BRITISH STANDARD

BS EN 15478:2009

Fertilizers — Determination of total nitrogen in urea

ICS 65.080

BSI
British Standards

National foreword

This British Standard is the UK implementation of EN 15478:2009. It supersedes DD CEN/TS 15478:2006 which is withdrawn.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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Engrais - Détermination de l'azote total dans l'urée

Düngemittel - Bestimmung von Gesamtstickstoff in Harnstoff

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Foreword

This document (EN 15478:2009) 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of an identical text or by endorsement, at the latest by July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.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 urea. This method is applied exclusively to urea fertilizers which are nitrate free.

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

Urea is transformed quantitatively into ammonia by boiling in the presence of sulfuric acid. The ammonia thus obtained is distilled from an alkaline medium, the distillate being collected in an excess of standard sulfuric acid. The excess acid is titrated by means of a standard alkaline 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 Kjeldahl tablets,

5 g/tablet containing 100 parts K_2SO_4 to 1 part selenium.

5.3 Sulfuric acid, concentrated (ρ_{20} = 1,84 g/ml).

5.4 Sodium hydroxide solution, approximately NaOH 500 g/l.

5.5 Sulfuric acid, c = 0,05 mol/l, to use for the blank test.

5.6 Sodium or potassium hydroxide solution, carbonate free, c = 0,1 mol/l, to use for the blank test.

5.7 Sulfuric acid, c = 0,5 mol/l.

5.8 Sodium or potassium hydroxide solution, carbonate free, c = 1,0 mol/l.

5.9 Indicator solutions

5.9.1 Mixed indicator

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

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

Mix one volume of A with two volumes of B.

This indicator is violet in an acid solution, grey in a neutral solution and green in an alkaline solution; use 0,5 ml (10 drops).

5.9.2 Methyl red indicator solution

Dissolve 0,1 g of methyl red in 50 ml of 95 % ethanol and make up to 100 ml with water. Filter if necessary. This indicator (4 or 5 drops) may be used instead of the preceding one. This indicator is red in acid solution and yellow in alkaline solution.

