BRITISH STANDARD

BS EN 15561:2009

Fertilizers — Determination of total nitrogen in calcium cyanamide containing nitrates

ICS 65.080

BSI
British Standards

National foreword

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The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Fertilizers - Determination of total nitrogen in calcium cyanamide containing nitrates

Engrais - Dosage de l'azote total dans la cyanamide calcique nitratée

Düngemittel - Bestimmung von Gesamtstickstoff in nitrathaltigem Kalkstickstoff

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Foreword

This document (EN 15561:2009) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.

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1 Scope

This European Standard specifies a method for the determination of total nitrogen in calcium cyanamide.

The method is applicable to calcium cyanamide containing nitrates.

2 Normative references

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

EN 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN 12944-1:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 1: General terms*

EN 12944-2:1999, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 2: Terms relating to fertilizers*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1:1999 and EN 12944-2:1999 apply.

4 Principle

Reduction of nitrate nitrogen to ammonia with metallic iron and stannous chloride solution. Digestion in sulfuric acid. Distillation of the ammonia from an alkaline solution, absorption in an excess of standard sulfuric acid solution and back-titration with standard sodium or potassium hydroxide solution.

5 Reagents

5.1 General

Use only reagents of recognized analytical grade and distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds (grade 3 according to EN ISO 3696:1995).

5.2 Sulfuric acid, ρ = 1,84 g/ml.

5.3 Powdered iron, reduced in hydrogen.

5.4 Potassium sulfate, p.a., finely pulverized.

5.5 Sulfuric acid (for variant a), c = 0,05 mol/l.

5.6 Sodium or potassium hydroxide standard solution (for variant a), carbonate free, c = 0,1 mol/l.

5.7 Sulfuric acid (for variant b, see NOTE in 8.2), c = 0,1 mol/l.

5.8 Sodium or potassium hydroxide standard solution (for variant b, see NOTE in 8.2), carbonate free, c = 0,2 mol/l.

5.9 Sulfuric acid (for variant c, see NOTE in 8.2), c = 0,25 mol/l.

5.10 Sodium or potassium hydroxide standard solution (for variant c, see NOTE in 8.2), carbonate free, c = 0,5 mol/l.

5.11 Indicator solutions

5.11.1 Mixed indicator

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

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

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.

5.11.2 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 may be used (4 to 5 drops) instead of that specified in 5.11.1.

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 completely clear and prepared immediately before use.

It is essential to check the reducing power of the 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 = 0,1 mol/l iodine solution (I_2) should be used.

5.13 Sodium hydroxide solution, containing about 30 % NaOH (ρ = 1,33 g/ml), ammonia free.

5.14 Standard nitrate-ammoniacal solution

Weigh 2,5 g of potassium nitrate and 10,16 g of ammonium sulfate and place them in a 250 ml graduated flask. Dissolve in water and make up to 250 ml. 1 ml of this solution contains 0,01 g of nitrogen.

