SLOVENSKI STANDARD

SIST-TS CEN/TS 15604:2008

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Gnojila - Določevanje različnih oblik dušika v istem vzorcu, ki vsebuje dušik v obliki nitrata, amonija, sečnine in cianoamida

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

Düngemittel - Bestimmung verschiedener, nebeneinander anwesender Stickstoff-Formen in derselben Probe mit Stickstoff in Form von Ammonium, Nitrat, Harnstoff und Cyanamid

Engrais - Détermination des différentes formes d'azote dans un meme échantillon contentant l'azote sous forme nitrique, ammoniacale, uréique et cyanamidique

Ta slovenski standard je istoveten z: **CEN/TS 15604:2007**

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65.080

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TECHNICAL SPECIFICATION

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CEN/TS 15604

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ICS 65.080

English Version

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COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This document (CEN/TS 15604:2007) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This Technical Specification 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 Annex I of the Regulation (EC) No 2003/2003 [1] containing nitrogen in various forms.

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*

CEN/TS 15475, *Fertilizers — Determination of ammoniacal nitrogen*

CEN/TS 15562, *Fertilizers — Determination of cyanamide nitrogen*

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

4.1 Total soluble and insoluble nitrogen

According to the list of standard fertilizers given in Annex I of [1], 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 CEN/TS 15475.

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 [1], Annex I.

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 CEN/TS 15475).

4.2.2.2 In the presence of nitrates, by Kjeldahl digestion on an aliqot part taken from the solution after reduction according to Ulsch. The ammonia is then determined (by the same method as that described in CEN/TS 15475).

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 sulphate. The ammonia is then determined (by the same method as that described in CEN/TS 15475).

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 (4.2.2.2) 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 + 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 CEN/TS 15475.

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 CEN/TS 15475.

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 EN ISO 3696:1995.

5.2 Potassium sulfate

p.a.

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 Diluted sulfuric acid

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

5.9 Standard solution of sulfuric acid

c = 0,1 mol/l

5.10 Sodium hydroxide solution

aqueous solution of about 30 % (mass concentration), free from ammonia

5.11 Standard solution of sodium or potassium hydroxide

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 (ρ_{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 (ρ_{20} = 1,18g/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 a 0,1 mol/l iodine solution in the presence of a starch solution as an indicator.

1 ml of 0,1 mol/l iodine solution corresponds to 0,01128 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 0,1 mol/l iodine solution shall therefore be used.

5.13 Sulfuric acid

ρ_{20}= 1,84 g/ml

5.14 Diluted hydrochloric acid

one volume of hydrochloric acid (ρ_{20} = 1,18 g/ml) plus 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 Standard sulfuric acid solution

c = 0,05 mol/l

5.19 Octyl alcohol

5.20 Saturated solution of potassium carbonate

5.21 Standard solution of sodium or potassium hydroxide

c = 0,1 mol/l (free from carbonates)

5.22 Saturated solution of barium hydroxide

5.23 Sodium carbonate solution

at 10 % (mass concentration)

5.24 Hydrochloric acid

c = 2 mol/l

5.25 Standard solution of hydrochloric acid

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

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

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.