5.10 Anti-bump granules, for example pumice stone, washed in hydrochloric acid and calcined.

5.11 Urea, p. a.

6 Apparatus

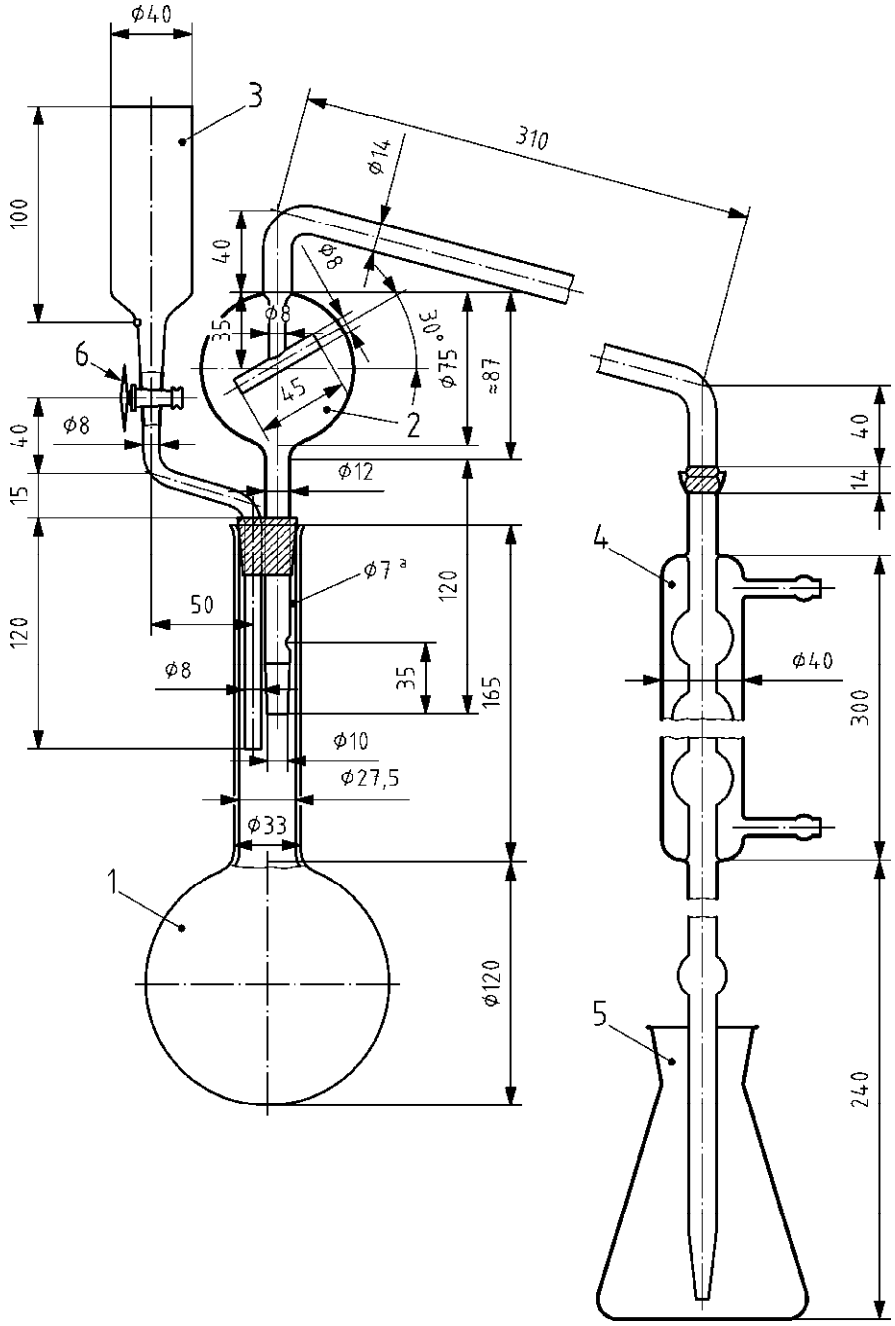
6.1 Distillation apparatus

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.

Automatic distillation apparatus may be used as well 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

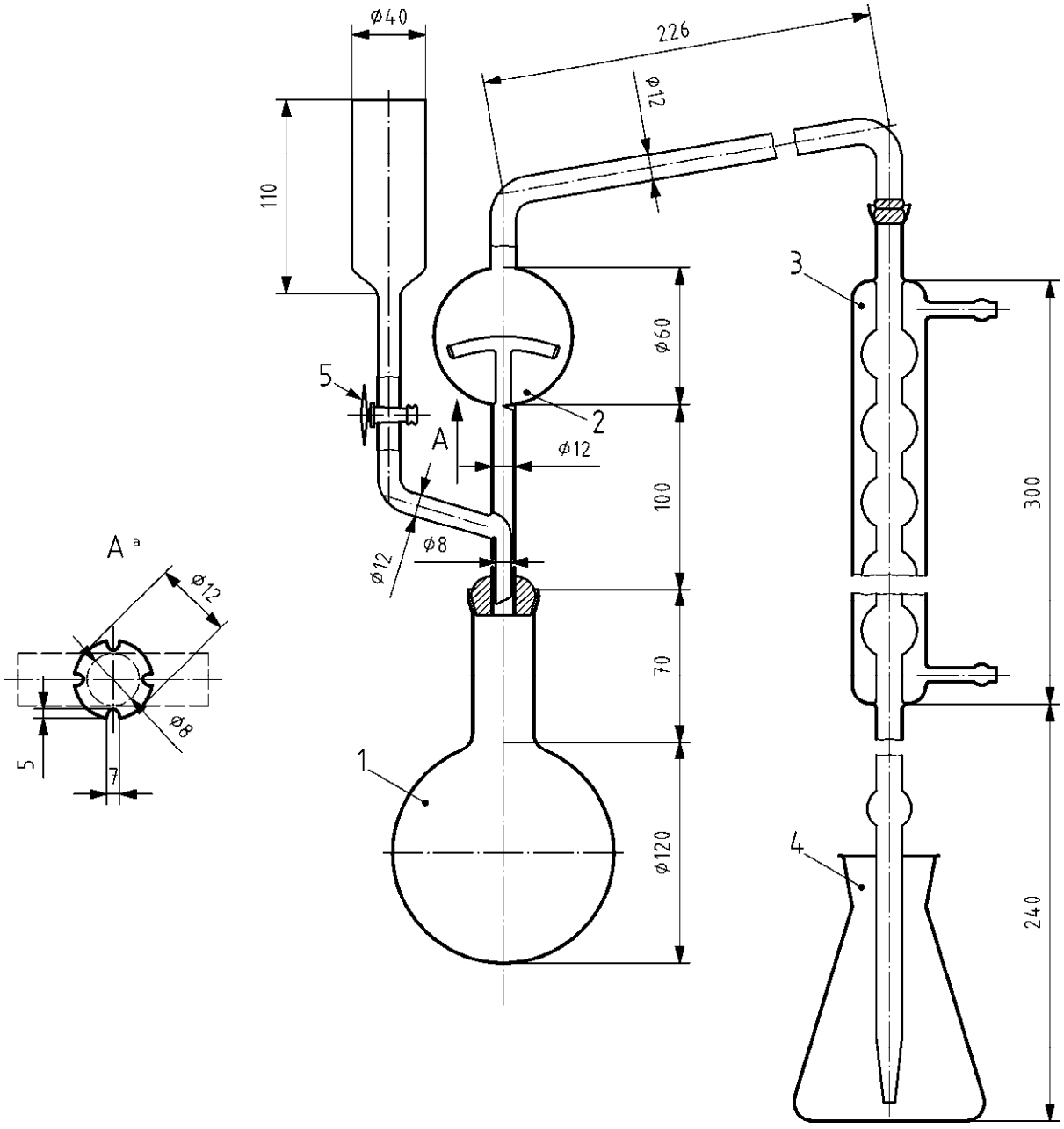
4 six-bulb condenser with spherical joint (No 18) at the entrance, and joined at the issue to a glass extension tube by means of a small rubber connection (when the connection to the distillation tube is effected by means of a rubber tube, the spherical joint may be replaced by a suitable rubber bung)

