BRITISH STANDARD

BS EN 15559:2009

Fertilizers — Determination of nitric and ammoniacal nitrogen according to Arnd

ICS 65.080

BSI
British Standards

National foreword

This British Standard is the UK implementation of EN 15559:2009. It supersedes DD CEN/TS 15559:2007 which is withdrawn.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 nitric and ammoniacal nitrogen according to Arnd

Engrais - Dosage de l'azote nitrique et ammoniacal selon Arnd

Düngemittel - Bestimmung von Nitrat- und Ammoniumstickstoff nach Arnd

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Foreword

This document (EN 15559:2009) 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of an identical text or by endorsement, at the latest by July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.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 nitric and ammoniacal nitrogen with reduction according to Arnd (modified for each of the variants a, b and c).

The method is applicable to all nitrogenous fertilizers, including compound fertilizers, in which nitrogen is found exclusively in nitrate form, or in ammoniacal and nitrate form.

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 nitrates and nitrites to ammonia in a neutral aqueous solution by means of a metallic alloy composed of 60 % Cu and 40 % Mg (Arnd's alloy) in the presence of magnesium chloride.

Distillation of the ammonia and determination of the yield in a known volume of standard sulfuric acid solution. 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 concentrated hydrochloric acid solution, 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 NOTES in 8.2), c = 0,1 mol/l.

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

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

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

5.9 Sodium hydroxide solution, approximately c = 2 mol/l.

5.10 Arnd's alloy, powdered so as to pass through a sieve with apertures less than 1 mm square.

5.11 Magnesium chloride solution, ρ = 20 %.

Dissolve 200 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) in approximately 600 ml to 700 ml of water in a 1 l flat-bottomed flask. To prevent frothing, add 15 g of magnesium sulfate ($MgSO_4.7H_2O$).

After dissolution add 2 g of magnesium oxide and a few anti-bump granules of pumice stone and concentrate the suspension to 200 ml by boiling, thus expelling any trace of ammonia from the reagents. Cool, make up the volume to 1 l and filter.

5.12 Indicator solutions

5.12.1 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.

5.12.2 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 5.12.1.

5.12.3 Congo red indicator solution

Dissolve 3 g of Congo red in 1 l of warm water and filter if necessary after cooling. This indicator may be used, instead of that specified in 5.12.1.or 5.12.2, in the neutralization of acid extracts before distillation, using 0,5 ml per 100 ml of liquid to be neutralized.

