

English Version

Fertilizers - Determination of nitric and ammoniacal nitrogen according to Ulsch

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

Düngemittel - Bestimmung von Nitrat- und
Ammoniumstickstoff nach Ulsch

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Contents

Foreword.....3

1 Scope4

2 Normative references4

3 Terms and definitions4

4 Principle4

5 Reagents4

6 Apparatus5

7 Sampling and sample preparation 10

8 Procedure 10

9 Calculation and expression of the result 11

10 Test report 12

Bibliography 13

Foreword

This document (EN 15558:2009) 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of an identical text or by endorsement, at the latest by July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TS 15558:2007.

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1 Scope

This European Standard specifies a method for the determination of nitrate and ammoniacal nitrogen with reduction according to Ulsch.

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 by means of metallic iron in an acid medium and displacement of the ammonia thus formed by the addition of an excess of sodium hydroxide: distillation of the ammonia and determination of the yield of ammonia in a known volume of standard sulfuric acid solution and titration of the excess sulfuric 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, $\rho(\text{HCl}) = 1,18 \text{ g/ml}$, with one volume of water.

5.3 Sulfuric acid, $c = 0,05 \text{ mol/l}$.

5.4 Sodium or potassium hydroxide solution, carbonate free, $c = 0,1 \text{ mol/l}$.

5.5 Sulfuric acid solution, approximately 30 % H_2SO_4 (mass concentration), ammonia free.

5.6 Powdered iron, reduced in hydrogen.

The prescribed quantity of iron shall be able to reduce at least 0,05 g of nitrate nitrogen.

5.7 Sodium hydroxide solution, 30 % mass concentration, of approximately $\rho(\text{NaOH}) = 1,33 \text{ g/ml}$, ammonia free.

5.8 Indicator solutions

5.8.1 Mixed indicator

Solution A: Dissolve 1 g of methyl red in 37 ml of sodium hydroxide solution $c = 0,1 \text{ mol/l}$ 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.

5.8.2 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 5.8.1.