5.15 Anti-bump granules of pumice stone, washed in hydrochloric acid and calcined.

6 Apparatus

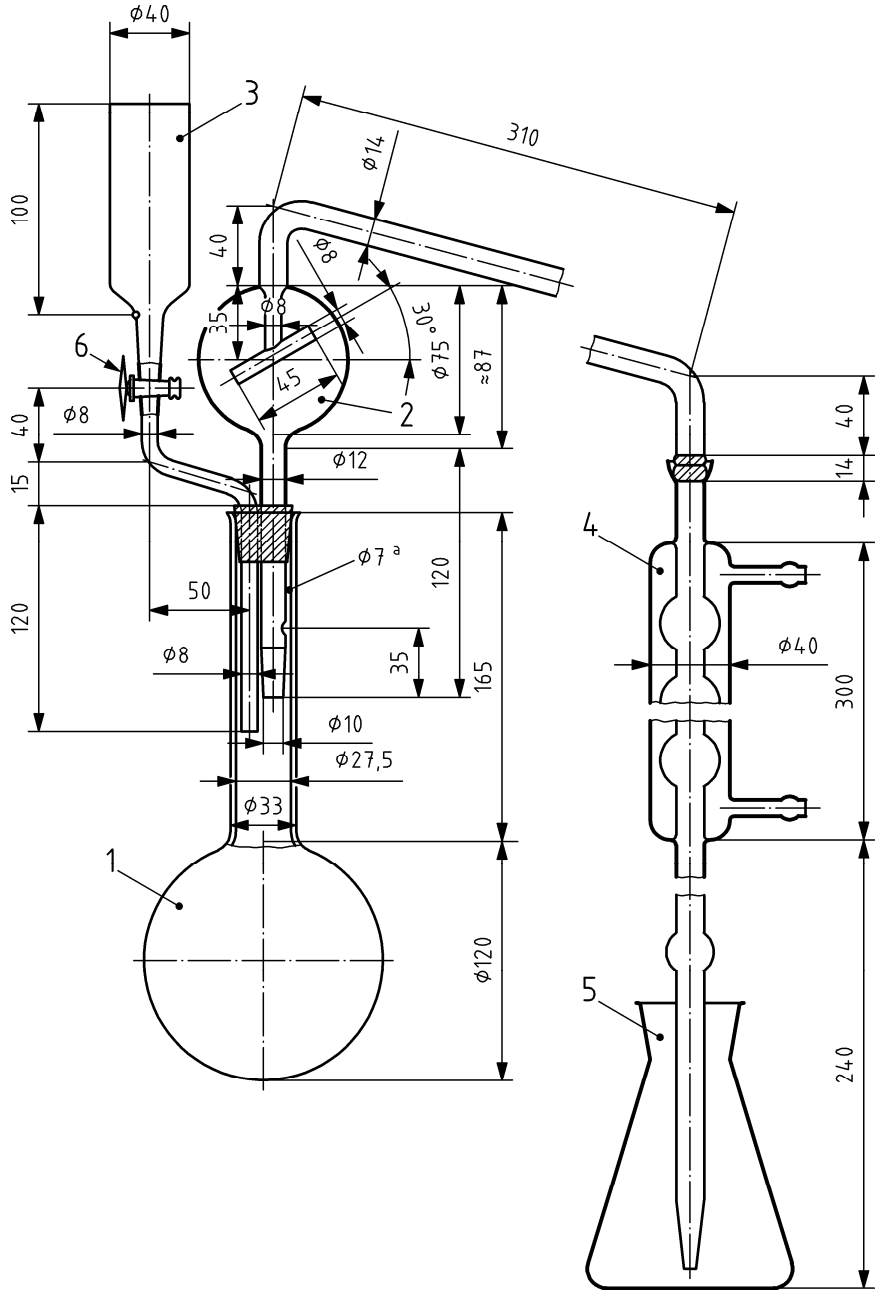
6.1 Distillation apparatus

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.

