In the absence of nitrates

8.1.1.1 Digestion

Weigh, to an accuracy of 0,001 g, a quantity of the sample containing 100 mg of nitrogen at the most. Place it in the flask of the distillation apparatus (see 6.1). Add 10 g to 15 g of potassium sulfate (see 5.2), the catalyst (see 5.28), and a few anti-bump granules (see 5.29). Then add 50 ml of diluted sulfuric acid (see 5.8), and mix thoroughly. First, heat gently, mixing from time to time, until foam no longer forms. Then heat in such a way that the liquid boils regularly and keep it boiling for 1 h 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 that the dissolution is as complete as possible. Allow to cool and connect the flask to the distillation apparatus (see 6.1).

8.1.1.2 Distillation of ammonia

Transfer with a precision pipette, into the receiver of the apparatus, 50 ml of a standard solution of sulfuric acid 0,1 mol/l (see 5.9). Add the indicator (see 5.30.3 or 5.30.4). 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 (see 5.10) to make the liquid strongly 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 shall still be clearly alkaline. Adjust the heating of the flask so as to distil 150 ml in 0,5 h. Test with indicator paper (see 5.31) 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 (see 5.31). Then, lower the receiver, distil a few millilitres more and rinse the tip of the condenser. Titrate the excess of acid with a standard solution of potassium or sodium hydroxide 0,2 mol/l (see 5.11) until the indicator changes colour.

8.1.1.3 Blank test

Carry out a blank test (omitting the sample) under the same conditions, and take account of it when calculating the final result.

8.1.1.4 Expression of the result

Express the result as the mass fraction in percent of nitrogen contained in the fertilizer as received for analysis.

$$w_{\mathrm{N}} = \frac{(50 - V) \times 0,28}{m} \tag{1}$$

where

50 is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the blank, carried out by pipetting into the receiver of the apparatus (see 6.1), in millilitre [50 ml of standard solution of sulfuric acid 0,1 mol/l (see 5.9)];

V is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the analysis, in millilitre;

m is the mass of the test sample, in grams.

8.1.2 In the presence of nitrate

8.1.2.1 Test sample

Weigh, to an accuracy of 0,001 g, a quantity of the sample containing not more than 40 mg of nitrate nitrogen.

8.1.2.2 Reduction of the nitrate

Mix the test sample in a small mortar with 50 ml of water. Transfer with the minimum amount of water into a 500 ml Kjeldahl flask. Add 5 g of reduced iron (see 5.3) and 50 ml of stannous chloride solution (see 5.12). Shake and leave it to stand for 0,5 h. During the time it is standing, stir again after 10 min and 20 min.

8.1.2.3 Kjeldahl digestion

Add 30 ml of sulfuric acid (see 5.13), 5 g of potassium sulfate (see 5.2), the prescribed quantity of catalyst (see 5.28), and some anti-bump granules (see 5.29). 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 sulfate suspension. Then, continue heating for 1 h after obtaining a clear solution, maintaining it at simmering point. Leave to cool. Cautiously take the contents of the flask up 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. Make up the volume with water. Mix. Filter through a dry filter into a dry receptacle.

8.1.2.4 Analysis of the solution

Transfer by pipette, into the flask of the distillation apparatus (see 6.1), an aliquot containing 100 mg of nitrogen at the most. Dilute to about 350 ml with water, add a few anti-bump granules (see 5.29), connect the flask to the distillation apparatus, and continue the determination as described in 8.1.1.2.

8.1.2.5 Blank test

See 8.1.1.3.

8.1.2.6 Expression of the result

Express the result as the mass fraction in percent of nitrogen contained in the fertilizer as received for analysis.

$$w_N = \frac{(50 - V) \times 0,28}{m} \quad (2)$$

where

50 is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the blank, carried out by pipetting into the receiver of the apparatus (see 6.1), in millilitre [50 ml of standard solution of sulfuric acid 0,1 mol/l (see 5.9)];

V is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the analysis, in millilitres;

m is the mass of the test sample, in grams, present in the aliquot part taken in 8.1.2.4.

