BRITISH STANDARD

BS EN 15475:2009

Fertilizers — Determination of ammoniacal nitrogen

ICS 65.080

British Standards

National foreword

This British Standard is the UK implementation of EN 15475:2009. It supersedes DD CEN/TS 15475:2006 which is withdrawn.

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 ammoniacal nitrogen

Engrais - Détermination de l'azote ammoniacal

Düngemittel - Bestimmung von Ammoniumstickstoff

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Foreword

This document (EN 15475:2009) 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of an identical text or by endorsement, at the latest by July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.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 the ammoniacal nitrogen content in fertilizers. The method is applicable to all nitrogenous fertilizers including compound fertilizers, in which nitrogen is found exclusively either in the form of ammonium salts or ammonium salts together with nitrates.

This European Standard is not applicable to fertilizers containing urea, cyanamide or other organic nitrogenous compounds.

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

Displacement of ammonia by means of an excess of sodium hydroxide, distillation and determining the yield of ammonia in a given volume of a standard sulfuric acid and titration of the excess acid by means of a standard solution of sodium or potassium hydroxide.

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 Diluted hydrochloric acid, mix one volume of ρ(HCl) = 1,18 g/ml with one volume of water.

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

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

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

5.6 Sodium or potassium hydroxide solution (for variant b, see NOTE in 8.2),

carbonate free, c = 0,2 mol/l.

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

5.8 Sodium or potassium hydroxide solution (for variant c, see NOTE in 8.2),

carbonate free, c = 0,5 mol/l.

5.9 Sodium hydroxide, 30 %, of approximately ρ(NaOH) = 1,33 g/ml, ammonia free.

5.10 Indicator solutions

5.10.1 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 A with two volumes of 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.

5.10.2 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 the preceding one. This indicator is red in acid solution and yellow in alkaline solution.