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

Dimensions in millimetres

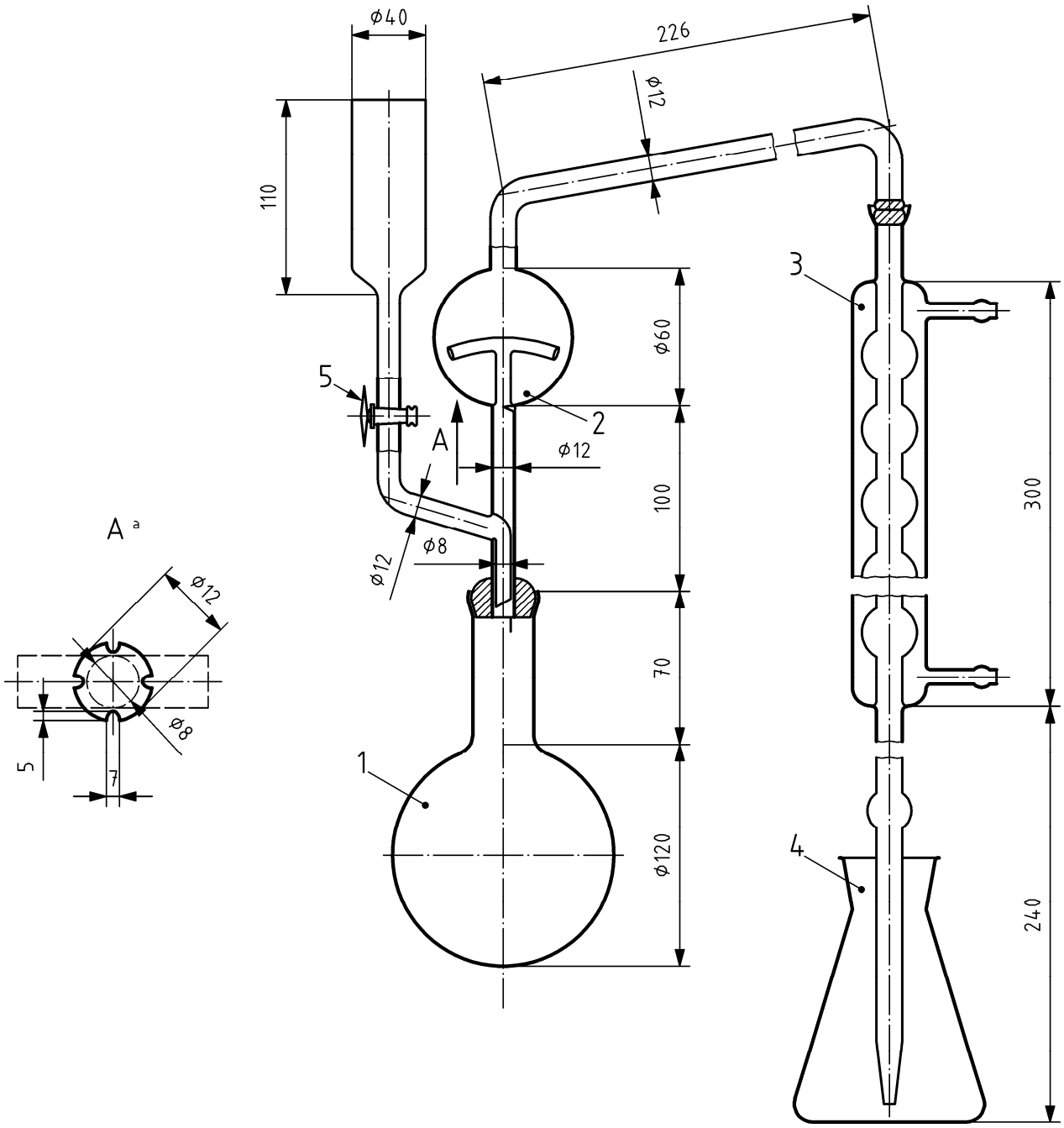


Key

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

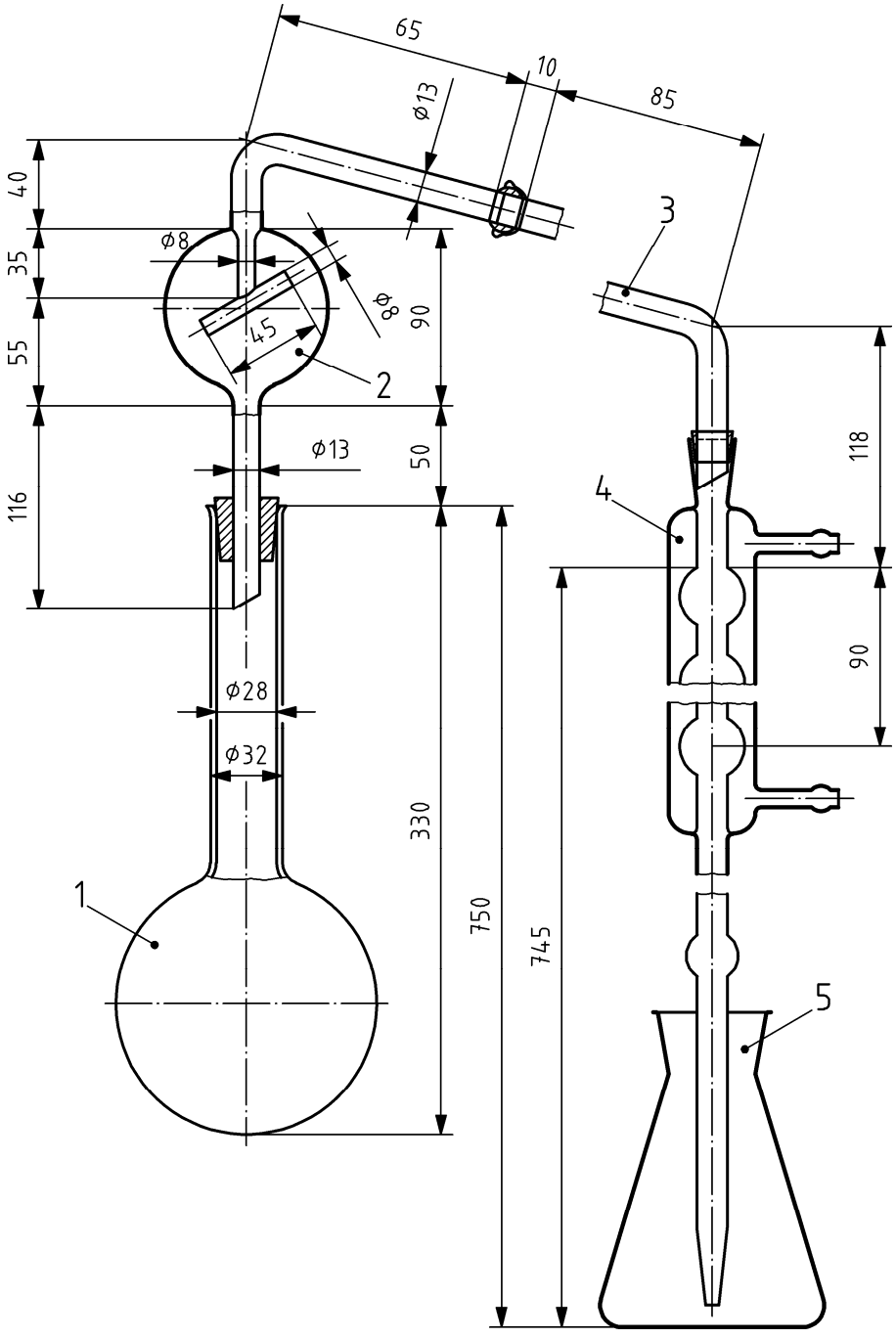


Key

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 description

Figure 2 — Distillation apparatus 2

Dimensions in millimetres

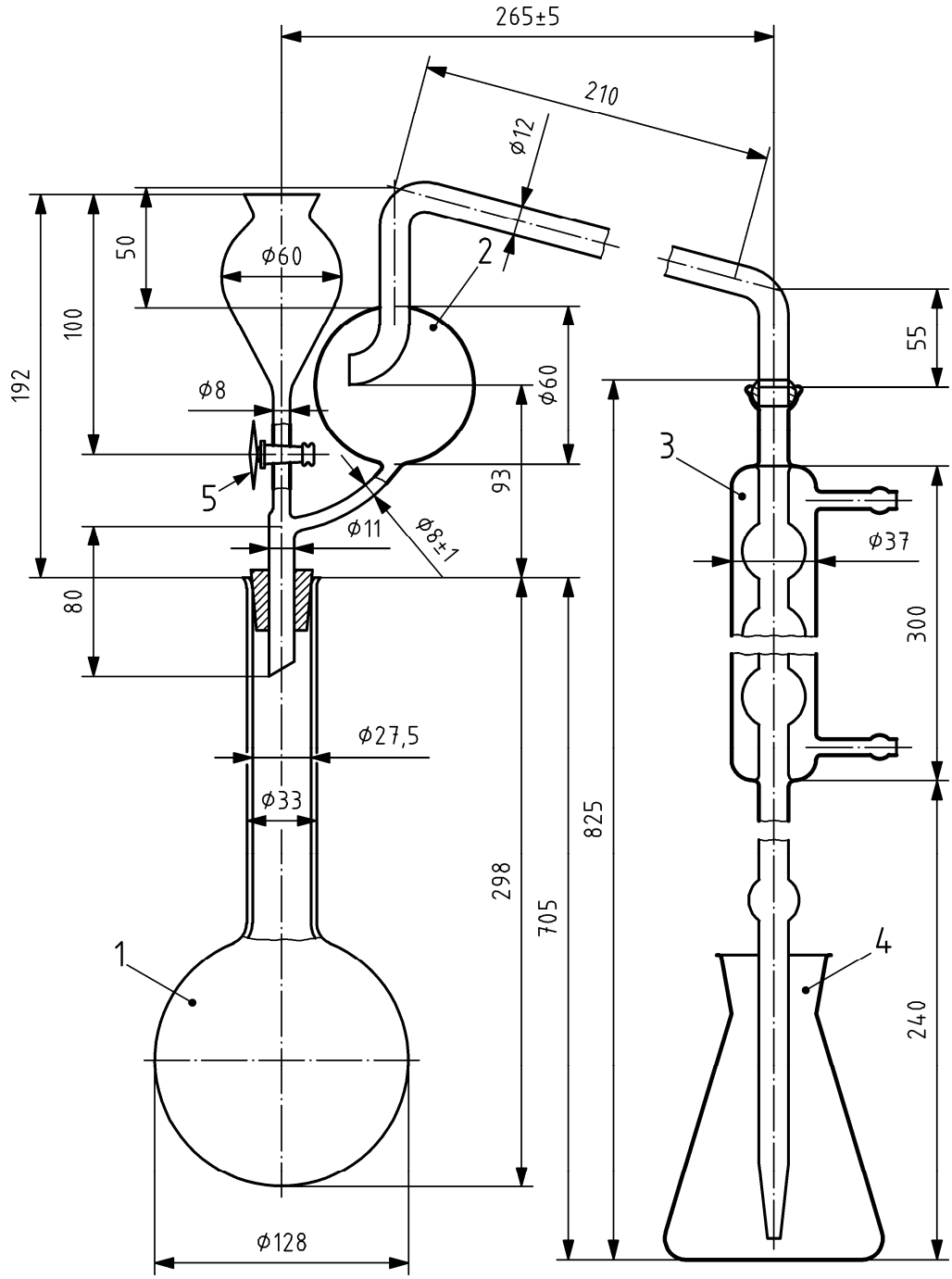


Key

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 Kjeldahl flask, long necked and of suitable capacity.

6.3 Pipettes, of capacity 50 ml, 100 ml and 200 ml.

6.4 Graduated flask, of capacity 250 ml.

7 Sampling and sample preparation

Sampling is not part of the method specified in this Technical Specification. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2.

8 Procedure

8.1 Preparation of the solution

Weigh, to the nearest 0,001 g, 1 g of the sample and place it in the Kjeldahl flask. Add 0,5 g of powdered iron (5.3) and 50 ml of the stannous chloride solution (5.12), stir and leave standing for 0,5 h. During the time it is left standing, stir again after 10 min and 20 min. Then add 10 g of potassium sulfate (5.4) and 30 ml of sulfuric acid (5.2). Bring to the boil and maintain boiling for 