8.2 Forms of soluble nitrogen

In the case of fertilizers not containing cyanamide nitrogen and in the case of fertilizers containing cyanamide nitrogen, 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.

8.2.1 Preparation of the solution to be analysed

8.2.1.1 Test portion

Weigh, to an accuracy of 1 mg, 10 g of the sample and place it in a 500 ml graduated flask.

8.2.1.2 In the case of fertilizers not containing cyanamide nitrogen

Add to the flask 50 ml of water and then 20 ml of diluted hydrochloric acid (see 5.14). Shake and leave it to stand until the evolution of carbon dioxide ceases. Then, add 400 ml of water and shake for 0,5 h on the rotary shaker (see 6.4). Make up to the volume with water, mix and filter through a dry filter into a dry receptacle.

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.

8.2.1.3 In the case of fertilizers containing cyanamide nitrogen

Add to the flask 400 ml of water and a few drops of methyl red (see 5.30.4). If necessary, make the solution acid by using acetic acid (see 5.15). Add 15 ml of acetic acid (see 5.15) in excess. Shake on the rotary shaker (see 6.4) for 2 h. If necessary, reacidify the solution during the operation, using acetic acid (see 5.15). Make up to the volume with water, mix, filter immediately through a dry filter into a dry receptacle, 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.

8.2.2 Total soluble nitrogen

8.2.2.1 In the absence of nitrate

Pipette into a 300 ml Kjeldahl flask, an aliquot of the filtrate (see 8.2.1.2 or 8.2.1.3) containing 100 mg of nitrogen at the most. Add 15 ml of concentrated sulfuric acid (see 5.13), 0,4 g of copper oxide or 1,25 g of copper sulfate (see 5.28), and a few anti-bump granules (see 5.29). 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 (see 5.29). Connect the flask to the distillation apparatus (see 6.1) and continue the determination as described in 8.1.1.2.

8.2.2.2 In the presence of nitrate

Transfer with a precision pipette into a 500 ml Erlenmeyer flask, an aliquot of the filtrate (see 8.2.1.2 or 8.2.1.3) containing not more than 40 mg of nitrate nitrogen. At this stage of the analysis, the total quantity of nitrogen is not important. Add 10 ml of sulfuric acid at 30 % (see 5.16), 5 g of reduced iron (see 5.3), 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 3 h 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 precision pipette into a 300 ml Kjeldahl flask an aliquot containing 100 mg of nitrogen at the most. Add 15 ml of concentrated sulfuric acid (see 5.13), 0,4 g of copper oxide or 1,25 g of copper sulfate (see 5.28), and some anti-bump granules (see 5.29). 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 (see 5.29). Connect the flask to the distillation apparatus (see 6.1) and continue the determination as described in 8.1.1.2.

8.2.2.3 Blank test

See 8.1.1.3.

8.2.2.4 Expression of the result

Express the result as the mass fraction in percent of nitrogen contained in the fertilizer as received for analysis.

$$w_{\mathrm{N}} = \frac{(50 - V) \times 0,28}{m} \tag{3}$$

where

50 is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the blank, carried out by pipetting into the receiver of the apparatus (see 6.1), in millilitres [50 ml of standard solution of sulfuric acid 0,1 mol/l (see 5.9)];

V is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the analysis, in millilitres;

m is the mass of the test sample, in grams, present in the aliquot part taken in 8.2.2.1 or 8.2.2.2.