5.13 Anti-bump granules, for example pumice stone, washed in hydrochloric acid and reclaimed.

5.14 Sodium nitrate, p.a.

6 Apparatus

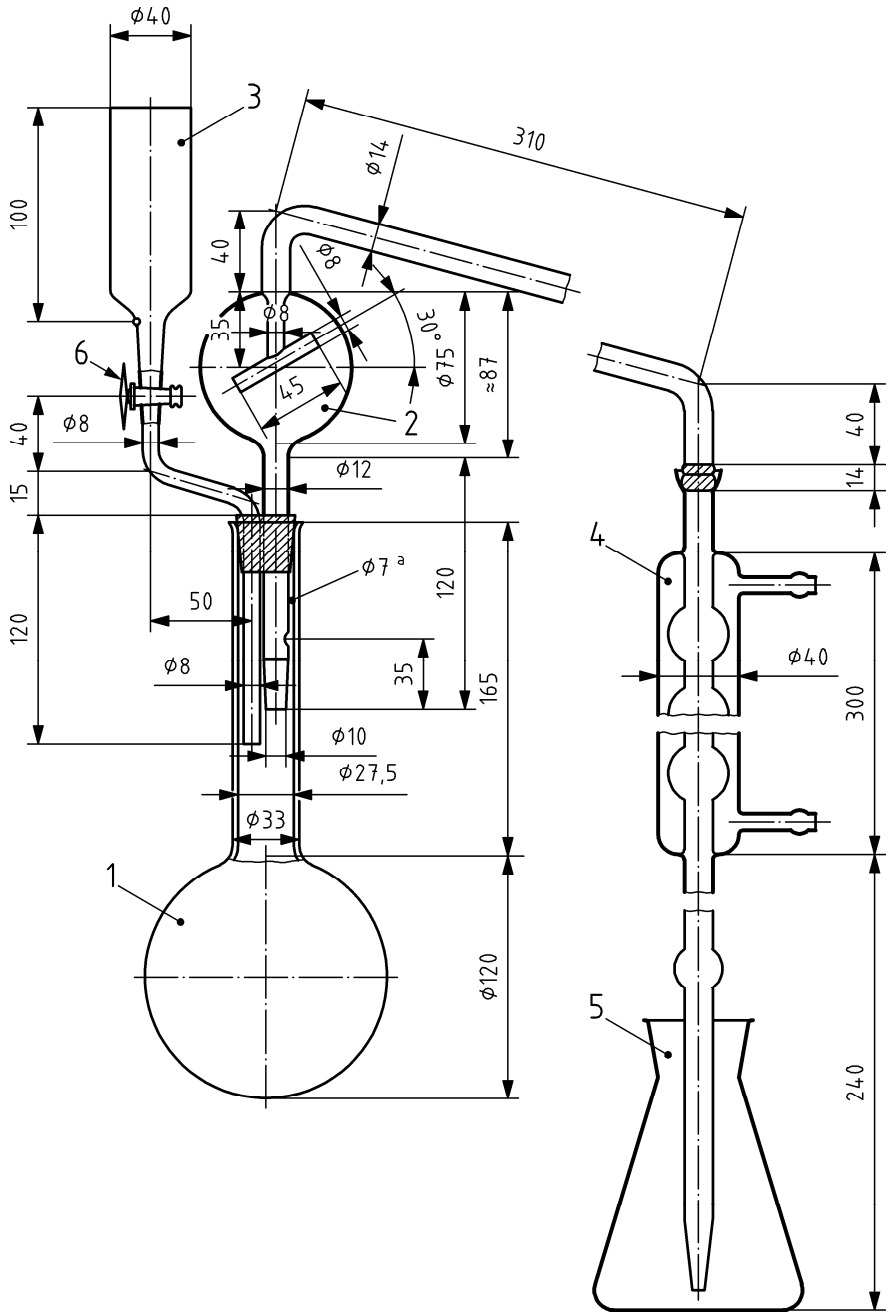
6.1 Distillation apparatus

