Annex D.3

Revision of CEN/TS 17403:2021, Inorganic fertilizers —Determination of cold water insoluble nitrogen and hot water insoluble nitrogen in solid urea formaldehyde and methylene urea slow-release fertilizers and determination of the solubility of nutrient polymers in phosphate buffer solution with a pH of 7,5 at 100 °C

Draft method

1 Scope

This document specifies a method for the determination of the cold and hot water insoluble nitrogen content in solid urea formaldehyde and methylene urea slow-release fertilizers and for the determination of the solubility of nutrient polymers in a phosphate buffer solution with a pH of 7,5 at 100 °C, in their pure form in inorganic fertilizers.

It is not applicable to the following nutrient polymers: liquid methylene urea, IBDU (isobutylidendiurea) and CDU (crotonylidendiurea) as they are almost completely soluble in hot water due to their chemical nature.

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*

ISO 5315, *Fertilizers — Determination of total nitrogen content — Titrimetric method after distillation*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 and the following 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 https://www.iso.org/obp

3.1
urea formaldehyde
UF
slow-release nitrogenous fertilizer obtained by the reaction between urea and formaldehyde to produce molecular chains of general formula NH_2-CO-NH$(CH_2NHCONH)_nH$

3.2
methylene urea
MU
slow-release nitrogenous fertilizer obtained by the reaction between urea and formaldehyde to produce oligomers such as MDU (methylendiurea), DMTU (dimethylentriurea), TMTU (trimethylentetraurea),

TMPU (tetramethylenpentaurea) and higher counterparts

3.3
CMC 8 nutrient polymers
component material of EU fertilising products consisting of polymers exclusively made of monomer substances complying with the criteria set out in points 1 and 2 of CMC 1, where the purpose of the polymerization is to control the release of nutrients from one or more of the monomer substances

Note 1 to entry: See [3], Annex II, Part I and Part II.

3.4
CMC 1
component material of EU fertilising products consisting of virgin material substances and mixtures

Note 1 to entry: See [3], Annex II, Part I and Part II.

Note 2 to entry: Excluded are the following products: waste and by-products according to [4], materials formerly having constituted in waste or by-products, animal by-products or derived products and polymers.

3.5
cold water insoluble nitrogen
CWIN
insoluble nitrogen fractions in urea formaldehyde or methylene urea products that are insoluble in phosphate buffer solution (pH 7,5) or distilled water at 25 °C during a 15 min period

[SOURCE: ISO 19670:2017, 3.2]

3.6
cold water soluble nitrogen
CWSN
soluble nitrogen fractions in urea formaldehyde or methylene urea products that are soluble in phosphate buffer solution (pH 7,5) or distilled water at 25 °C during a 15 min period

Note 1 to entry: CWSN = Total nitrogen - CWIN.

[SOURCE: ISO 19670:2017, 3.3]

3.7
hot water insoluble nitrogen
HWIN
insoluble nitrogen fractions in urea formaldehyde or methylene urea products that are insoluble in phosphate buffer solution (pH 7,5) at 100 °C during a 30 min period

[SOURCE: ISO 19670:2017, 3.4]

3.8
hot water soluble nitrogen
HWSN
soluble nitrogen fractions in urea formaldehyde or methylene urea products and in nutrient polymers that are soluble in phosphate buffer solution (pH 7,5) at 100 °C during a 30 min period

Note 1 to entry: HWSN = Total nitrogen - HWIN.

[SOURCE: ISO 19670:2017, 3.5, modified – “and in nutrient polymers” has been added to the definition.]

3.9
hot water soluble nitrogen only
HWSN only
soluble nitrogen fractions in urea formaldehyde or methylene urea products that are soluble in

phosphate buffer solution (pH 7,5) at 100 °C during a 30 min period and insoluble in phosphate buffer solution (pH 7,5) or distilled water at 25 °C during a 15 min period

Note 1 to entry: HWSN only = HWSN – CWSN = CWIN - HWIN.

[SOURCE: ISO 19670:2017, 3.6]

4 Sampling and sample preparation

4.1 Sampling of products in bags and in bulk

Sampling is not part of the method specified in this document. Recommended sampling methods are given in EN 1482-1.

4.2 Reduction of samples

Reduction, labelling and sample preparation shall be carried out in accordance with EN 1482-2.

For the size reduction of samples to be used for the determinations according to Clause 5 and Clause 6 the laboratory sample shall be reduced to 100 g. Grind this test sample in the grinder. Avoid any warming of the sample on grinding. Take the portion of the grinded sample that passed at 0,500 mm sieve and pass it through a 0,212 mm sieve; use only the portion of the grinded sample that does not pass the 0,212 mm sieve. Put the prepared samples into clean and dry bottles to be used for further analysis.

5 Determination of the mass fraction of CWIN in solid UF/MU

5.1 Principle

Extraction of the test portion in phosphate buffer solution (pH 7,5) or distilled water at 25 °C. Filtration of the insoluble residue, washing and determination of the nitrogen content in the insoluble residue.

5.2 Reagents

5.2.1 Distilled water.

5.2.2 Phosphate buffer solution, pH 7,5.

Dissolve 14,3 g KH_2PO_4 and 91,0 g K_2HPO_4 in water and dilute to 1 l. Dilute 100 ml of this solution to 1 l.

