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# Fertilizers — Determination of different forms of nitrogen in the same sample, containing nitrogen as nitric, ammoniacal, urea and cyanamide nitrogen

*Engrais — Détermination des différentes formes d'azote dans un même échantillon contenant l'azote sous forme nitrique, ammoniacale, uréique et cyanamidique*

Reference number
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# Foreword

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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).

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ISO 15604 was prepared by CEN/TC 260 as EN 15604:2009 and was adopted (without modification other than those stipulated below) by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners*.

Modifications were made as follows:

a) 5.2: p.a. = pro analysis = analytical grade;

b) 6.2: add "Refer to Figure 1".

# Fertilizers — Determination of different forms of nitrogen in the same sample, containing nitrogen as nitric, ammoniacal, urea and cyanamide nitrogen

## 1 Scope

This International Standard specifies a method for the determination of any one form of nitrogen in the presence of any other form.

The method is applicable to any fertilizer provided for in the Regulation (EC) No 2003/2003, Annex I[2] containing nitrogen in various forms.

## 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*

ISO 25475, *Fertilizers — Determination of ammoniacal nitrogen*

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*

EN 15562, *Fertilizers — Determination of cyanamide nitrogen*

## 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

### 4.1 Total soluble and insoluble nitrogen

According to the list of standard fertilizers given in Regulation (EC) No 2003/2003, Annex I,[2] this determination is applicable to products containing calcium cyanamide.

In the absence of nitrates, the test sample is mineralized by direct Kjeldahl digestion.

In the presence of nitrates, the test sample is mineralized by Kjeldahl digestion after reduction with the aid of metallic iron and stannous chloride.

In both cases, the ammonia is determined according to ISO 25475.

NOTE If analysis shows an insoluble nitrogen content of more than 0,5 %, one concludes that the fertilizer contains other forms of insoluble nitrogen not included in the list in Regulation (EC) No 2003/2003, Annex I.[2]

## 4.2 Forms of soluble nitrogen

### 4.2.1 General

The forms of soluble nitrogen referred to in 4.2.2 to 4.2.7 are determined from different aliquots taken from the same solution of the test sample.

### 4.2.2 Total soluble nitrogen

**4.2.2.1** In the absence of nitrates, by direct Kjeldahl digestion. The ammonia is then determined (by the same method as that described in ISO 25475).

**4.2.2.2** In the presence of nitrates, by Kjeldahl digestion on an aliquot part taken from the solution after reduction according to Ulsch. The ammonia is then determined (by the same method as that described in ISO 25475).

### 4.2.3 Total soluble nitrogen with the exception of nitrate nitrogen

By Kjeldahl digestion after elimination in an acid medium of nitrate nitrogen with ferrous sulfate. The ammonia is then determined (by the same method as that described in ISO 25475).

### 4.2.4 Nitrate nitrogen by difference

**4.2.4.1** In the absence of calcium cyanamide, by determining the difference between the nitrogen determined as summarized in 4.2.2.2 and that determined as summarized in 4.2.3 or between total soluble nitrogen (see 4.2.2) and the sum of ammoniacal nitrogen and ureic organic nitrogen (4.2.5 + 4.2.6).

**4.2.4.2** In the presence of calcium cyanamide, by determining the difference between the nitrogen determined as summarized in 4.2.2.2 and that determined as summarized in 4.2.3 or between the nitrogen determined as summarized in 4.2.2.2 and the sum of that determined as summarized in 4.2.5, 4.2.6 and 4.2.7.

### 4.2.5 Ammoniacal nitrogen

**4.2.5.1** Solely in the presence of ammoniacal nitrogen and ammoniacal plus nitrate nitrogen, according to ISO 25475.

**4.2.5.2** In the presence of urea nitrogen and/or cyanamide nitrogen by cold distillation after making slightly alkaline, the ammonia is absorbed in a standard solution of sulfuric acid and determined according to ISO 25475.

