
Fertilizers — Determination of ammoniacal nitrogen

Engrais — Détermination de l'azote ammoniacal





COPYRIGHT PROTECTED DOCUMENT

© ISO 2016, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

| | |
|--|-----------|
| Foreword | iv |
| 1 Scope | 1 |
| 2 Normative references | 1 |
| 3 Terms and definitions | 1 |
| 4 Principle | 1 |
| 5 Reagents | 1 |
| 6 Apparatus | 2 |
| 7 Sampling and sample preparation | 7 |
| 8 Procedure | 7 |
| 8.1 Preparation of the solution..... | 7 |
| 8.2 Analysis of the solution..... | 7 |
| 8.3 Blank..... | 9 |
| 8.4 Control test..... | 9 |
| 9 Calculation and expression of the result | 9 |
| 10 Precision | 9 |
| 10.1 Inter-laboratory test..... | 9 |
| 10.2 Repeatability..... | 9 |
| 10.3 Reproducibility..... | 10 |
| 11 Test report | 10 |
| Annex A (informative) Results of the inter-laboratory tests | 11 |
| Bibliography | 12 |

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

ISO 25475 was prepared by CEN/TC 260 as EN 15475:2009 and was adopted (without modification other than those stipulated below) by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners*.

Modifications were made in the following subclauses:

- a) General: The references to EN 1482-1 and -2 were changed to ISO 14820-1 and -2;
- b) [5.9](#): added “mass fraction”;
- c) [5.12](#): p.a. = pro analysis = analytical grade;
- d) [6.1](#): First two sentences joined together.
- e) [6.4](#): “35 to 40 revolutions per minute” was changed to “35 r/min to 40 r/min”;
- f) [8.1](#): “Filter through a filter into a 500 ml graduated flask and make up to the volume with water” was changed to “Pass the solution through a filter into a 500 ml graduated flask and make up to the volume with water”;
- g) [8.2](#), [Table 3](#): “ 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” was changed to “ F = factor comprising the amount weighed, the dilution, the aliquot part of the solution of the sample to be distilled and the volumetric equivalent”.
- h) [10.1](#) Line 1: “Test was carried out in 2004 with 24, respectively 22 participating labs” was changed to “A test was carried out in 2004 with 24 participating labs”;
- i) Bibliography: Reference [3] was removed.

Fertilizers — Determination of ammoniacal nitrogen

1 Scope

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 14820-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

EN 12944-1, *Fertilizers and liming materials — Vocabulary — Part 1: General terms*

EN 12944-2, *Fertilizers and liming materials — Vocabulary — Part 2: Terms relating to fertilizers*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 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 ISO 3696).

5.2 Hydrochloric acid, diluted. Mix one volume of $\rho(\text{HCl}) = 1,18 \text{ g/ml}$ with one volume of water.

5.3 Sulfuric acid (for variant a), $c = 0,05 \text{ mol/l}$.

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

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

5.6 Sodium or potassium hydroxide solution (for variant b, see NOTE in [8.2](#)), carbonate free, $c = 0,2 \text{ mol/l}$.

5.7 Sulfuric acid (for variant c, see NOTE in [8.2](#)), $c = 0,25 \text{ mol/l}$.

5.8 Sodium or potassium hydroxide solution (for variant c, see NOTE in [8.2](#)), carbonate free, $c = 0,5 \text{ mol/l}$.

5.9 Sodium hydroxide, 30 % (mass fraction), of approximately $\rho(\text{NaOH}) = 1,33 \text{ g/ml}$, 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 ([5.4](#)) $c = 0,1 \text{ mol/l}$ 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 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 (four to five 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. (p.a. = pro analysis = analytical grade).

