BRITISH STANDARD

BS EN 15562:2009

Fertilizers — Determination of cyanamide nitrogen

ICS 65.080

BSI
British Standards

National foreword

This British Standard is the UK implementation of EN 15562:2009. It supersedes DD CEN/TS 15562:2007 which is withdrawn.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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Engrais - Détermination de l'azote cyanamidé

Düngemittel - Bestimmung von Cyanamidstickstoff

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Foreword

This document (EN 15562:2009) 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of an identical text or by endorsement, at the latest by July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.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 cyanamide nitrogen in fertilizers. The method is applicable to calcium cyanamide and calcium cyanamide/nitrate mixtures.

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

Precipitation of cyanamide nitrogen as a silver complex. Digestion in sulfuric acid with the aid of a catalyst. 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 Glacial acetic acid

5.3 Ammonia solution, containing 10 % of ammonia gas by mass (ρ_{20} = 0,96 g/ml).

5.4 Ammoniacal silver solution, according to Tollens.

Mix 500 ml of 10 % silver nitrate ($AgNO_3$) solution in water with 500 ml of 10 % ammonia solution (5.3).

Do not expose unnecessarily to light, heat or air. The solution normally keeps for years. As long as the solution remains clear, the reagent is of good quality.

5.5 Concentrated sulfuric acid, ρ_{20} = 1,84 g/ml.

5.6 Potassium sulfate, p.a.

5.7 Catalyst

Use 0,3 g to 0,4 g of copper(II) oxide or 0,95 g to 1,25 g of copper(II) sulfate pentahydrate for each determination.

5.8 Sodium hydroxide solution, approximately 30 % NaOH (ρ_{20} = 1,33 g/ml), ammonia free.

5.9 Sulfuric acid, c = 0,05 mol/l.

5.10 Sodium or potassium hydroxide solution, c = 0,1 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 Anti-bump granules (i.e. pumice stone, glass pearls), washed in hydrochloric acid and calcined.