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

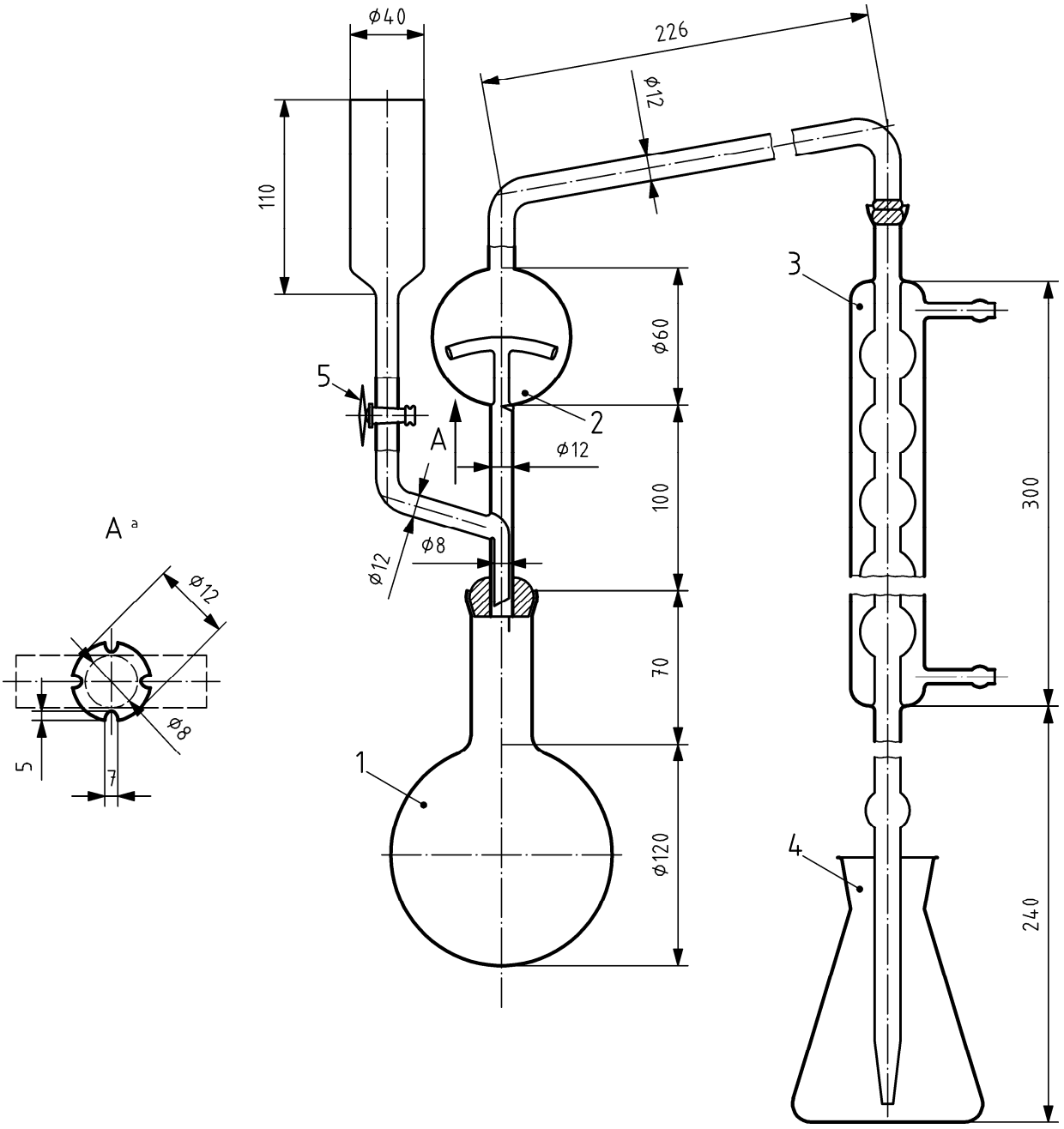


Key

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 (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