6 Apparatus

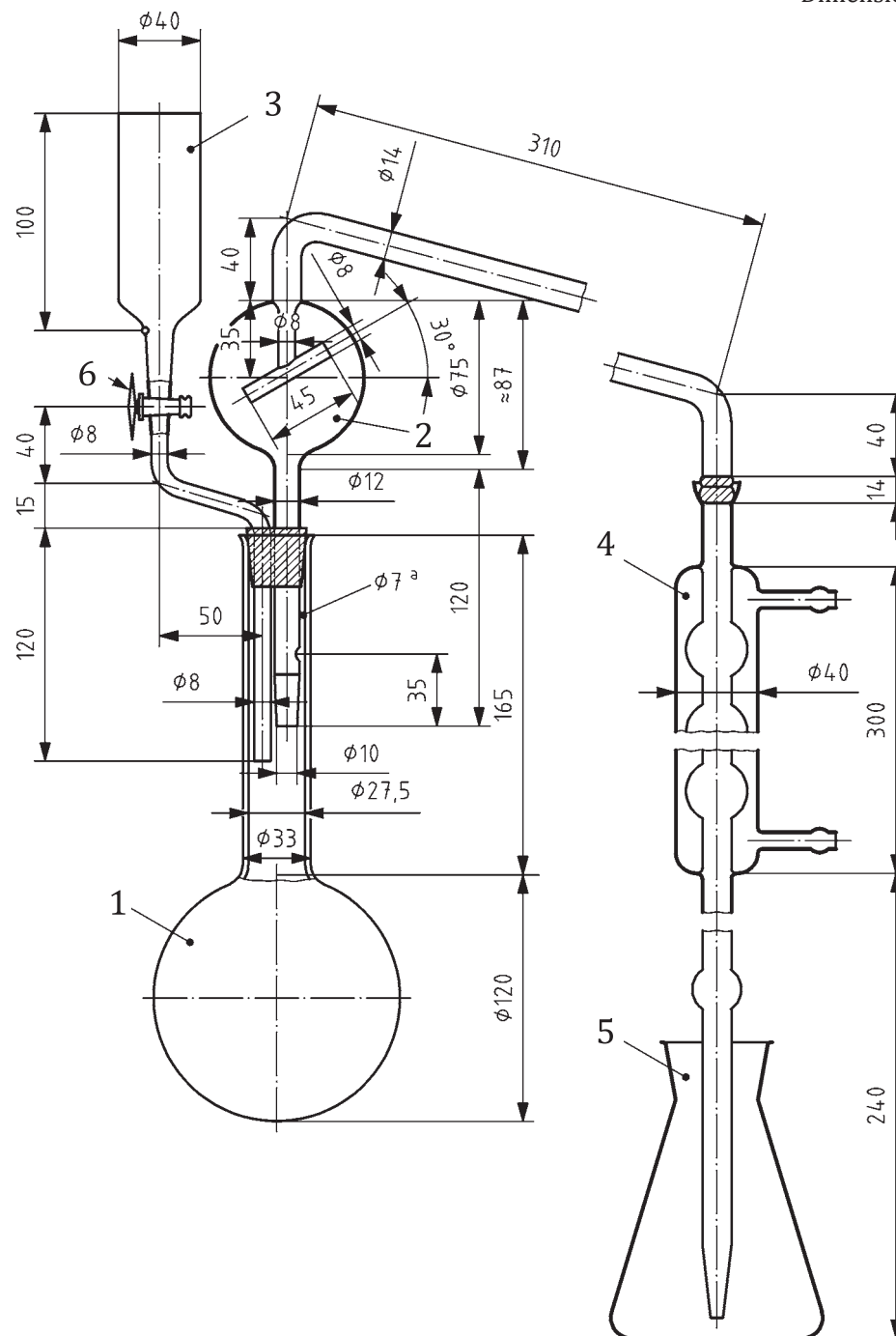
6.1 Distillation apparatus

The equipment is made of borosilicate glass and consists of a round-bottomed flask of suitable capacity connected to a condenser by means of a splash head.