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

5.10 Sodium nitrate, p. a.

6 Apparatus

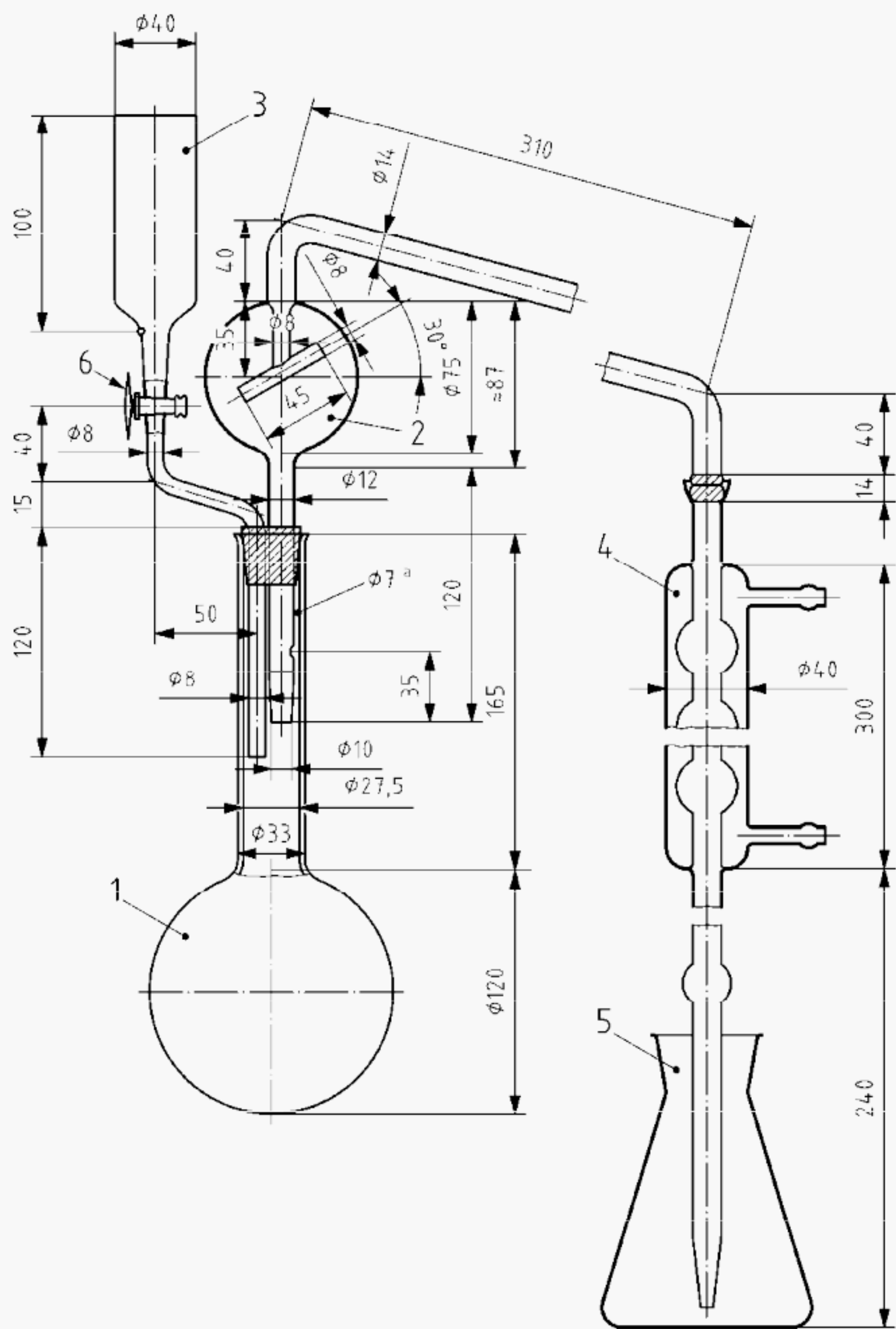
6.1 Distillation apparatus

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

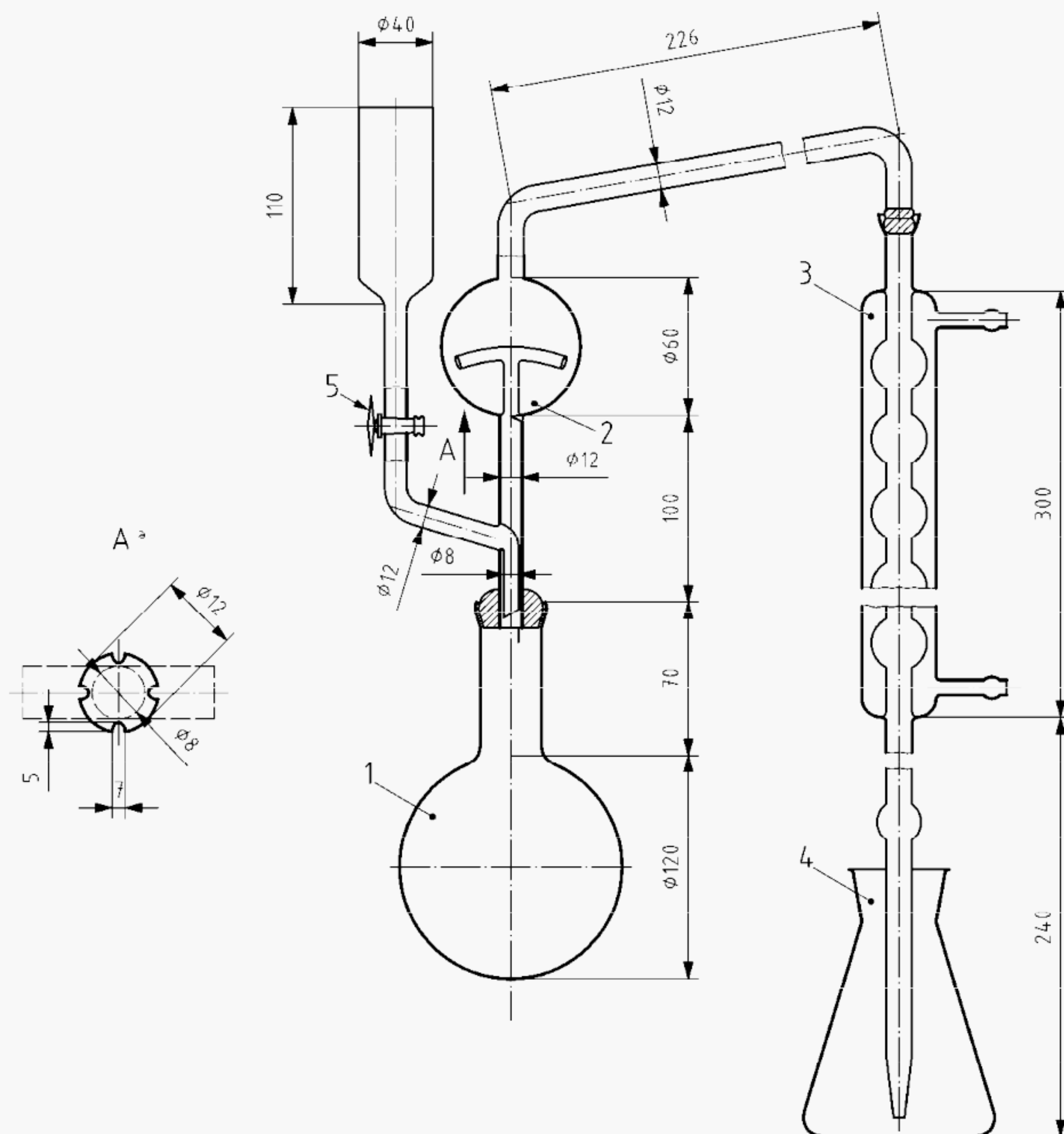


Key

- 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



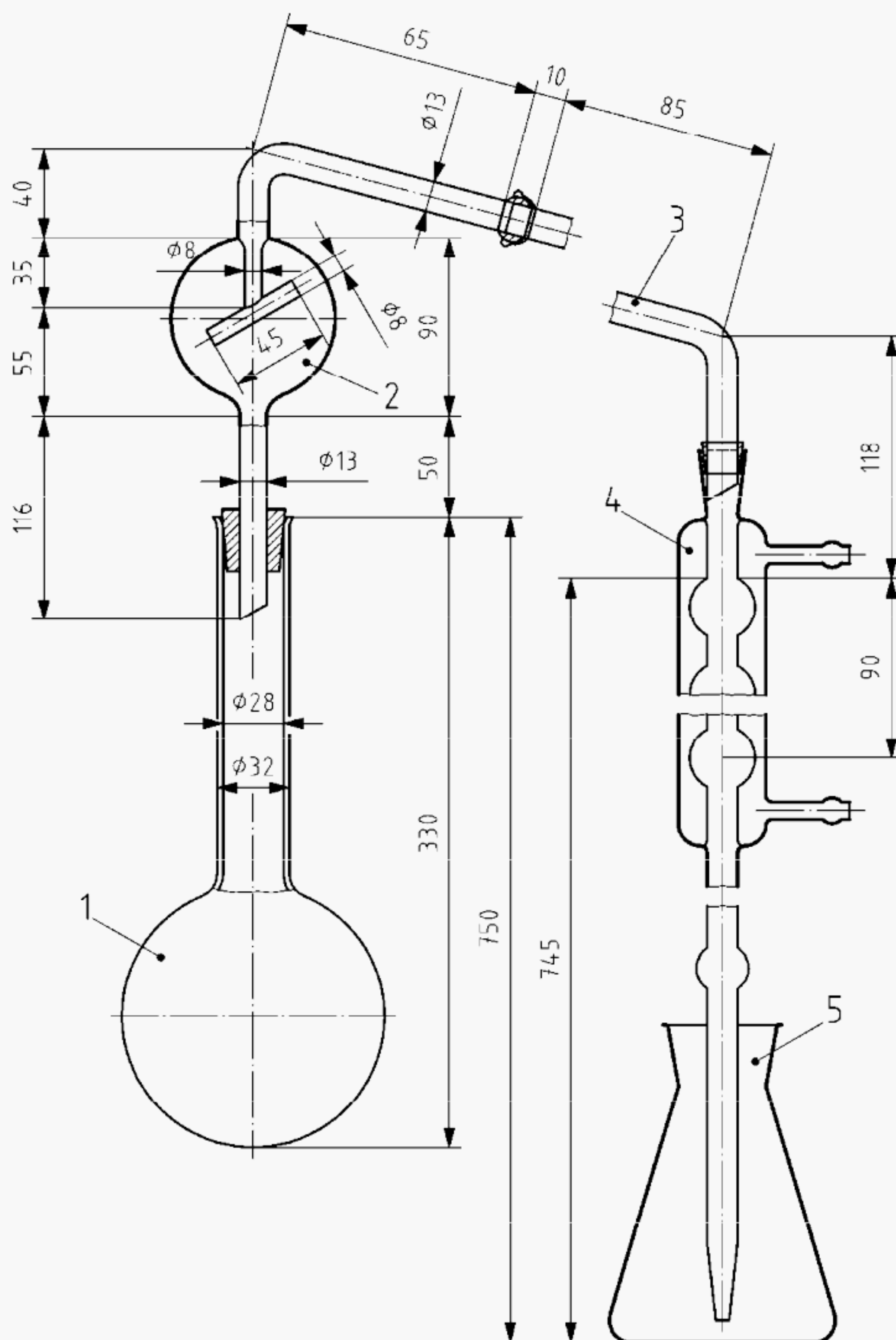
Key

- 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

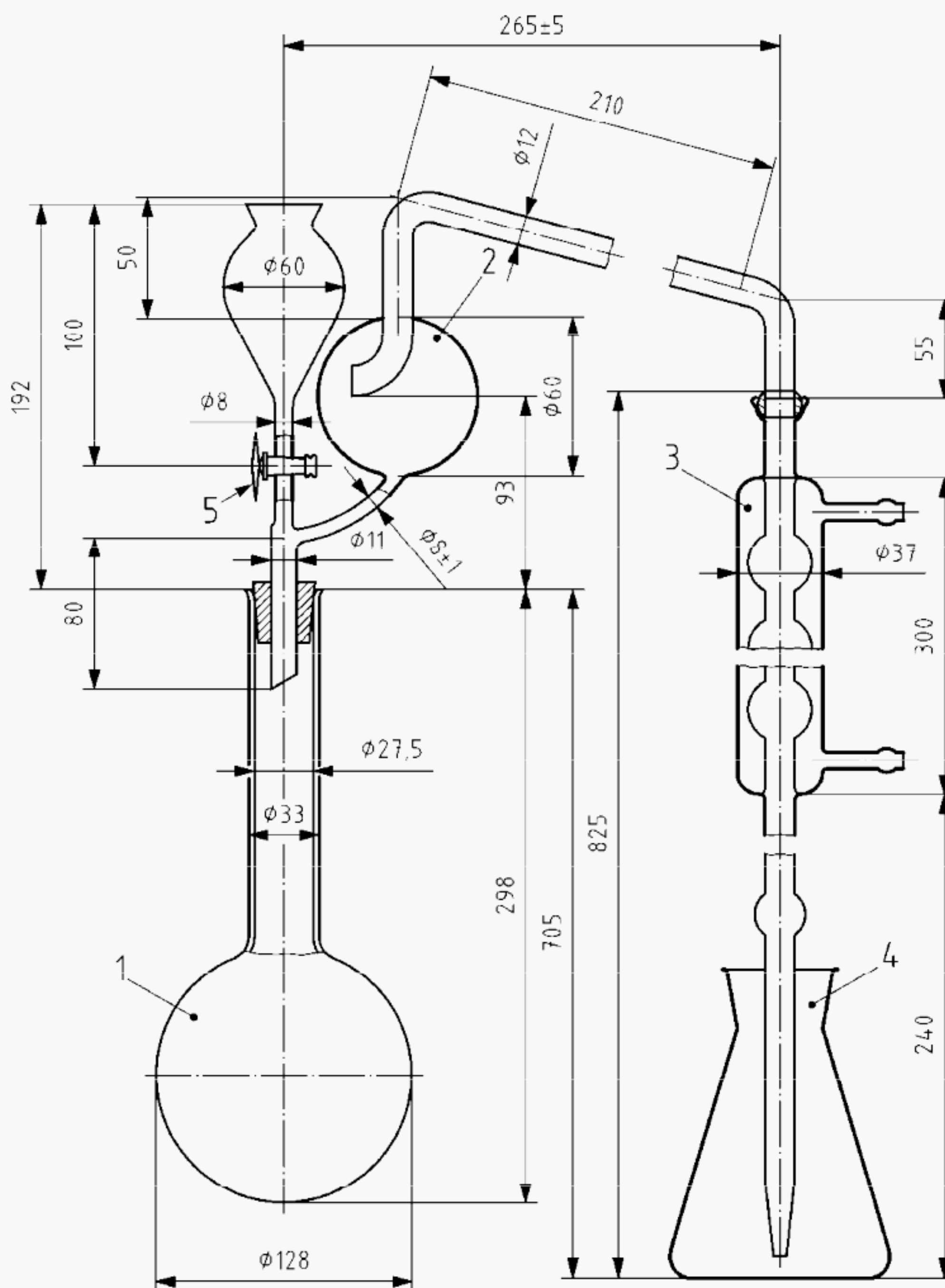


Key

- 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 flasks, 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 Procedure