5.13 Potassium thiocyanate, for the control test.

6 Apparatus

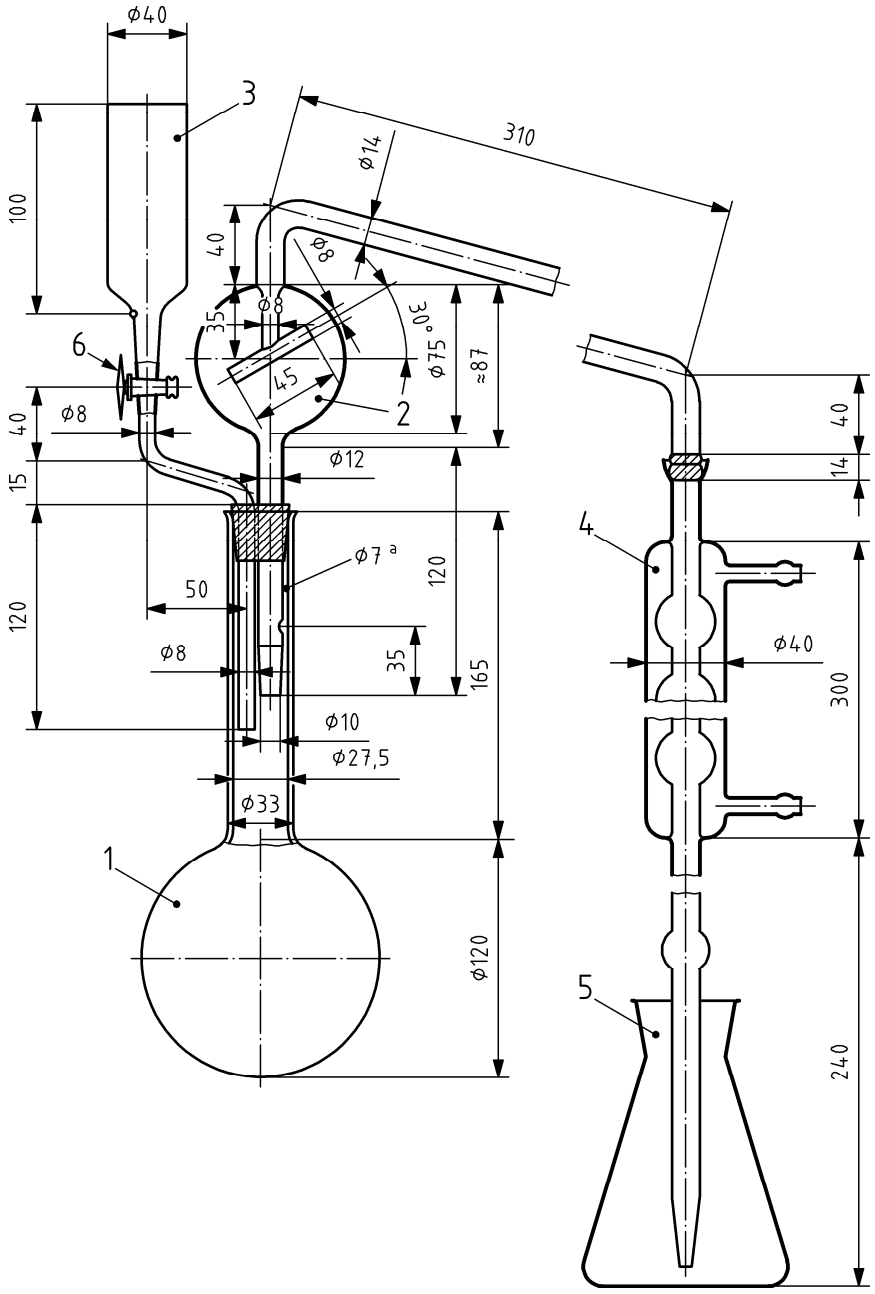
6.1 Distillation apparatus

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

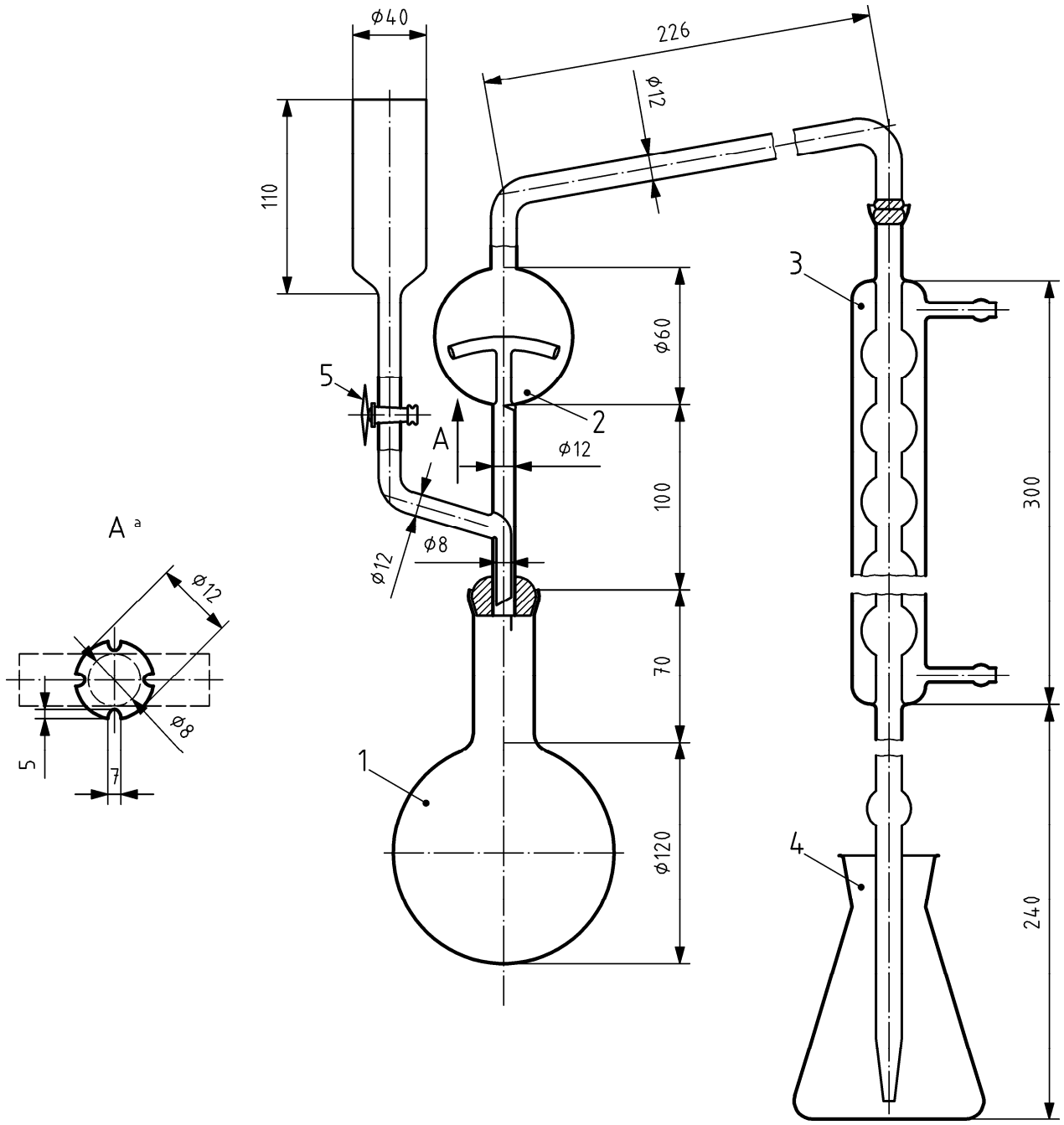


Key

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

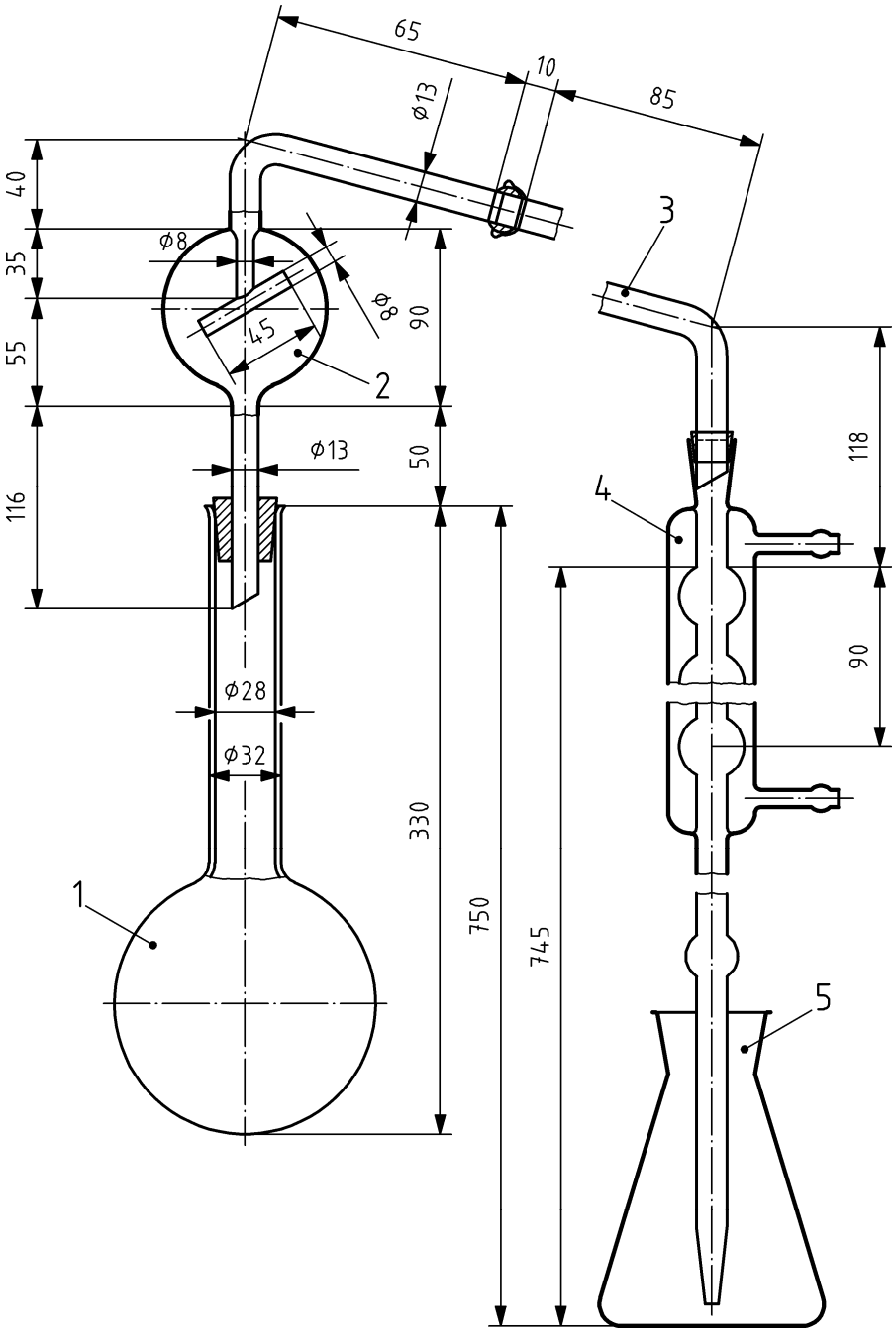


Key

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

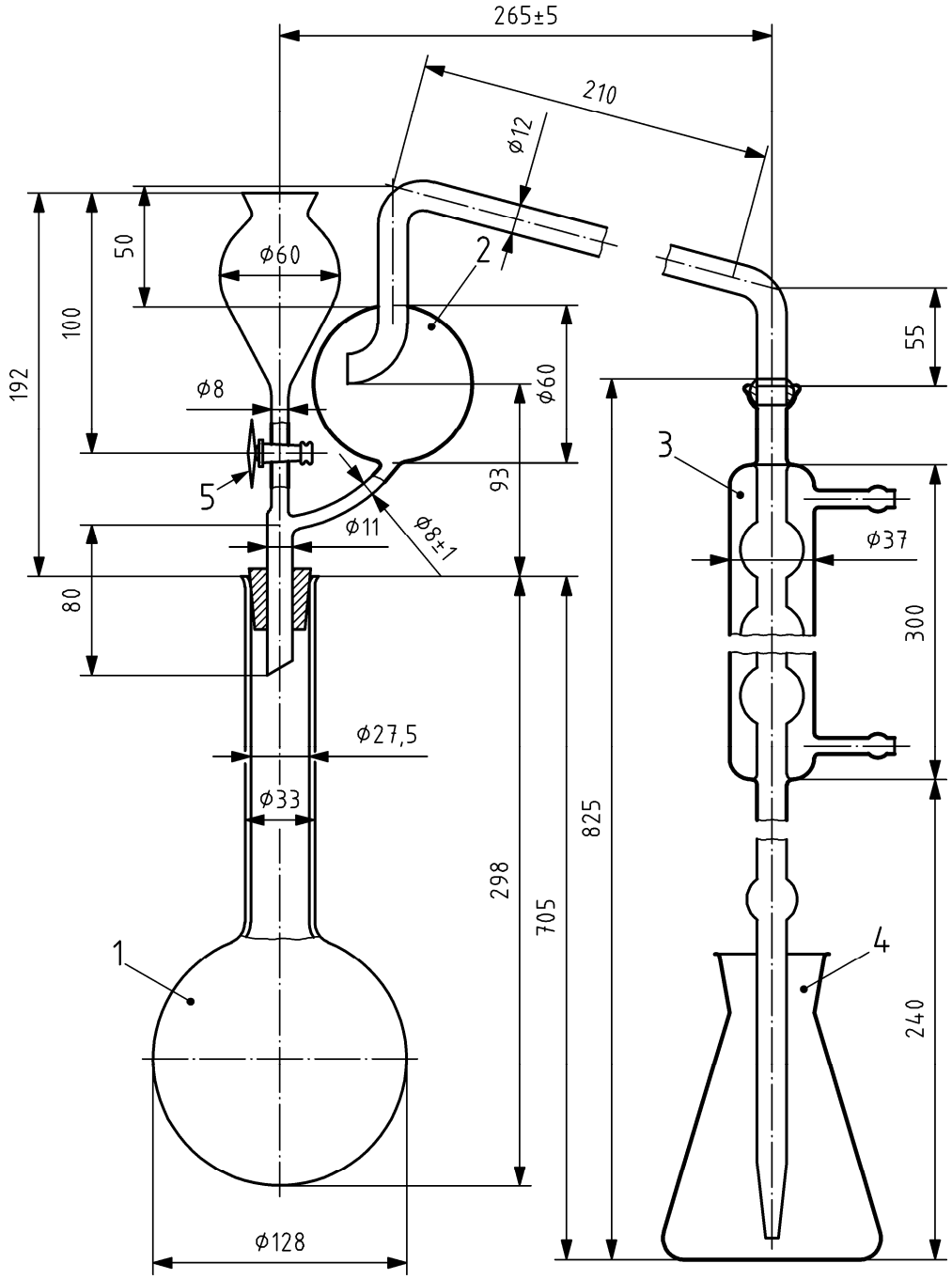


Key

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 Graduated flask, capacity 500 ml.

6.3 Long-necked Kjeldahl flask, of suitable capacity (300 ml to 500 ml).

6.4 Pipette, capacity 50 ml.

6.5 Rotary shaker, 35 to 40 turns per minute.

7 Sampling and sample preparation

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

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

8 Procedure

SAFETY PRECAUTIONS — When using any ammoniacal silver solution safety goggles shall be worn. As soon as a thin membrane forms on the surface of the liquid, an explosion can be produced by agitation and the greatest caution is essential.