### 4.2.6 Urea nitrogen

**4.2.6.1** By conversion using urease into ammonia which is titrated with a standard solution of hydrochloric acid.

or

**4.2.6.2** By gravimetry with xanthydrol: the co-precipitated biuret can be counted with urea nitrogen without great error, its content remaining generally low in absolute value in compound fertilizers.

or

**4.2.6.3** By difference according to Table 1.

**Table 1 — Determination of urea nitrogen by difference**

| Case | Nitrate nitrogen | Ammoniacal nitrogen | Cyanamidic nitrogen | Difference |
|---|---|---|---|---|
| 1 | Absent | Present | Present | (4.2.2.1) - (4.2.5.2 + 4.2.7) |
| 2 | Present | Present | Present | (4.2.3) - (4.2.5.2 + 4.2.7) |
| 3 | Absent | Present | Absent | (4.2.2.1) - (4.2.5.2) |
| 4 | Present | Present | Absent | (4.2.3) - (4.2.5.2) |

### 4.2.7 Cyanamide nitrogen

By precipitation as a silver compound, the nitrogen being determined in the precipitate by the Kjeldahl method.

## 5 Reagents

### 5.1 General.

Use only reagents of recognized analytical grade and distilled or de-mineralized water of grade 3 according to ISO 3696.

**5.2 Potassium sulfate**, p.a. (p.a. = pro analysis = analytical grade).

**5.3 Iron powder**, reduced with hydrogen.

The prescribed quantity of iron shall be able to reduce at least 50 mg of nitrate nitrogen.

**5.4 Potassium thiocyanate**, p.a.

**5.5 Potassium nitrate**, p.a.

**5.6 Ammonium sulfate**, p.a.

**5.7 Urea**, p.a.

### 5.8 Sulfuric acid diluted.

Dilute one volume of sulfuric acid ($\rho_{20}$ = 1,84 g/ml) in one volume of water.

**5.9 Sulfuric acid, standard solution**, $c$ = 0,1 mol/l.

**5.10 Sodium hydroxide solution**, aqueous solution of about 30 % (mass concentration), free from ammonia.

**5.11 Sodium or potassium hydroxide, standard solution,** $c$ = 0,2 mol/l, free from carbonates.

### 5.12 Stannous chloride solution.

Dissolve 120 g of $SnCl_2 \cdot 2H_2O$ in 400 ml of concentrated hydrochloric acid ($\rho_{20}$ = 1,18 g/ml) and make up to 1 l with water. The solution shall be perfectly clear and prepared immediately before use.

It is essential to check the reducing power of stannous chloride: dissolve 0,5 g of $SnCl_2 \cdot 2H_2O$ in 2 ml of concentrated hydrochloric acid ($\rho_{20}$ = 1,18 g/ml) and make up to 50 ml with water. Then, add 5 g of Rochelle salt (potassium sodium tartrate), then a sufficient quantity of sodium bicarbonate for the solution to be alkaline to litmus paper.

Titrate with an iodine solution ($I_2$) of $c$ = 0,05 mol/l in the presence of a starch solution as an indicator.

1 ml of iodine solution ($I_2$) of $c$ = 0,05 mol/l corresponds to 0,011 28 g of $SnCl_2 \cdot 2H_2O$.

At least 80 % of the total tin present in the solution thus prepared shall be in bivalent form. For the titration, at least 35 ml of the $c$ = 0,05 mol/l iodine solution ($I_2$) should be used.

**5.13 Sulfuric acid**, $\rho_{20}$ = 1,84 g/ml.

### 5.14 Hydrochloric acid diluted.

Mix one volume of hydrochloric acid ($\rho_{20}$ = 1,18 g/ml) with one volume of water.

**5.15 Acetic acid**, 96 % to 100 %.

**5.16 Sulfuric acid solution**, containing about 30 % of $H_2SO_4$ (mass concentration).

**5.17 Ferrous sulfate**, crystalline, $FeSO_4 \cdot 7H_2O$.

**5.18 Sulfuric acid standard solution**, $c$ = 0,05 mol/l.

**5.19 Octyl alcohol**.

**5.20 Potassium carbonate, saturated solution.**.

**5.21 Sodium or potassium hydroxide standard solution**, $c$ = 0,1 mol/l (free from carbonates).

**5.22 Barium hydroxide saturated solution.**

**5.23 Sodium carbonate solution**, at 10 % (mass concentration).

**5.24 Hydrochloric acid**, $c$ = 2 mol/l.

**5.25 Hydrochloric acid standard solution**, $c$ = 0,1 mol/l.

### 5.26 Urease solution.

Suspend 0,5 g of active urease in 100 ml of water. Using hydrochloric acid 0,1 mol/l (5.25), adjust the pH to 5,4, measured by a pH-meter.

### 5.27 Xanthydrol.

Use a solution at 5 % in ethanol or methanol (5.32) (do not use products giving a high proportion of insoluble matter). The solution may be kept for three months in a well-stoppered bottle, away from the light.