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 (6) 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

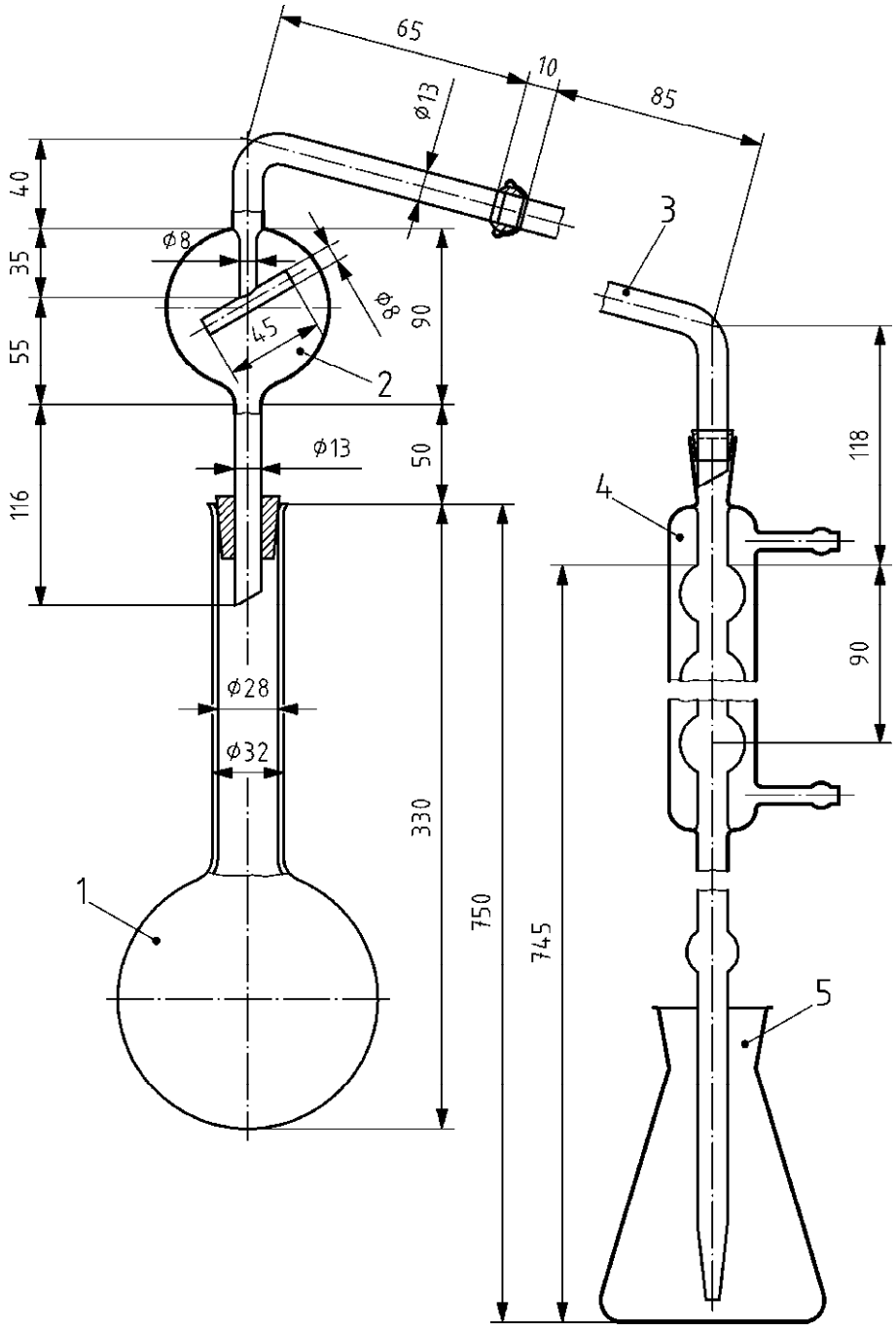
4 500 ml flask in which the distillate is collected