5.11 Anti-bump granules (i. e. pumice stone, glass pearls), washed in hydrochloric acid and calcined.

5.12 Ammonium sulfate, p. a.

6 Apparatus

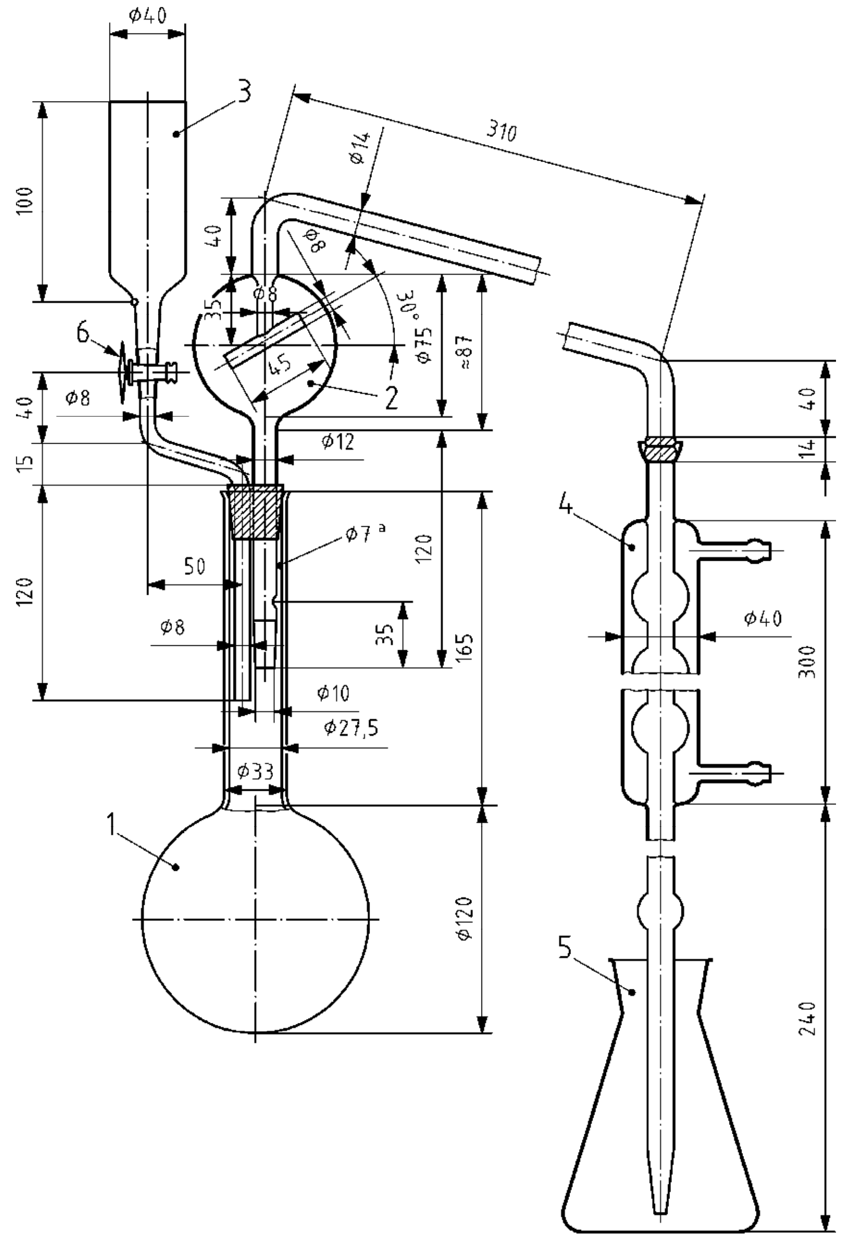
6.1 Distillation apparatus

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

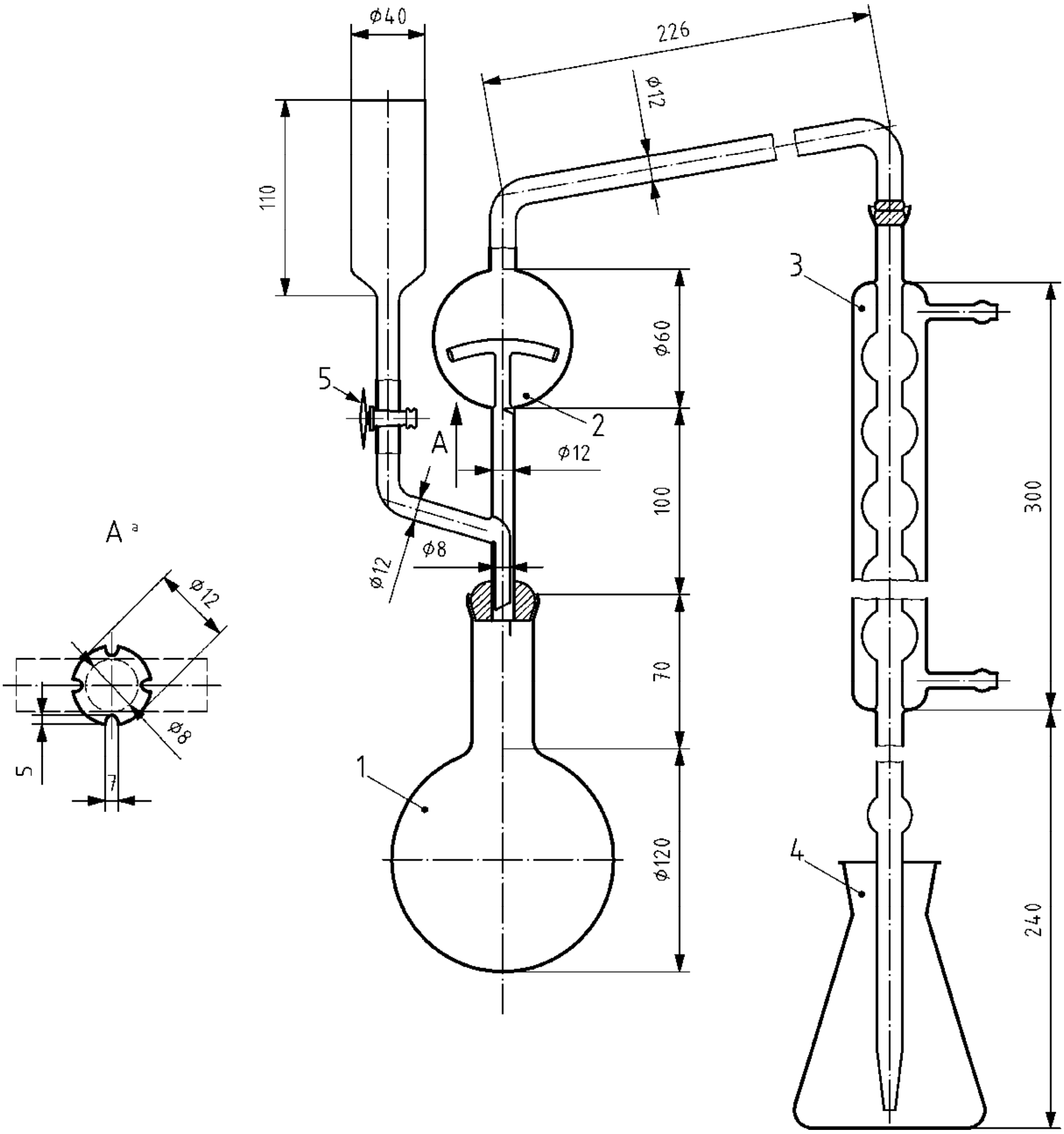
4 six-bulb condenser with spherical joint (No 18) at the entrance, and joined at the issue to a glass extension tube by means of a small rubber connection (when the connection to the distillation tube is effected by means of a rubber tube, the spherical joint may be replaced by a suitable rubber bung)