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

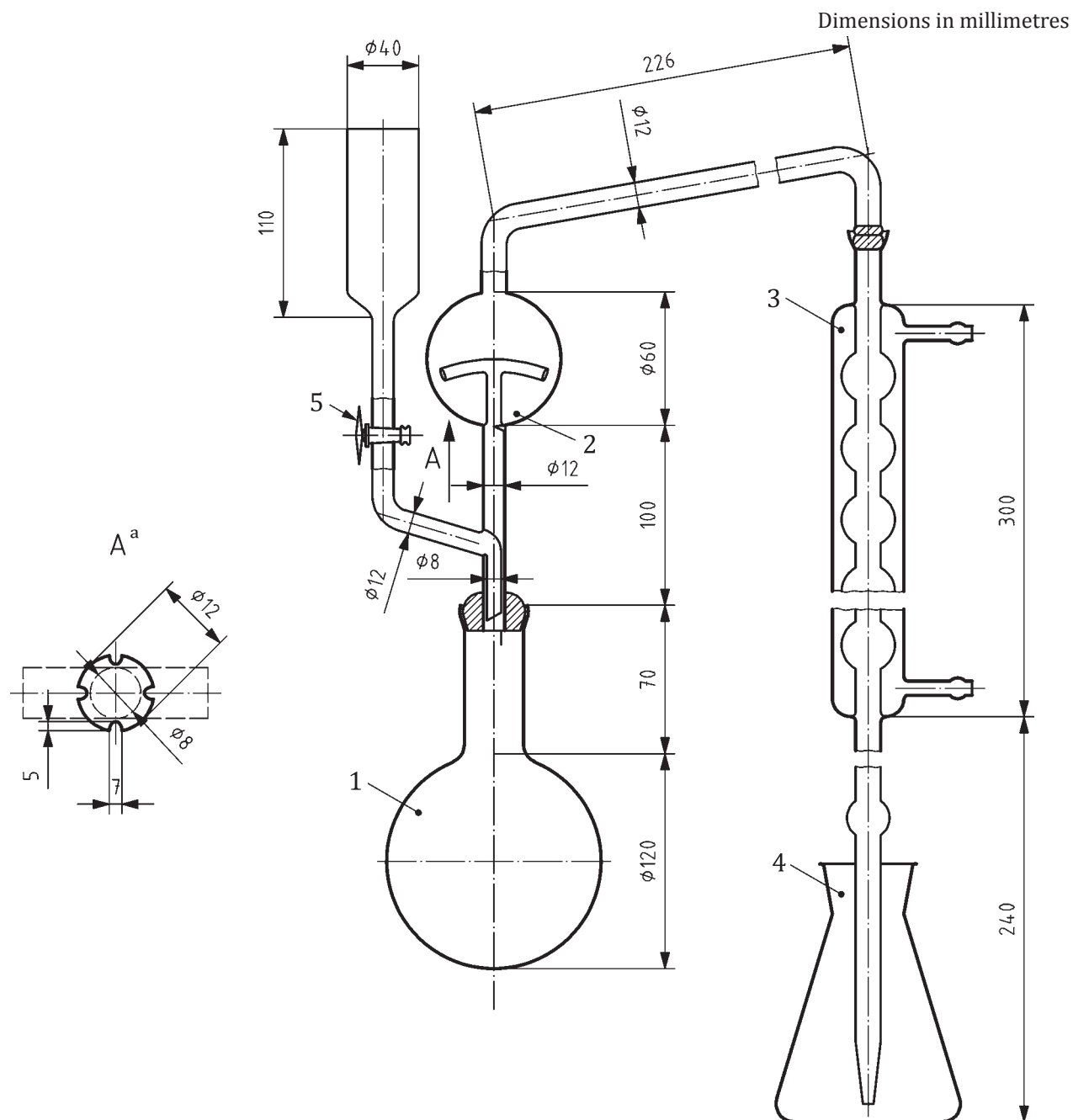
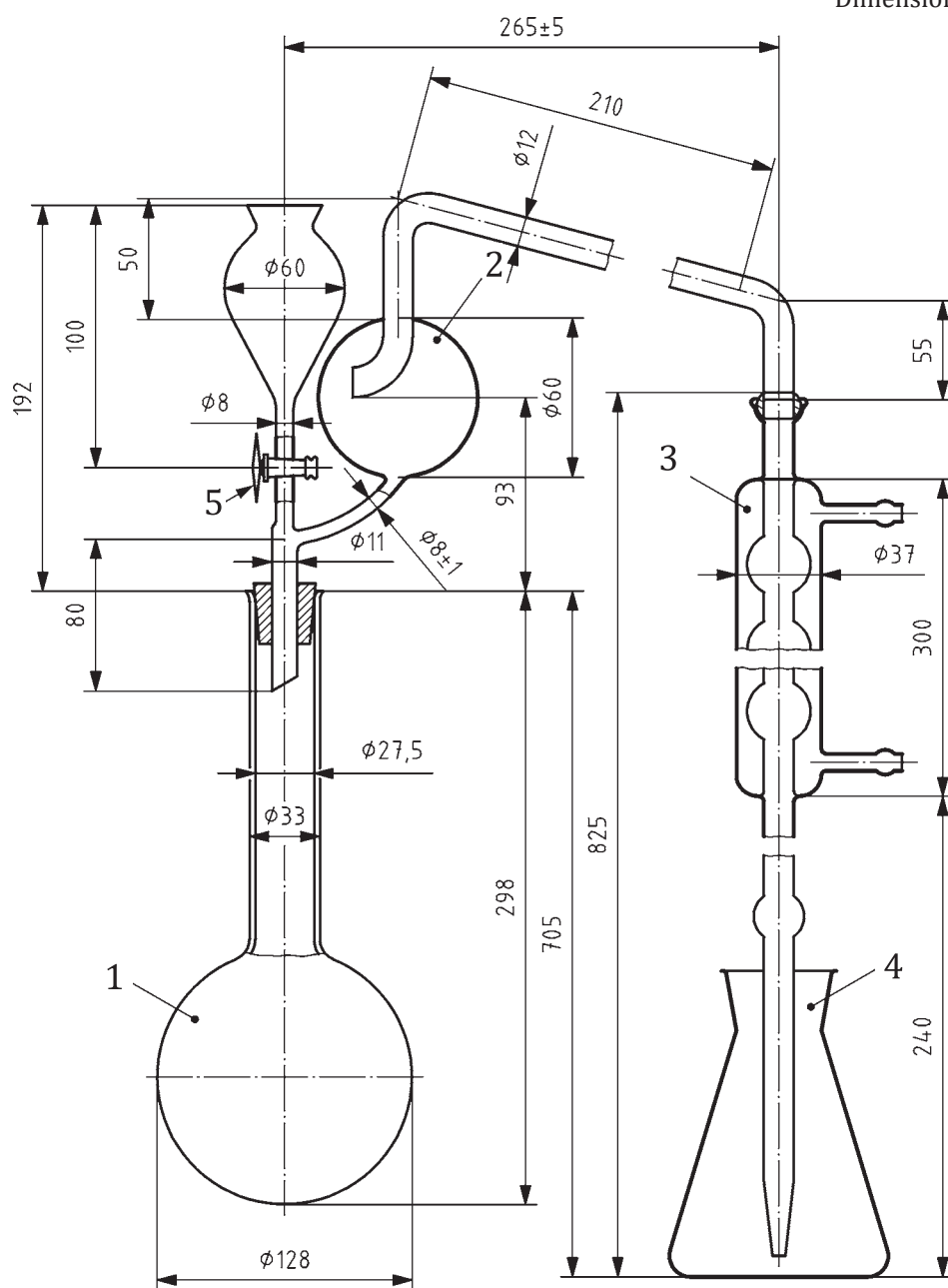