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

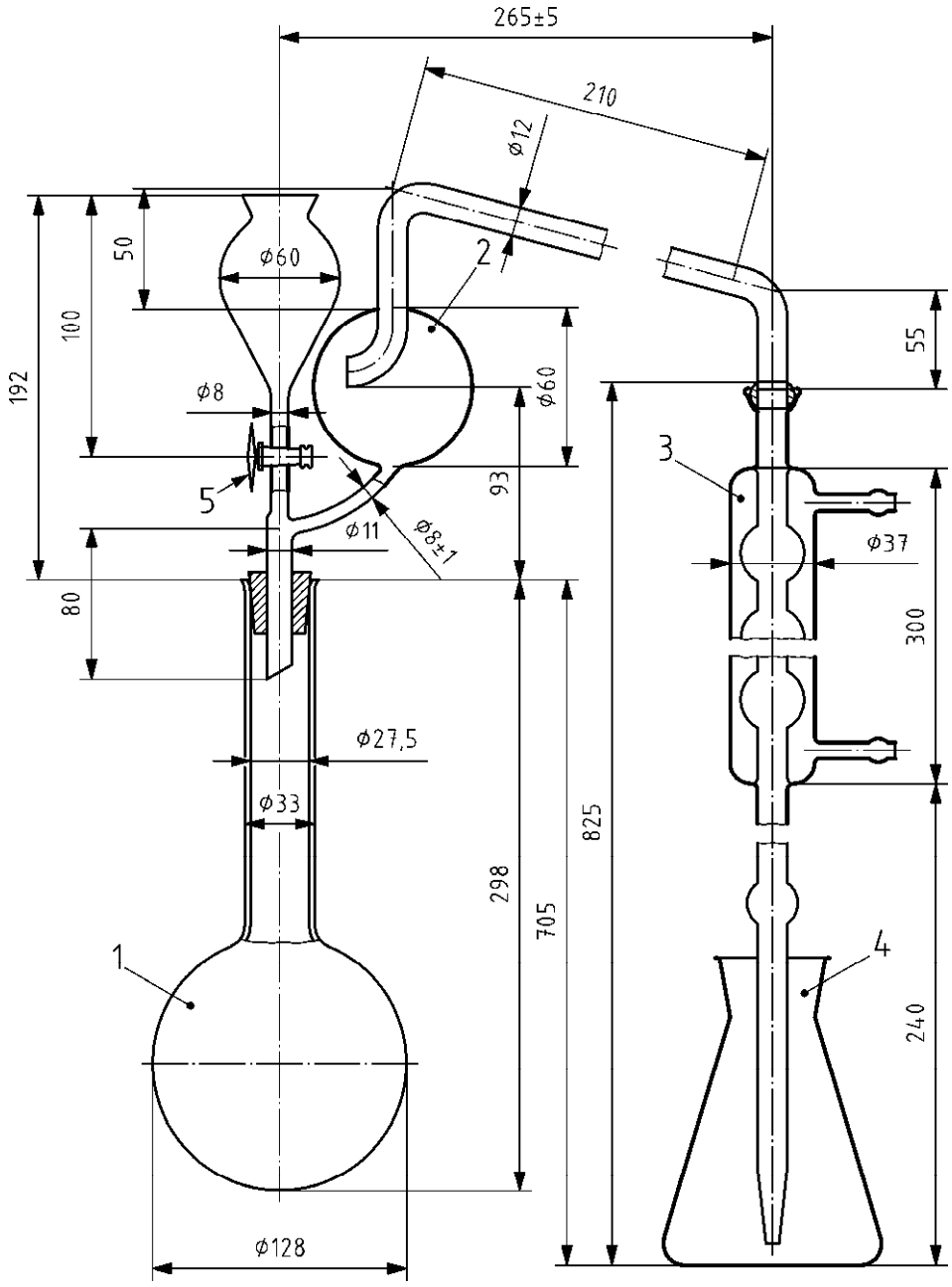
3 elbow tube with a spherical joint (No 18) at the entrance, and a drip cone (the connection to the distillation tube may be effected by means of a rubber tube instead of a spherical joint)

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

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 (the tap may be replaced by a rubber connection with an appropriate clip)

Figure 4 — Distillation apparatus 4

6.2 Graduated flask, capacity 500 ml.

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

Weigh to the nearest 0,001 g about 500 mg of the prepared sample and transfer with 10 ml demineralised water to a 800 ml Kjeldahl flask. Add, while gently swirling 30 ml sulfuric acid (5.3) and 1 Kjeldahl tablet (5.2).