5 500-ml-flask in which the distillate is collected

6 PTFE-tap (the tap may likewise be replaced by a rubber connection with a clip)

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

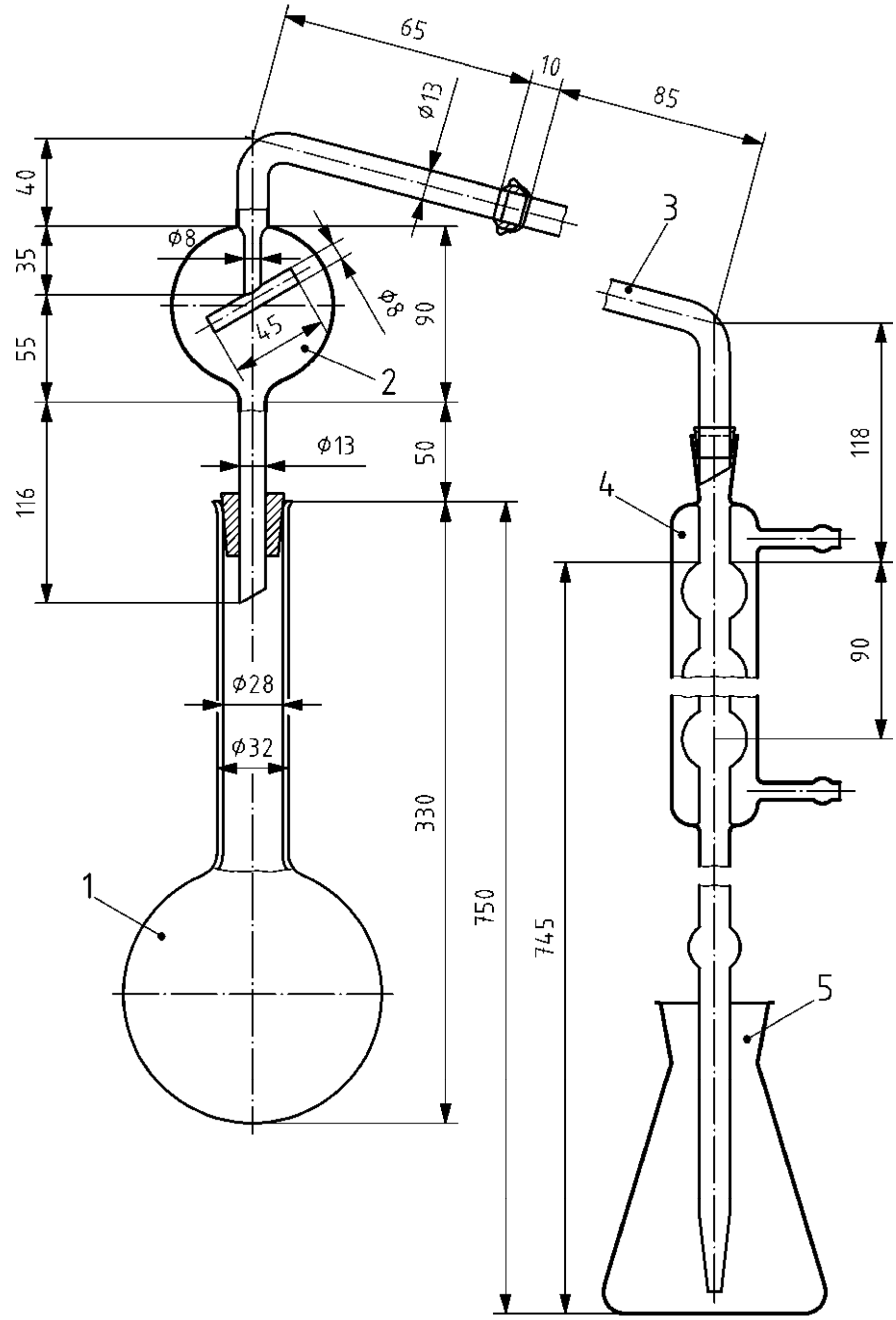
4 500-ml-flask in which the distillate is collected