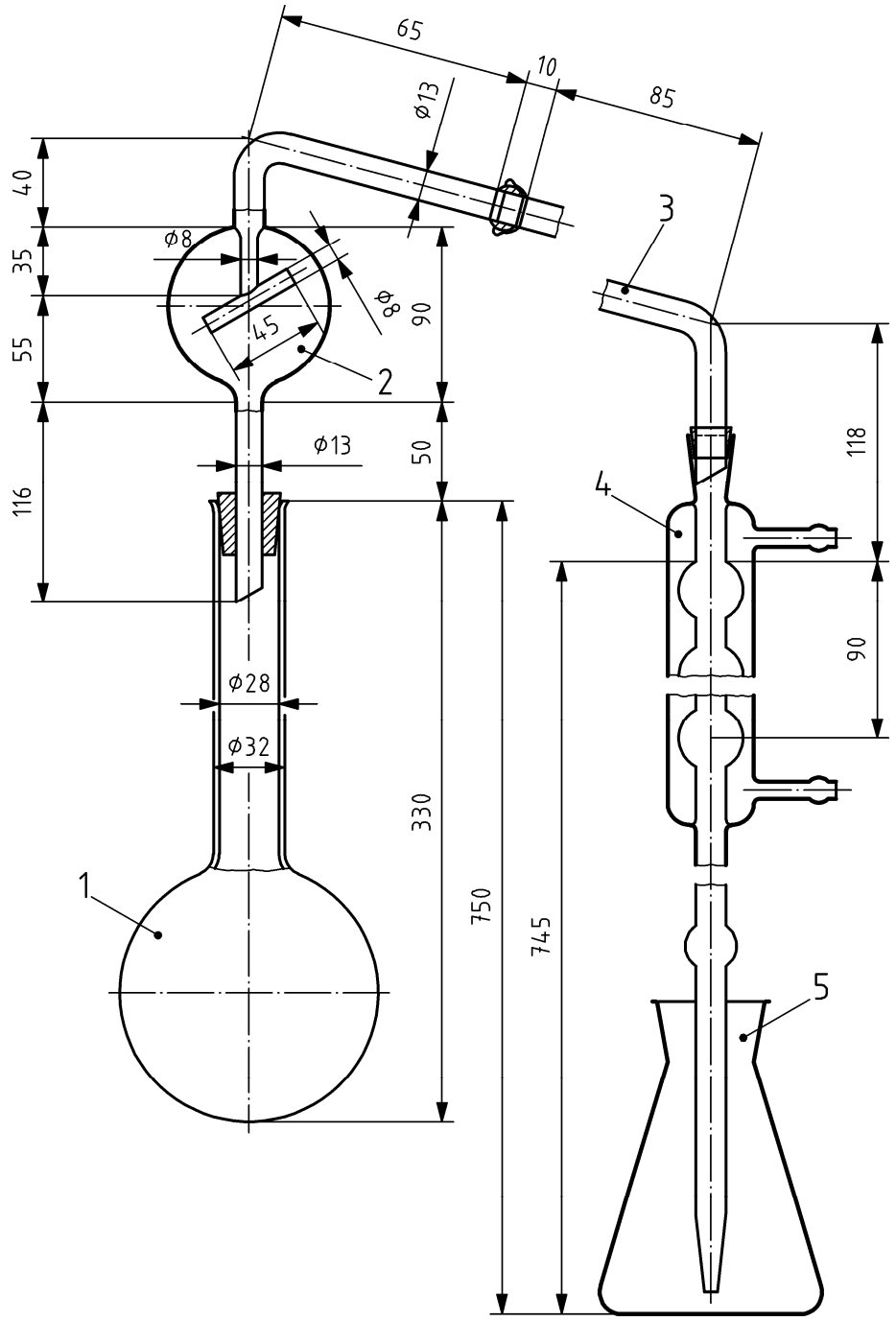


Key

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

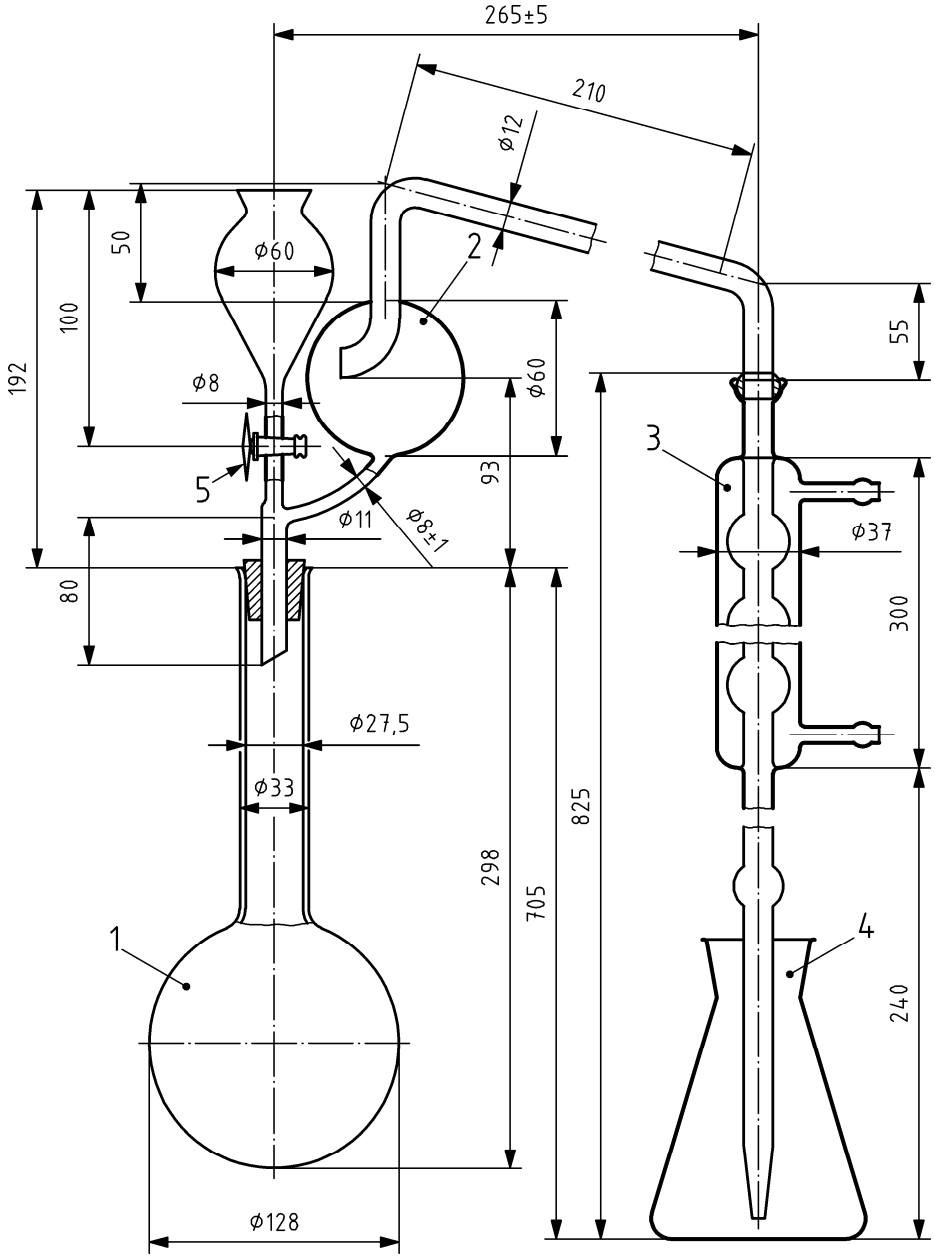


Key

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

6.3 Graduated flask, of capacity 500 ml.

6.4 Rotary shaker, 35 to 40 turns per minute.

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

8.1.1 General

Carry out a solubility test on the sample in water at room temperature and in the proportion of 2 % (mass concentration). Weigh to 0,001 g, according to the indications given in Table 1, a quantity of 5 g or 7 g or 10 g of the prepared sample and place it in a 500 ml graduated flask. According to the result of the solubility test, proceed as follows:

8.1.2 Products completely soluble in water

Add to the flask the quantity of water needed to dissolve the sample; shake, and when completely dissolved, make up the volume and mix thoroughly.

8.1.3 Products not completely soluble in water

Add to the flask 50 ml of water and then 20 ml of hydrochloric acid (5.2). Shake and leave undisturbed until the evolution of carbon dioxide has ceased. Add 400 ml of water and shake for half an hour with the rotary shaker (6.4). Make up the volume with water, mix and filter through a dry filter into a dry receptacle.

8.2 Analysis of the solution

According to the chosen variant, place in the receiving flask the exactly measured quantity of standard sulfuric acid as indicated in Table 1, Table 2 or Table 3. Add the appropriate quantity of chosen indicator solution (5.12.1 or 5.12.2) and finally, sufficient water to give a volume of at least 50 ml. The end of the extension tube of the condenser shall be below the surface of the solution.

Using a precision pipette, take, according to Table 1, Table 2 or Table 3, an adequate aliquot of the clear solution. Place it in the distillation flask.