8.2 Analysis of the solution

8.2.1 Digestion step

Put the Kjeldahl flask in a fume cupboard. Place on a heating device and heat until boiling, with an input that is required to bring 250 ml of water at 25 °C to a "rolling boil" in 20 min to 30 min.

Continue to heat the flask and contents for approximately 1 h, until dense white fumes of sulfuric acid are escaping for at least 15 min. Allow the flask to cool to 25 °C.

8.2.2 Distillation step

Measure into a 500 ml Erlenmeyer receiving flask 30,00 ml of the 0,5 mol/l sulfuric acid solution (5.7). Add 270 ml water and add four or five drops of the indicator solution (5.9.) and place the Erlenmeyer flask in such a way that the end of the delivery tube is at least 3 cm below the surface of the liquid. Add 250 ml water to the Kjeldahl flask and several grains of pumice stone (5.10) 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 Kjeldahl flask carefully 120 ml of the sodium hydroxide solution (5.4). Agitate the flask to thoroughly mix the contents. Apply heat increasing the rate of heating progressively until finally the contents of the flask are boiling briskly.

Most of the ammonia is expelled within 15 min. Continue the distillation until 150 ml of distillate has been collected. Then lower the Erlenmeyer flask receiver so that the end of the delivery tube is out of the liquid and continue the distillation for a few more minutes. Rinse the outside of the delivery tube with a small amount of water into the Erlenmeyer flask. Back titrate the excess of acid with the 1,0 mol/l sodium hydroxide solution (5.8) to the neutral colour of the indicator (5.9).

8.3 Blank

At the same time as the determination carry out a blank test, using the same apparatus and the same quantities of all the reagents and water, but omitting the test portion and using 20,00 ml of the 0,05 mol/l sulfuric acid solution (5.5) and back titrating with the 0,1 mol/l sodium hydroxide solution (5.6).

8.4 Control test

Before carrying out the analysis, 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 urea (5.11).

9 Calculation and expression of the result

Express the result of the analysis as a percentage of nitrogen (*N*) contained in the fertilizer as received for analysis. Calculate the mass fraction of total nitrogen, w_N in percent, using the following equation:

$$w_N = \frac{(30 \times t_1 \times 2 - V_1 \times t_2) - (20 \times t_3 \times 2 - V_2 \times t_4) \times 14 \times 100}{m} \quad (1)$$

where

30 is the volume, in millilitres of the 0,5 mol/l sulfuric acid solution (5.7);

20 is the volume, in millilitres of the 0,05 mol/l sulfuric acid solution (5.5);

V_1 is the volume, in millilitres of the 1,0 mol/l sodium hydroxide solution (5.8) used for the determination;

V_2 is the volume, in millilitres of the 0,1 mol/l sodium hydroxide solution (5.6) used for the blank test;

t_1 is the titre of H_2SO_4 0,5 mol/l;

t_2 is the titre of NaOH 1,0 mol/l;

t_3 is the titre of H_2SO_4 0,05 mol/l;

t_4 is the titre of NaOH 0,1 mol/l;

m is the mass, in milligrams, of the sample taken for the determination.

10 Precision

10.1 Inter-laboratory test

An inter-laboratory test was carried out in 2004 with 19 participating laboratories and one sample of urea. 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 1.

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 1.

Table 1 — Mean value, repeatability and reproducibility limit

Sample	$\bar{x}$ %	r %	R %
Urea	46,26	0,24	0,74

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 the 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) 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 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
	Urea
Number of participating laboratories	19
Number of laboratories after elimination of outliers (accepted test results)	16
Mean value $\bar{x}$ (%)	46,26
Repeatability standard deviation s_r (%)	0,11
RSD_r (%)	0,30
Repeatability limit r (%)	0,24
Reproducibility standard deviation s_R (%)	0,27
RSD_R (%)	0,57
Reproducibility limit R (%)	0,74

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 2.3.3

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