Annex D.2

Revision of EN 15478:2009, Inorganic fertilizers — Determination of total nitrogen in methylene-urea and urea formaldehyde

Draft method

1 Scope

This document specifies a method for the determination of the content of total nitrogen from methylene-urea and urea formaldehyde in their pure form in inorganic fertilizers.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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, liming materials and inhibitors — Sampling and sample preparation — Part 2: General sample preparation provisions*

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 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 and EN 12944-2 apply.
ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

The nitrogen is transformed quantitatively into ammoniacal salt by boiling in the presence of sulfuric acid. The ammoniacal solution thus obtained is distilled through 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

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).

5.1 Kjeldahl tablets.

5.1.1 5 g/tablet containing 100 parts K_2SO_4 to 1 part selenium.

or, in alternative,

5.1.2 5 g of pure K_2SO_4 in powder (recommended).

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

5.3 Sodium hydroxide solution, NaOH 30 % w/w.

5.4 Sulfuric acid standard solution, molar concentration *c* = 0,25 mol/l (0,5 N/l)

5.5 Sodium or potassium hydroxide standard solution, carbonate free, c = 0,5 mol/l.

5.6 Indicator for ammonia nitrogen, ready for use.

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

5.8 Melamine, analytical grade.

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	definition for Y
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

Annex D.2

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

Annex D.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)

Annex D.2

Figure 4 — Distillation apparatus 4

6.2 **Graduated Erlenmeyer flask,** capacity 400 or 500 ml.

6.3 **25 ml burettes,** with a precision of 0,03 ml and a division of 0,05 ml (class AS).

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 0,0001 g about 300 mg of the prepared sample and transfer with 50 ml demineralised water to a suitable Kjeldahl flask, depending to the distillation apparatus. Add 1 Kjeldahl tablet (5.1.1) or, in alternative, 5 g of potassium sulphate (5.1.2) and add, while gently swirling, 30 ml sulfuric acid (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 gradually 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 for approximately 2 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 with the burette (6.3) into a graduated Erlenmeyer receiving flask (6.2) 25,00 ml of the sulfuric acid solution (5.4) and add 25 ml of water.
Add fifteen drops of the indicator solution (5.7) and place the graduated Erlenmeyer flask (6.2) in such a way that the end of the delivery tube is 1 cm below the surface of the liquid. Add a suitable quantity of water to the Kjeldahl flask and several grains of pumice stone (5.8) in order to control the boiling.
Assemble the distillation apparatus taking care to avoid any loss of ammonia. If the distillation apparatus is automatic, the water is automatically added.
Add to the contents of the Kjeldahl flask carefully, manually or automatically, 120 ml of the sodium hydroxide solution (5.3). 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 a total of 300 ml of distillate has been collected. Rinse the outside of the delivery tube with a small amount of water into the Erlenmeyer flask. Back titrate the excess of acid with sodium or potassium hydroxide standard solution (5.6) to the green colour of the indicator (5.7).

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.

8.4 Control test

To check that the apparatus is working properly and that the correct application of the method is used, perform two analysis simultaneously using melamine (5.9) as standard.

9 Calculation and expression of the result

Express the result of the analysis as a percentage of total 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:

$$w_N = \frac{(V_2 - V_1) \times 0{,}5 \times 14{,}008 \times 100}{m} \qquad (1)$$

where

V_1	is the volume of the 0,5 mol/l sodium or potassium hydroxide standard solution (5.6) used for the determination, in millilitres;
V_2	is the volume of the 0,5 mol/l sodium or potassium hydroxide standard solution (5.6) used for the blank test, in millilitres;
m	is the mass, of the sample taken for the determination, in milligrams.

10 Precision

10.1 Inter-laboratory test

<to be added>
An inter-laboratory test was carried out in 20** with ** participating laboratories and several samples of methylene-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*** %
<to be added>			

11 Test report

The test report shall contain at least the following information:

Annex D.2

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this document, including its year of publication;

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).

Bibliography

[1] EN 1482-1, *Fertilizers, liming materials and inhibitors — Sampling and sample preparation — Part 1: General sampling provisions*

[2] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*