8.2.3 Total soluble nitrogen with the exception of nitrate nitrogen

8.2.3.1 Determination

Transfer with a precision pipette into a 300 ml Kjeldahl flask, an aliquot of the filtrate (see 8.2.1.2 or 8.2.1.3) containing not more than 50 mg of nitrogen to be determined. Dilute to 100 ml with water, add 5 g of ferrous sulfate (see 5.17), 20 ml of concentrated sulfuric acid (see 5.13), and some anti-bump granules (see 5.29). First, heat gently and then increase the heat until white fumes appear. Continue the digestion for 15 min. Stop the heating, introduce the catalyst (see 5.28), and keep it at a temperature such that white fumes are emitted for a further 10 min to 15 min. After cooling, quantitatively transfer the contents of the Kjeldahl flask into the distillation flask of the apparatus (see 6.1). Dilute to approximately 500 ml with water and add a few anti-bump granules (see 5.29). Connect the flask to the distillation apparatus and continue the determination as described in 8.1.1.2.

8.2.3.2 Blank test

See 8.1.1.3.

8.2.3.3 Expression of the result

Express the result as the mass fraction in percent of nitrogen in the fertilizer as received for analysis.

$$w_N = \frac{(50 - V) \times 0,28}{m} \quad (4)$$

where

50 is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the blank, carried out by pipetting into the receiver of the apparatus (see 6.1), in millilitres [50 ml of standard solution of sulfuric acid 0,1 mol/l (see 5.9)];

V is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the analysis, in millilitres;

m is the mass of the test sample, in grams, present in the aliquot part taken for the determination.

8.2.4 Nitrate nitrogen

8.2.4.1 In the absence of calcium cyanamide

The nitrogen content is determined by calculating the difference between the results obtained in 8.2.2.4 and 8.2.3.3, and/or the result obtained in 8.2.2.4, and the sum of the results obtained in (8.2.5.2 or 8.2.5.5) and (8.2.6.3 or 8.2.6.5 or 8.2.6.6).

8.2.4.2 In the presence of calcium cyanamide

The nitrogen content is determined by calculating the difference between the results obtained in 8.2.2.4 and 8.2.3.3 and between the result obtained in 8.2.2.4 and the sum of the results obtained in (8.2.5.5), (8.2.6.3 or 8.2.6.5 or 8.2.6.6) and (8.2.7).

8.2.5 Ammoniacal nitrogen

8.2.5.1 Solely in the presence of ammoniacal nitrogen and ammoniacal plus nitrate nitrogen

Transfer with a precision pipette into the flask of the distillation apparatus (see 6.1), an aliquot of the filtrate (see 8.2.1.2) 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 (see 5.29) to facilitate boiling. Connect the flask to the distillation apparatus (see 6.1), add 20 ml of sodium hydroxide solution (5.10), and distil and determine as described in 8.1.1.2.

8.2.5.2 Expression of the result

Express the result as the mass fraction in percent of ammoniacal nitrogen contained in the fertilizer as received for analysis.

$$w_{\text{N (ammoniacal)}} = \frac{(50 - V) \times 0,28}{m} \tag{5}$$

where

50 is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the blank, carried out by pipetting into the receiver of the apparatus (see 6.1), in millilitres [50 ml of standard solution of sulfuric acid 0,1 mol/l (see 5.9)];

V is the volume of the standard solution of sodium or potassium hydroxide 0,2 mol/l used for the analysis, in millilitres;

m is the mass of the test sample, in grams, present in the aliquot part taken for the determination.

8.2.5.3 In the presence of urea and/or cyanamide nitrogen

Transfer with a precision pipette, into the dry flask of the apparatus (see 6.2), an aliquot of the filtrate (8.2.1.2 or 8.2.1.3) containing 20 mg of ammoniacal nitrogen at the most. Then, assemble the apparatus. Pipette, into the 300 ml Erlenmeyer flask, 50 ml of the standard sulfuric acid solution 0,05 mol/l (see 5.18) and enough water for the level of the liquid to be approximately 5 cm above the opening of the delivery tube. Introduce, through the side neck of the reaction flask, water so as to make up the volume to about 50 ml. Mix. To avoid foaming during aeration, add a few drops of octyl alcohol (see 5.19). Then, make the solution alkaline by using 50 ml of saturated potassium carbonate solution (see 5.20) and immediately begin to expel the ammonia thus liberated from the cold suspension.