1 h after the appearance of white fumes. Leave to cool and dilute with 100 ml to 150 ml of water. Transfer the suspension quantitatively into a 250 ml graduated flask, cool and make up the volume with water, stir and filter through a dry filter into a dry container. Instead of then siphoning off the suspension in order to apply the variant a, b or c, the ammoniacal nitrogen in this solution may also be distilled directly, after adding sufficient sodium hydroxide to ensure a large surplus (5.13).

8.2 Analysis of the solution

According to the variant chosen, place in the receiving flask a measured quantity of standard sulfuric acid as indicated in Table 1, Table 2 or Table 3. Add the appropriate quantity of the chosen indicator solution (5.11.1 or 5.11.2) and, if necessary, water in order to obtain a volume of at least 50 ml. The end of the extension tube of the condenser shall be below the surface of the solution.

With a pipette, transfer, according to the variant chosen, 50 ml, 100 ml or 200 ml of the solution obtained as described in 8.1, and distil the ammonia as described below, adding sufficient NaOH solution (5.13) to ensure a considerable excess. Add water in order to obtain a total volume of about 350 ml, and several grains of pumice in order to control the boiling.

Assemble the distillation apparatus and, taking care to avoid any loss of ammonia, add to the contents of the distillation flask 10 ml of concentrated sodium hydroxide solution (5.13). Gradually warm the flask, to avoid boiling vigorously. When boiling commences, distil at the rate of about 100 ml in 10 min to 15 min; the total volume of distillate should be about 250 ml. The condenser shall be regulated so that a continuous flow of condensate is ensured. The distillation should be completed in 30 min to 40 min. When no more ammonia is likely to be evolved, lower the receiving flask so that the tip of the condenser extension is above the surface of the liquid.

Test the subsequent distillate by means of an appropriate reagent to ensure that all the ammonia is completely distilled. Wash the condenser extension with a little water and titrate the surplus acid with the standard solution of sodium or potassium hydroxide prescribed for the variant adopted (see NOTE).

NOTE Standard solutions of different strengths may be used for the back titration provided that the volumes used for the titration do not, as far as possible, exceed 45 ml.