8.1 Preparation of the solution for analysis

Weigh, to the nearest 0,001 g, about 2,5 g of the prepared sample and place it in a small glass mortar. Grind the sample three times with water, pouring off the water after each grinding into a 500 ml graduated flask (6.2). Transfer quantitatively the sample into the 500 ml graduated flask, washing the mortar, pestle and funnel with water. Make up with water to approximately 400 ml. Add 15 ml of acetic acid (5.2). Shake on the rotary shaker (6.5) for 2 h.

Make up to 500 ml with water, mix and filter.

The analysis shall be carried out as quickly as possible.

8.2 Analysis of the solution

Transfer 50 ml of the filtrate into a 250 ml beaker.

Add ammonia solution (5.3) until slightly alkaline and add 30 ml of warm ammoniacal silver nitrate (5.4) in order to precipitate the yellow silver complex of the cyanamide.

Leave overnight, filter and wash the precipitate with cold water until it is completely free of ammonia.

Place the filter and the precipitate, still moist, in a Kjeldahl flask, add 10 g to 15 g of potassium sulfate (5.6), the catalyst (5.7), in the prescribed proportion, then 50 ml of water and 25 ml of concentrated sulfuric acid (5.5).

Warm the flask slowly, while shaking it gently until the contents come to the boil. Increase the heat, boil until the contents of the flask become colourless or pale green.

Continue boiling for 1 h, then leave to cool.

Place in the receiving flask 50 ml of standard sulfuric acid. 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.

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 (5.8) (add sufficient NaOH solution (5.8) to ensure the presence of a considerable excess). 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 (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

Declaration w_N **%**	**Amount to be weighed g**	**Dilution ml**	**Solution of sample to be distilled ml**	**Expression of the result** [a] $w_N = (50 - V)\,F$
0 to 5	10	500	50	$(50 - V) \times 0{,}14$
5 to 10	10	500	25	$(50 - V) \times 0{,}28$
10 to 15	7	500	25	$(50 - V) \times 0{,}40$
15 to 20	5	500	25	$(50 - V) \times 0{,}56$
20 to 40	7	500	10	$(50 - V) \times 1{,}00$
Approximate maximum quantity of nitrogen to be distilled: 50 mg. Back-titration with NaOH or KOH 0,1 mol/l.				

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

- 50 is the volume of the standard solution of sulfuric acid to be placed in the receiving flask, in millilitres;
- V is the volume of the sodium or potassium hydroxide used for the back titration;
- F is the 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 test

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 using an aliquot part of a standard solution of potassium thiocyanate (5.13) corresponding to 0,05 g of nitrogen.

9 Calculation and expression of the result

Calculate the content of cyanamide nitrogen as a percentage mass fraction of the fertilizer as received for analysis according to Table 1.

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 15562;

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 2.4

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