The strong current of air necessary (flow of approximately 3 l per min) shall be purified beforehand by passing it through washing flasks containing dilute sulfuric acid and dilute sodium hydroxide. Instead of using pressurized air, it is also possible to work in a vacuum (water pump) provided that the inflow tube is connected in a sufficiently airtight manner to the receptacle used to recover the ammonia. The elimination of the ammonia is generally complete after 3 h. It is nevertheless wise to make sure of that by changing the receiving flask. When the operation is finished, separate the flask from the apparatus, rinse the tip of the tube and the sides of the flask with a little water. Titrate the excess of acid with a standard solution of sodium or potassium hydroxide 0,1 mol/l (see 5.21) until the indicator (see 5.30.3 or 5.30.4) turns grey.

8.2.5.4 Blank test

See 8.1.1.3.

8.2.5.5 Expression of the result

Express the result as the mass fraction in percent of ammoniacal nitrogen contained in the fertilizer as received for analysis.

$$w_{\text{N (ammoniacal)}} = \frac{(50 - V) \times 0,14}{m} \quad (6)$$

where

50 is the volume of the standard solution of sodium or potassium hydroxide 0,1 mol/l used for the blank, carried out by pipetting into the 300 ml Erlenmeyer flask of the apparatus (see 6.2), in millilitres [50 ml of standard solution of sulfuric acid 0,05 mol/l (see 5.16)];

V is the volume of the standard solution of sodium or potassium hydroxide 0,1 mol/l used for the analysis, in millilitres;

m is the mass of the test sample, in grams, present in the aliquot part taken for the analysis.

8.2.6 Urea nitrogen

8.2.6.1 Urease method

Transfer with a precision pipette, into a 500 ml graduated flask, an aliquot of the filtrate (see 8.2.1.2. or 8.2.1.3) containing not more than 250 mg of urea nitrogen. To precipitate the phosphates, add some saturated barium hydroxide solution (see 5.22) until no further precipitation occurs. Then, eliminate the excess of barium ions (and any dissolved calcium ions) with the aid off the sodium carbonate solution at 10 % (see 5.23).

Leave it to settle and check whether total precipitation has occurred. Make up to the mark, mix and filter through a pleated filter. Pipette 50 ml of the filtrate into the 300 ml Erlenmeyer flask of the apparatus (see 6.3). Acidify the filtrate with hydrochloric acid 2 mol/l (see 5.24) until pH = 3 measured by the pH meter (see 6.5) is obtained. Then raise to pH = 5,4 with sodium or potassium hydroxide 0,1 mol/l (see 5.21).

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 a standard solution of hydrochloric acid 0,1 mol/l (see 5.25). Introduce through the separating funnel 20 ml of urease solution (see 5.26), and leave it to stand for 1 h at 20 °C to 25 °C. Then, pipette 25 ml of the standard solution of hydrochloric acid 0,1 mol/l (see 5.25) 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 protective receptacle into the solution contained in the Erlenmeyer flask. Titrate the excess of acid with the standard solution of sodium hydroxide 0,1 mol/l (see 5.21), until a pH = 5,4 is obtained, measured by the pH-meter.

After precipitation by the solutions of barium hydroxide and sodium carbonate, it should be made up to the mark, filtered and neutralized as rapidly as possible.

NOTE The titration may also be carried out with the indicator (5.30.3), but the end point is then more difficult to observe.

8.2.6.2 Blank test

See 8.1.1.3.

8.2.6.3 Expression of the result

Express the result as the mass fraction in percent of urea nitrogen contained in the fertilizer as received for analysis.

$$w_{\text{N (urea)}} = \frac{(V_1 - V_2) \times 0,14}{m} \tag{7}$$

where

V_1 is the volume of the standard solution of sodium or potassium hydroxide 0,1 mol/l used for the blank, in millilitres;

V_2 is the volume of the standard solution of sodium or potassium hydroxide 0,1 mol/l used for the analysis, in millilitres;

m is the mass of the test sample, in grams, present in the aliquot part taken for the analysis.