Add sufficient water to obtain a total volume of about 350 ml (see NOTE 1), 10 g of Arnd's alloy (5.10), 50 ml of magnesium chloride solution (5.11) and a few fragments of pumice stone (5.13). Rapidly connect the flask to the distillation apparatus. Heat gently for about 30 min. Then increase the heating to distil the ammonia. Continue the distillation for about 1 h. After this time, the residue in the flask ought to have a syrupy consistency. When the distillation has finished, 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 2).

NOTE 1 When the sample solution is acid (addition of 20 ml of HCl (1 + 1) (5.2) to dissolve the sample) the aliquot part taken for analysis is neutralized in the following way: to the distillation flask containing the taken aliquot part about 250 ml of water is added, the necessary quantity of one of the indicators (5.12.1, 5.12.2, 5.12.3) is added and shaken carefully. It is neutralized with 2 mol/l sodium hydroxide solution (5.9) and acidified again with a drop of hydrochloric acid (1 + 1) (5.2). Then it is treated as indicated in 8.2.

NOTE 2 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	**Amount to be weighed**	**Dilution**	**Solution of sample to be distilled**	**Expression of the result** [a]
% *N*	**g**	**ml**	**ml**	**% *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, expressed as percentage of ammoniacal nitrogen in the fertilizer.				

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 analysis, check that the apparatus is working properly and that the correct technique is applied using a freshly prepared solution of sodium nitrate (5.14) containing 0,050 g to 0,150 g of nitrate nitrogen depending on the variant chosen.

9 Calculation and expression of the result

Express the result of analysis as a percentage mass fraction of nitrate nitrogen or combined ammoniacal and nitrate nitrogen contained in the fertilizer as received for analysis. Calculation shall be performed in accordance with Table 1, Table 2 or Table 3.

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) the test method used with reference to this European Standard, i.e. EN 15559;

c) the test results obtained expressed as percentage mass fraction of nitrate and ammoniacal 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 2.2.2

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