### 5.28 Catalyst.

Use 0,3 g to 0,4 g of copper oxide per determination or an equivalent quantity of copper sulfate pentahydrate of 0,95 g to 1,25 g per determination.

**5.29 Anti-bump granules**, washed in hydrochloric acid and calcined.

### 5.30 Indicator solutions.

#### 5.30.1 Solution A.

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

#### 5.30.2 Solution B.

Dissolve 1 g of methylene blue in water and make up to 1 l.

#### 5.30.3 Combined indicator solution.

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.

#### 5.30.4 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 (four or five drops) may be used instead of that described in 5.30.3.

**5.31 Indicator papers**, litmus bromothymol blue (or other papers sensitive to pH = 6 to pH = 8).

**5.32 Ethanol or methanol**, solution 95 %.

## 6 Apparatus

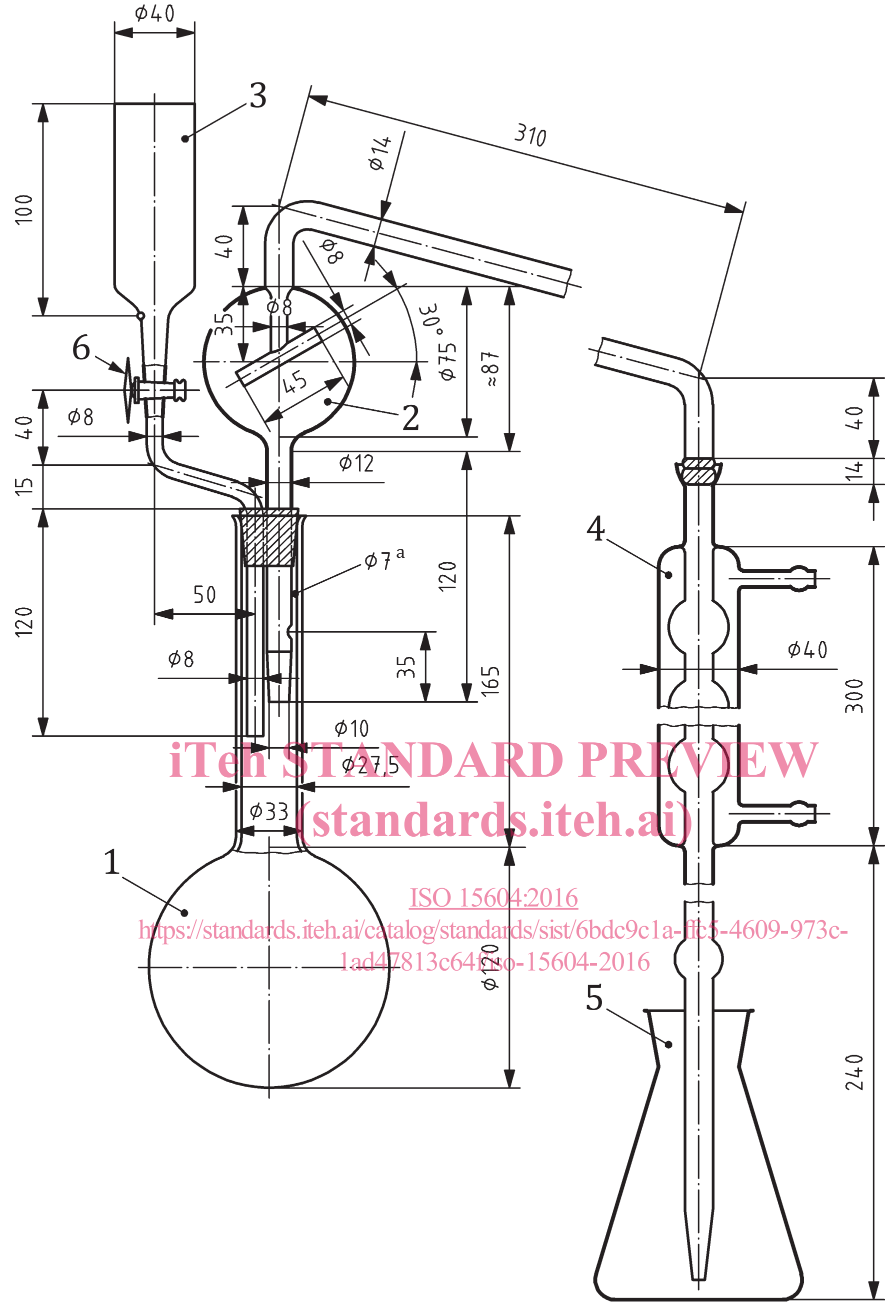
### 6.1 Distillation apparatus.