8.2.6.4 Gravimetric method with xanthydrol

Transfer with a precision pipette, into a 250 ml beaker, an aliquot of the filtrate (see 8.2.1.2 or 8.2.1.3) containing not more than 20 mg of urea. Add 40 ml of acetic acid (see 5.15). Stir with a glass rod for 1 min, leave any precipitate to settle for 5 min. Filter on a flat bed into a 100 ml beaker, wash with several millilitres of acetic acid (see 5.15), then add to the filtrate drop by drop 10 ml of xanthydrol (see 5.27), stirring continuously with a glass rod. Leave it to settle until the precipitate appears. At that juncture, stir again for 1 min or 2 min. Leave it to stand for 1,5 h. Filter through a glass filtering crucible, which has been previously dried and weighed, pressing it down slightly; wash three times with 5 ml of ethanol (see 5.32) without trying to eliminate all the acetic acid. Place it in the oven. and keep it at a temperature of 130 °C for 1 h (do not go above 145 °C). Leave it to cool in a desiccator and weigh.

8.2.6.5 Expression of the result

Express the result as the mass fraction in percent of urea nitrogen plus biuret contained in the fertilizer as received for analysis.

$$w_{\text{urea N + biuret}} = \frac{6,67 \times m_1}{m_2} \tag{8}$$

where

m_1 is the mass of the precipitate, in grams;

m_2 is the mass of the sample, in grams, present in the aliquot part taken for the determination.

Correct for a blank. Biuret may, generally speaking, be measured with the urea nitrogen without any great error, since its content remains small in absolute value in compound fertilizers.

8.2.6.6 Method by difference

Urea nitrogen may also be calculated according to Table 2.

Table 2 — Calculation of urea nitrogen

Case	Nitrate nitrogen	Ammoniacal nitrogen	Cyanamide nitrogen	Urea nitrogen
1	Absent	Present	Present	(8.2.2.4) - (8.2.5.5 + 8.2.7)
2	Present	Present	Present	(8.2.3.3) - (8.2.5.5 + 8.2.7)
3	Absent	Present	Absent	(8.2.2.4) - (8.2.5.5)
4	Present	Present	Absent	(8.2.3.3) - (8.2.5.5)

8.2.7 Cyanamide nitrogen

Take one aliquot part of the filtrate (see 8.2.1.3), containing 10 mg to 30 mg of cyanamide nitrogen and place it in a 250 ml beaker. Continue the analysis according to EN 15562.

9 Verification of the result

9.1 In certain cases, a difference can be found between the total nitrogen obtained directly from a weighed out sample (see 8.1) and total soluble nitrogen (see 8.2.2). Nevertheless, the difference should not be greater than 0,5 %. If this is not the case, the fertilizer contains forms of insoluble nitrogen not contained in the list in Regulation (EC) No 2003/2003, Annex I.[2]

9.2 Before each analysis, check that the apparatus is working properly and that the correct technique is applied, 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 standard solutions of potassium thiocyanate (see 5.4), potassium nitrate (see 5.5), ammonium sulfate (see 5.6), and urea (see 5.7).

10 Test report

The test report shall contain the following information:

a) all information necessary for the complete identification of the sample;

b) the test method used with reference to this International Standard, i.e. ISO 15604:2016;

c) the results of the determination, expressed as percentage mass fractions of the forms of nitrogen in the fertilizer;

d) the date of sampling and sampling procedure (if known);

e) the date when the analysis was finished;

f) all operating details not specified in this International Standard, or regarded as optional, together with details of any incidents that occurred when performing the method which might have influenced the test result(s).

Bibliography

[1] ISO 14820-1, *Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling*

[2] *Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers*. Official Journal L 304, 21/11/2003 P. 0001-0194, Annex I, Annex IV, method 2.6.1

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