Table 1 — Weighing, dilution and calculation variant a

Declaration % *N*	Amount to be weighed g	Dilution ml	Solution of sample to be distilled ml	Expression of the result [a] % *N* = (50 – *A*) *F*
0 to 5	10	500	50	$(50 - A) \times 0{,}14$
5 to 10	10	500	25	$(50 - A) \times 0{,}28$
10 to 15	7	500	25	$(50 - A) \times 0{,}40$
15 to 20	5	500	25	$(50 - A) \times 0{,}56$
20 to 40	7	500	10	$(50 - A) \times 1{,}00$
Approximate maximum quantity of nitrogen to be distilled: 50 mg. Sulfuric acid 0,05 mol/l to be placed in the receiving flask: 50 ml. Back titration with NaOH or KOH 0,1 mol/l.				
a For the purposes of the equation for expression of the result: — 50 = volume of standard solution of sulfuric acid to be placed in the receiving flask, in millilitres; — *A* = volume of sodium or potassium hydroxide used for the back titration, in millilitres; — *F* = factor comprising the amount weighed, the dilution, the aliquot part of solution of the sample to be distilled and the volumetric equivalent.				

Table 2 — Weighing, dilution and calculation variant b

Declaration % *N*	Amount to be weighed g	Dilution ml	Solution of sample to be distilled ml	Expression of the result [a] (% *N* = (50 – *A*) *F*)
0 to 5	10	500	100	$(50 - A) \times 0{,}14$
5 to 10	10	500	50	$(50 - A) \times 0{,}28$
10 to 15	7	500	50	$(50 - A) \times 0{,}40$
15 to 20	5	500	50	$(50 - A) \times 0{,}56$
20 to 40	7	500	20	$(50 - A) \times 1{,}00$
Approximate maximum quantity of nitrogen to be distilled: 100 mg. Sulfuric acid 0,1 mol/l to be placed in the receiving flask: 50 ml. Back titration with NaOH or KOH 0,2 mol/l.				
a For the purposes of the equation for expression of the result: — 50 = volume of standard solution of sulfuric acid to be placed in the receiving flask, in millilitres; — *A* = volume of sodium or potassium hydroxide used for the back titration, in millilitres; — *F* = factor comprising the amount weighed, the dilution, the aliquot part of solution of the sample to be distilled and the volumetric equivalent.				

Table 3 — Weighing, dilution and calculation variant c

Declaration % *N*	Amount to be weighed g	Dilution ml	Solution of sample to be distilled ml	Expression of the result [a] % *N* = (35 – *A*) *F*
0 to 5	10	500	200	$(35 - A) \times 0{,}175$
5 to 10	10	500	100	$(35 - A) \times 0{,}350$
10 to 15	7	500	100	$(35 - A) \times 0{,}500$
15 to 20	5	500	100	$(35 - A) \times 0{,}700$
20 to 40	5	500	50	$(35 - A) \times 1{,}400$
Approximate maximum quantity of nitrogen to be distilled: 200 mg. Sulfuric acid 0,25 mol/l to be placed in the receiving flask: 35 ml. Back titration with NaOH or KOH 0,5 mol/l.				
a For the purposes of the equation for expression of the result: — 35 = volume of standard solution of sulfuric acid to be placed in the receiving flask, in millilitres; — *A* = volume of sodium or potassium hydroxide used for the back titration, in millilitres; — *F* = factor comprising the amount weighed, the dilution, the aliquot part of solution of the sample to be distilled and the volumetric equivalent.				

8.3 Blank

Carry out a blank test (omitting the sample) under the same conditions and refer to this in the calculation of the final result.

8.4 Control test

Before carrying out the analysis, check that the apparatus is working properly and that the correct technique is applied with a standard solution containing quantities of ammoniacal and nitrate nitrogen comparable to the quantities of cyanamide and nitrate nitrogen contained in nitrated calcium cyanamide.

For this purpose place 20 ml of the standard solution (5.14) in the Kjeldahl flask.

Carry out the analysis according to the method described in 8.1 and 8.2.

9 Calculation and expression of the result

Calculate the *N* content as a percentage mass fraction of the fertilizer as received for analysis according to Table 1 for variant a, Table 2 for variant b and Table 3 for variant c.

10 Test report

The test report shall contain at least the following information:

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

b) test method used with reference to this European Standard, i.e. EN 15561;

c) test results obtained expressed as percentage mass fraction of total nitrogen in the fertilizer;

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

e) date when the analysis was finished;

f) all operating details not specified in this document, 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] EN 1482-1, 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 IV, method 2.3.2

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