5.2.3 Anhydrous ethanol.

5.2.4 Reagents listed in ISO 5315 for the determination of the nitrogen content.

5.3 Apparatus

5.3.1 Usual laboratory apparatus.

5.3.2 Water bath, capable of being maintained at (25 ± 2) °C.

5.3.3 Quantitative filter paper (intermediate speed), nitrogen free.

5.3.4 Apparatus listed in ISO 5315 for the determination of the nitrogen content.

5.4 Procedure

5.4.1 Two analyses shall be performed simultaneously for the determination.

5.4.2 Place 1 g to 1,4 g test portion (accurate to 0,000 1 g) in a 50 ml beaker and wet the test portion with ethanol (5.2.3). Add 20 ml phosphate buffer solution (5.2.2) or distilled water (5.2.1) and let stand for 15 min in the water bath maintained at (25 ± 2) °C (5.3.2) and stir at 5 min intervals during

standing. Transfer the supernate to a piece of filter paper (5.3.3) in long-stem funnel and wash the residue four or five times by decanting with water (5.2.1) at (25 ± 2) °C. Finally, transfer all the residue to the filter paper and complete washing with water (5.2.1) at (25 ± 2) °C until the filtrate measures 250 ml. Determine the nitrogen content in the filter paper and the residue in accordance with ISO 5315.

5.4.3 Carry out a blank test at the same time as the determination, using the same procedure, using the same reagents, but omitting the test portion.

5.5 Calculation and expression of results

The CWIN content, w_1, expressed as a mass fraction in percent, is given by Formula (1):

$$w_1 = \frac{(V_1 - V_2) \times c_1 \times 14{,}01}{m_1 \times 1000} \times 100 \qquad (1)$$

where:

V_1 is the volume, in millilitres, of sodium hydroxide standard solution used for the blank test;

V_2 is the volume, in millilitres, of sodium hydroxide standard solution used for the determination;

c_1 is the concentration, in mol per litres, of sodium hydroxide standard solution used;

m_1 is the mass, in grams, of the test portion.

The calculation results are accurate to two digits after the decimal point. The determination result is the arithmetic average of the duplicate determination results.

6 Determination of the mass fraction of HWIN in solid UF/MU

6.1 Principle

Extraction of the test portion in phosphate buffer solution (pH 7,5) (5.2.2) at 100 °C. Filtration of the insoluble residue, washing and determination of the nitrogen content in the insoluble residue.

6.2 Reagents

6.2.1 Reagents listed in 5.2.

6.2.2 Celite.

6.3 Apparatus

6.3.1 Usual laboratory apparatus.

6.3.2 Water bath, capable of being maintained at (100 ± 2) °C.

6.3.3 Apparatus listed in 5.3.3 and 5.3.4.

6.4 Procedure

6.4.1 Two analyses shall be performed simultaneously for the determination.
6.4.2 Place 0,5 g of the test portion (accurate to 0,000 1 g) in a 250 ml tall-form beaker. Add 100 ml of the phosphate buffer solution (5.2.2) at 100 °C using a graduated cylinder to the test portion, stir, cover with a watch glass and immerse promptly in a boiling water bath (6.3.2) so that the liquid in the beaker is below the water level in the water bath. Maintain the water bath at 100 °C, check with a thermometer and stir at 10 min intervals. After exactly 30 min, remove the beaker from the water bath and filter promptly through a piece of filter paper (5.3.3). If filtration takes more than 4 min, discard determination: in this case repeat the determination adding 1 g celite (6.2.2) as filter-aid just before removing the beaker from the water bath, stir and filter.

6.4.3 Wash the insoluble residue completely onto the filter paper with boiling water (5.2.1) and continue washing with water (5.2.1) at (100 ± 2) °C until the total volume used is 100 ml. Complete washing before the filtrate becomes cloudy or its temperature drops to below 60 °C. Determine total nitrogen in the filter paper and residue in accordance with ISO 5315.

6.4.4 Carry out a blank test at the same time as the determination, using the same procedure and reagents, but omitting the test portion.

6.5 Calculation and expression of results

The HWIN content, w_2, expressed as a mass fraction in percent, is given by Formula (2):

$$w_2 = \frac{(V_3 - V_4) \times c_2 \times 14{,}01}{m_2 \times 1\,000} \times 100 \qquad (2)$$

where:

V_3 is the volume, in millilitres, of sodium hydroxide standard solution used for the blank test;

V_4 is the volume, in millilitres, of sodium hydroxide standard solution used for the determination;

c_2 is the concentration, in mol per litres, of sodium hydroxide standard solution used;

m_2 is the mass, in grams, of the test portion.

The calculation results are accurate to two digits after the decimal point. The determination result is the arithmetic average of the duplicate determination results.

7 Determination of the solubility of nutrient polymers in phosphate buffer solution with a pH of 7,5 at 100 °C

The HWSN content, w_3, expressed as a mass fraction in percent, is given by Formula (3):

$$w_3 = w_4 - w_2 \qquad (3)$$

where:

w_2 is the HWIN content expressed as a mass fraction, in percent;

w_4 is the total nitrogen content expressed as a mass fraction, in percent.

8 Precision

8.1 Inter-laboratory tests

Inter-laboratory tests have been carried out in 20**. The number of participating laboratories and different fertilizer samples are mentioned in Annex A. Repeatability and reproducibility were calculated according to ISO 5725-2.

The values derived from these inter-laboratory tests may not be applicable to concentration ranges and matrices other than those given in Annex A.

8.2 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.

8.3 Reproducibility

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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 values of *R* given in Table 1.

Table 1 — Mean values, repeatability and reproducibility limits

Sample	$\bar{x}$ %	r %	R %
<to be added>			

9 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 document, including its year of publication;

c) the test results obtained;

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 occurred when performing the method, which might have influenced the test result(s).

Annex A
(informative)

Statistical results of the inter-laboratory tests

<to be added>

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*

[3] Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003

[4] Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives

[5] ISO 19670:2017, *Fertilizers and soil conditioners — Solid urea aldehyde slow release fertilizer — General requirements*

[6] Method BNL-N-12*, Determination of the activity index and of nitrogen insoluble in cold water*