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

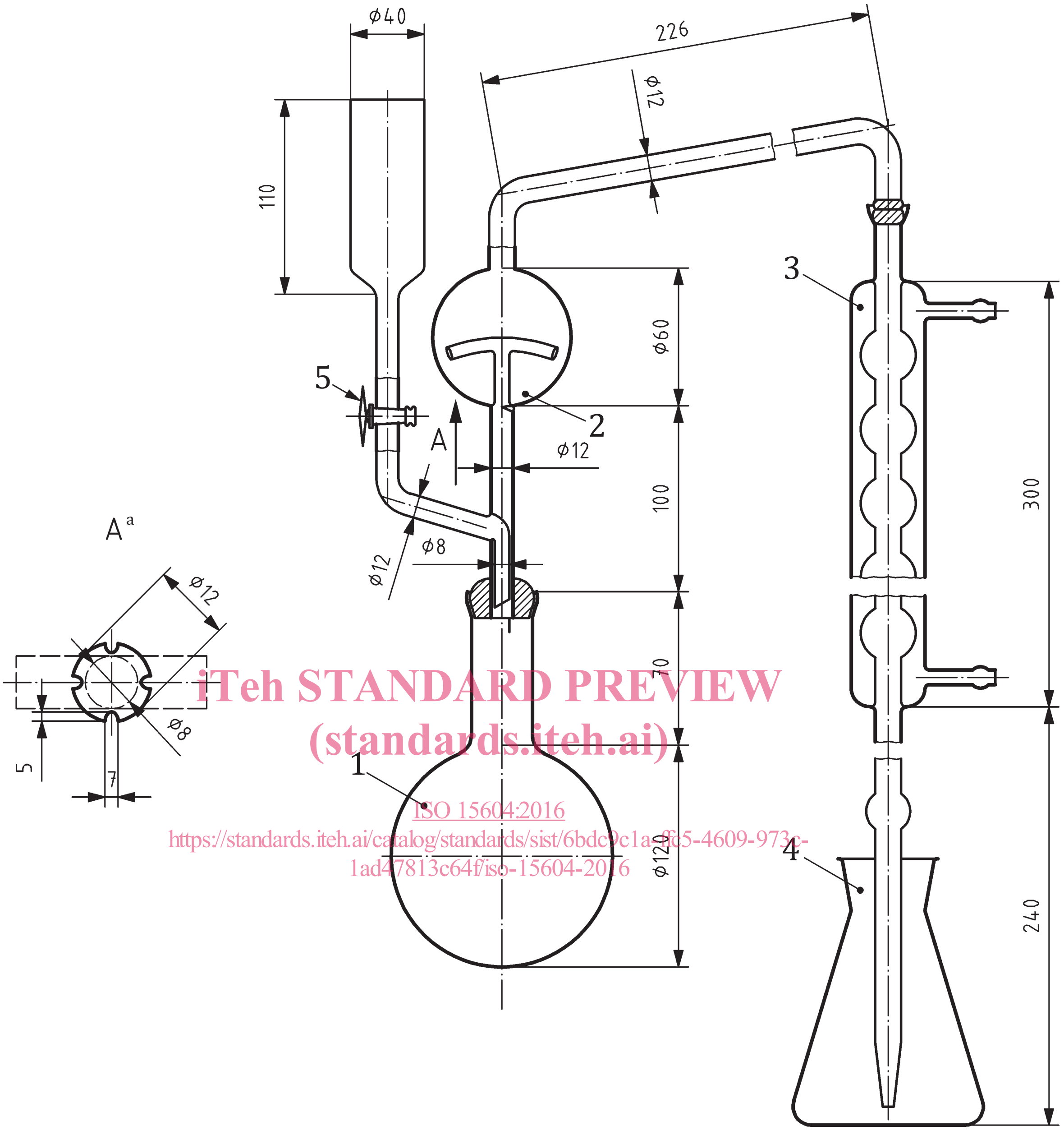


**Key**

| | |
|---|---|
| 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 cross-section. |

**Figure 2 — Distillation apparatus 2**