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

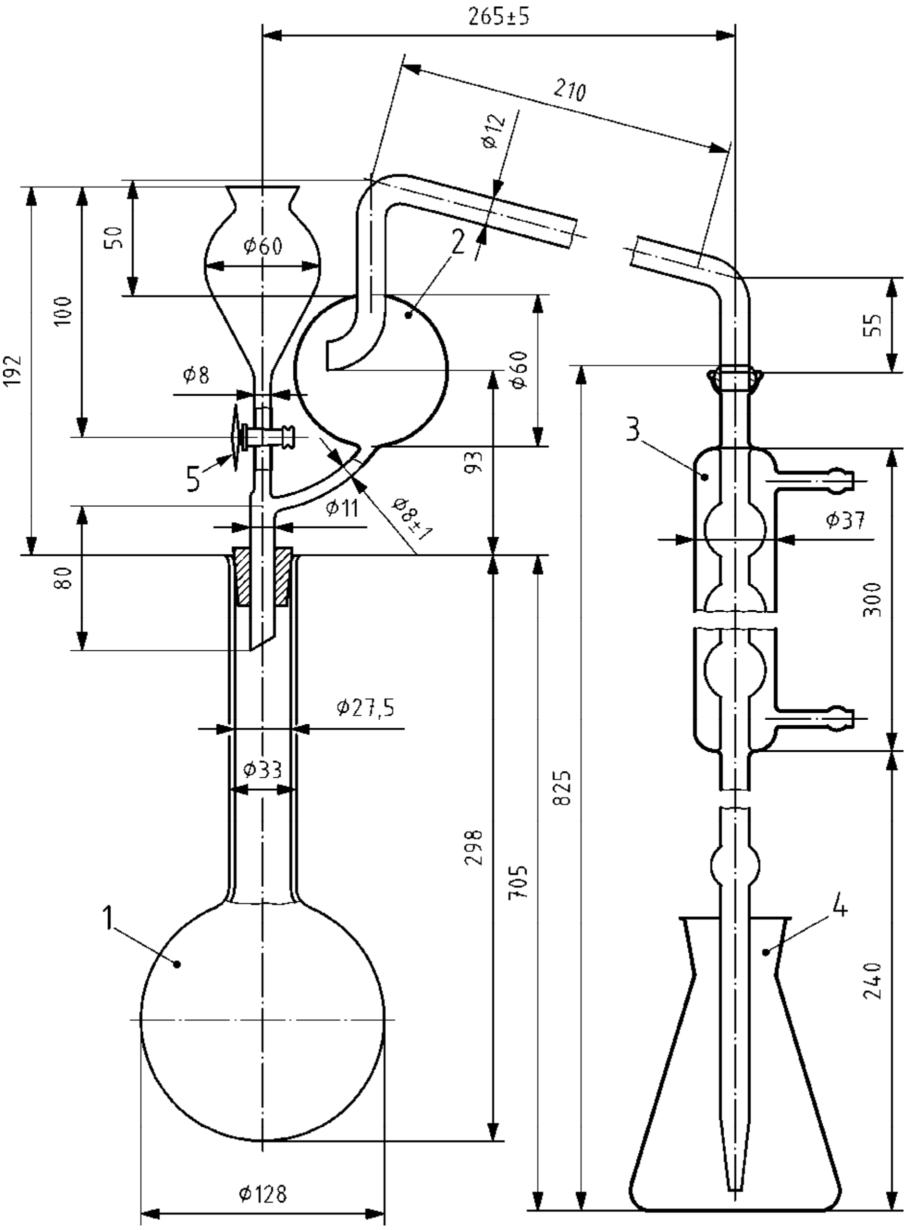
3 elbow tube with a spherical joint (No 18) at the entrance, and a drip cone (the connection to the distillation tube may be effected by means of a rubber tube instead of a spherical joint)

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 Pipettes, capacity of 10 ml, 20 ml, 25 ml, 50 ml, 100 ml and 200 ml.

6.3 Graduated flasks, capacity 500 ml.

6.4 Rotary shaker, 35 to 40 revolutions per minute.

7 Sampling and sample preparation

Sampling is not part of the method specified in this document. 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

According to Table 1, Table 2 or Table 3, depending on the variant chosen, weigh to the nearest 0,001 g a quantity of 5 g, 7 g, or 10 g of the prepared sample and transfer it into a 500-ml flask.

Add 50 ml of water and then 20 ml of hydrochloric acid (5.2). Shake. Leave undisturbed until the evolution of carbon dioxide has ceased. Add 200 ml of water and shake for half an hour with the rotary shaker (6.4). Filter through a filter into a 500-ml graduated flask and make up to the volume with water.

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 (5.10.1 or 5.10.2) 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.

Transfer by precision pipette, according to the details given in Table 1, an aliquot portion of the clear solution, into the distillation flask of the apparatus. 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 (5.9) or 20 ml of the sodium hydroxide solution (5.9) in the cases where one has used 20 ml hydrochloric acid (5.2) in order to dissolve the test sample. Gradually warm the flask; avoid boiling vigorously. When boiling commences, distil at a 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 40 ml to 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 *c*=0,1 mol/l.

[a] For the purposes of the formula for expression of the result:

- 50 = millilitres of standard solution of sulfuric acid to be placed in the receiving flask;
- *A* = millilitres of sodium or potassium hydroxide used for the back titration;
- *F* = factor comprising the amount weighed, the dilution, the aliquot part of solution of the sample to be distilled and the volumetric equivalent;
- *N* = percentage mass fraction of nitrogen.

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 *c*=0,2 mol/l.