Place in the receiving flask an exactly measured quantity of 50 ml standard sulfuric acid and add the appropriate quantity of indicator solution 5.8.1 or 5.8.2. The end of the extension tube of the condenser shall be below the surface of the standard acid in the receiving flask.

Using a precision pipette, transfer an aliquot part of the clear solution as indicated in Table 1 and place it in the distillation flask of the apparatus. Add 350 ml of water, 20 ml of 30 % sulfuric acid solution (5.5) stir, and add 5 g of reduced iron (5.6). Wash the neck of the flask with several millilitres of water, and place in the neck of the flask a small, long-stemmed funnel. Heat in a boiling water bath for an hour and then wash the stem of the funnel with a few millilitres of water.

Taking care to avoid any loss of ammonia, add to the contents of the distillation flask 50 ml of concentrated sodium hydroxide solution (5.7), or in the cases where 20 ml of hydrochloric acid (5.2) has been used to dissolve the sample, add 60 ml of concentrated sodium hydroxide solution (5.7). Assemble the distillation apparatus. 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 in such a way 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

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) × 0,14
5 to 10	10	500	25	(50 – A) × 0,28
10 to 15	7	500	25	(50 – A) × 0,40
15 to 20	5	500	25	(50 – A) × 0,56
20 to 40	7	500	10	(50 – A) × 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 millilitre; — A = volume of sodium or potassium hydroxide used for the back titration, in millilitre; — 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 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 analysis, check that the apparatus is working properly and that the method is correctly applied by using an aliquot part of a freshly prepared solution of sodium nitrate (5.10) containing 0,045 g to 0,050 g of nitrogen.

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.

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 15558;
- c) the 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) 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 2.2.1