Figure 2 — Distillation apparatus 2



- 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 r/min to 40 r/min.

7 Sampling and sample preparation

Sampling is not part of the method specified in this International Standard. A recommended sampling method is given in ISO 14820-1.

Sample preparation shall be carried out in accordance with ISO 14820-2.

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](#)). Pass the solution 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.

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 % <i>N</i> | 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 | $(50 - A) \times 1,00$ |

NOTE 1 Approximate maximum quantity of nitrogen to be distilled: 50 mg.

NOTE 2 Sulfuric acid 0,05 mol/l to be placed in the receiving flask: 50 ml.

NOTE 3 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 the 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 % <i>N</i> | 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 | $(50 - A) \times 1,00$ |

NOTE 1 Approximate maximum quantity of nitrogen to be distilled: 100 mg.

NOTE 2 Sulfuric acid 0,1 mol/l to be placed in the receiving flask: 50 ml.

NOTE 3 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 the 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 % <i>N</i> | 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 | $(35 - A) \times 1,400$ |

NOTE 1 Approximate maximum quantity of nitrogen to be distilled: 200 mg.

NOTE 2 Sulfuric acid 0,25 mol/l to be placed in the receiving flask: 35 ml.

NOTE 3 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 the solution of the sample to be distilled and the volumetric equivalent;
- *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

A test was carried out in 2004 with 24 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:

- all information necessary for the complete identification of the sample;
- the test method used with reference to International Standard, i.e. ISO 25475:2016;
- the test results obtained expressed as percentage mass fraction of ammoniacal nitrogen in the fertilizer;
- the date of sampling and sampling procedure (if known);
- the date when the analysis was finished;
- the whether the requirement of the repeatability limit has been fulfilled;
- all operating details not specified in this International Standard, 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 CEN/TC 260 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] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*
- [2] ISO 14820-1, *Fertilizers and liming materials — Sampling and sample preparation — Part 1: Sampling*