[a] For the purposes of the formula for expression of the result:

- 50 = millilitres of standard solution of sulfuric acid to be placed in the receiving flask;
- *A* = millilitres of sodium or potassium hydroxide used for the back titration;
- *F* = factor comprising the amount weighed, the dilution, the aliquot part of solution of the sample to be distilled and the volumetric equivalent;
- *N* = percentage mass fraction of nitrogen.

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 formula for expression of the result:

- 35 = millilitres of standard solution of sulfuric acid to be placed in the receiving flask;
- A = millilitres of sodium or potassium hydroxide used for the back titration;
- F = factor comprising the amount weighed, the dilution, the aliquot part of solution of the sample to be distilled and the volumetric equivalent. expressed as percentage of ammoniacal nitrogen in the fertilizer;
- N = percentage mass fraction of nitrogen.

8.3 Blank

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

8.4 Control test

Before carrying out analyses, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a freshly prepared solution of ammonium sulfate (5.12) containing the maximum quantity of nitrogen prescribed for the chosen variant.

9 Calculation and expression of the result

Express the result of the analysis as the percentage of ammoniacal nitrogen in the fertilizer as received for analysis. Calculation shall be performed in accordance with Table 1 (variant a), Table 2 (variant b) or Table 3 (variant c).

10 Precision

10.1 Inter-laboratory test

An inter-laboratory test was carried out in 2004 with 24, respectively 22 participating laboratories and five different samples of fertilizers and phosphate types. This test yielded the data given in Annex A. Repeatability and reproducibility were calculated according to ISO 5725-1.

The values derived from this inter-laboratory test might not be applicable to concentration ranges and matrices other than those given in Annex A.

10.2 Repeatability

The absolute difference between two independent single test results, obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will in not more than 5 % of the cases exceed the values of *r* given in Table 4.

10.3 Reproducibility

The absolute difference between two single test results, obtained with the same method on identical test material in different laboratories by different operators using different equipment, will in not more than 5 % of the cases exceed the values of *R* given in Table 4.

Table 4 — Mean values, repeatability and reproducibility limits

Sample	$\bar{x}$ %	***r*** %	***R*** %
Ammonium nitrate 33,5 % (AN 33,5)	16,67	0,13	0,63
Calcium ammonium nitrate 27 % (CAN 27)	13,53	0,14	0,39
NPK1 (14-8-24+8S)	8,38	0,09	0,34
NPK2 (16-16-8+4S)	10,02	0,08	0,45
Di-ammonium phosphate (DAP)	17,64	0,10	0,65

11 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 document;

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

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

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

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

Annex A
(informative)

Results of the inter-laboratory tests

The precision of the method was established in 2004 by Working Group 7 “Chemical analysis” of CEN/TC 260 “Fertilizers and liming materials” in an inter-laboratory test evaluated in accordance with ISO 5725-1. The statistical results are given in Table A.1.

Table A.1 — Statistical results of the inter-laboratory test

Parameter	**Sample**				
	AN 33.5	CAN 27	NPK1 (14-8-24+8S)	NPK2 (16-16-8+4S)	DAP
Number of participating laboratories	22	24	24	24	24
Number of laboratories after elimination of outliers (accepted test results)	18	24	23	21	21
Mean value $\bar{x}$ (%)	16,67	13,53	8,38	10,02	17,64
Repeatability standard deviation s_r (%)	0,05	0,05	0,03	0,03	0,04
RSD_r (%)	0,29	0,36	0,38	0,28	0,20
Repeatability limit r (%)	0,13	0,14	0,09	0,08	0,10
Reproducibility standard deviation s_R (%)	0,23	0,14	0,12	0,16	0,23
RSD_R (%)	1,36	1,02	1,43	1,59	1,31
Reproducibility limit R (%)	0,63	0,39	0,34	0,45	0,65

Bibliography

[1] EN 1482-1, Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling

[2] ISO 5725-1, Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions

[3] 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 2.1

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