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Fertilizers — Determination of 1H-1,2,4-triazole in urea and in fertilizers containing urea — Method using high-performance liquid chromatography (HPLC)

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Engrais - Dosage du 1H-1,2,4-triazole dans l'urée et les engrais contenant de l'urée - Méthode par chromatographie liquide à haute performance (HPLC)

Düngemittel - Bestimmung von 1H-1,2,4-Triazol in Harnstoff und harnstoffhaltigen Düngemitteln - Verfahren mit Hochleistungs-Flüssigchromatographie (HPLC)

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Foreword

This document (EN 16024:2011) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2011, and conflicting national standards shall be withdrawn at the latest by October 2011.

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1 Scope

This European Standard specifies a method for the determination of triazole (TZ) in urea or in fertilizers containing urea in the presence of dicyandiamide or methylpyrazole respectively using high-performance liquid chromatography (HPLC).

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*

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

The sample of fertilizer is dissolved in water or extracted with water. The triazole content is determined in the solution using reversed phase high-performance liquid chromatography with an electrochemical pulsed detector.

5 Reagents

Use only reagents of recognized analytical grade.

5.1 Water, distilled or demineralised, conductivity less than 0,5 mS/m, according to EN ISO 3696:1995, grade 3.

5.2 1H-1,2,4-triazole.

5.3 Triazole standard solution, ρ=1 g/l.

Weigh 1 g of triazole to the nearest of 0,1 mg into a 1 000 ml measuring flask. Dissolve with water, make up to the mark with water and mix well.

5.4 Acetonitrile, gradient grade.

5.5 Buffer solution.

Weigh 8,9 g of dipotassium hydrogen phosphate trihydrate and 35,93 g of potassium dihydrogen phosphate in a 1 000 ml measuring flask, add approximately 750 ml of water, dissolve in the ultrasonic bath and make up to the mark with water.

6 Apparatus

6.1 Analytical balance, measuring accuracy 0,01 mg.

6.2 Ultrasonic bath.

6.3 Syringe filter, for aqueous solutions; pore size 0,25 µm.

6.4 HPLC device.

6.5 Sampling issuing system.

6.6 Electrochemical detector.

— Working electrode: gold,

— Reference electrode: Ag+AgCl, 3 mol/l KCl.

6.7 Reversed phase HPLC separator column, e. g. C8 10 µm, 250 mm × 4 mm.

6.8 Laboratory glassware.

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 test solution

Weigh approximately 0,2 g of the sample (m) in a 100 ml volumetric flask to the nearest 0,1 mg, add approximately 70 ml of water (5.1), dissolve in the ultrasonic bath (6.2) and make up to the mark with water (5.1). Filtrate this solution straight into a vial through a syringe filter (6.3) to remove any conditioning agents. This solution is used for the determination.

8.2 Preparation of the calibration solutions

To obtain the calibration curve, prepare the following dilution series according to Table 1 from the triazole standard solution (5.3) (each in a 100 ml measuring flask):

Table 1 — Preparation of the dilution series

Mass concentration of triazole mg/l	**Volume of standard solution (5.3)** µl
0,1	10
0,3	30
0,7	70
1,0	100
3,0	300
5,0	500
7,0	700
10,0	1 000

8.3 HPLC conditions

Separation column: filling for reversed phase HPLC (6.7)

Column temperature: 20 °C

Elution agent: buffer solution (5.5) / acetonitrile (5.4) mixture 85 + 15 (volume fraction)

Flow rate: 0,7 ml/min

Injection volume: 10 µl

Detector programme: according to Table 2

Table 2 — Detector programme

waveform time s	potential	integration
0,00	0,25 V	
0,30	0,25 V	begin
0,60	0,25 V	end
0,61	1,00 V	
0,80	1,00 V	
0,81	-0,60 V	
1,00	-0,60 V	

The elution agent shall be degassed, e. g. in the ultrasonic bath (6.2).

8.4 HPLC determination

To determine the calibration curve, inject an amount of 10 µl of each calibration solution (see 8.2) three times. The calibration curve may be used for the content determination when the correlation coefficient exceeds 0,99.

NOTE The correlation coefficient is calculated in accordance with the method of smallest squares.

To verify the equipment system, inject a calibration solution, prepared according to 8.2, with a content of 1 mg/l triazole and inject 10 µl three times in succession. Once the determined content is within the tolerance of ± 0,05 mg/l (5 % rel.) , the equipment system satisfies the requirements for continuing the measurements on the test solution. Inject 10 µl of the test solution three times in succession.

Special care has to be taken to obtain good peak separation in order to avoid interference from other substances present in the sample.

9 Calculation and expression of the results

9.1 Calculation

Carry out the evaluation on the basis of the calibration curve over the peak areas.

Calculate the mass fraction of 1H-1,2,4-triazole, w_{TZ}, in percent according to the following equation:

$$w_{TZ} = \frac{(A_{pk} - b) \times F_d \times 100}{a \times m} \quad (1)$$

where

A_{pk} is the peak area;

b is the ordinate section of the calibration curve;

a is the slope of the calibration curve;

F_d is the dilution factor;

m is the mass of the test portion, in milligrams.

9.2 Expression of results

Calculate the arithmetic mean from both values obtained. Indicate the result to the nearest 0,001 %.

10 Precision

10.1 Inter-laboratory test

An inter-laboratory test has been carried out in 2009 with 8 participating laboratories and 4 different samples of fertilizers. This test yielded the data given in Annex A. Repeatability and reproducibility were calculated according to ISO 5725-1 and ISO 5725-2.

The values derived from this inter-laboratory test may 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 3.

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 3.

Table 3 — Mean values, repeatability and reproducibility limits

Sample	$\bar{x}$	r	R
UAN 1	0,057 6	0,002 4	0,007 4
UAN 2	0,071 8	0,00 40	0,021 1
Urea 1	0,063 6	0,004 83	0,020 9
Urea 2	0,070 1	0,005 68	0,019 5

11 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;

c) the test results obtained;

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

Annex A
(informative)

Statistical results of the inter-laboratory test

The precision of the method has been determined in the year 2009 in an inter-laboratory test with eight laboratories participating and carried out on four samples of fertilizer. The statistical results are given in Table A.1.

Table A.1 — Statistical results of the inter-laboratory test

Parameter	UAN 1	UAN 2	Urea 1	Urea 2
Year of the test	2009	2009	2009	2009
Number of participating laboratories	8	8	8	8
Number of laboratories after eliminating outliers	7	7	5	5
mean value, $\bar{x}$, (%)	0,057 6	0,071 8	0,063 6	0,070 1
Repeatability standard deviation s_r, (%)	0,000 88	0,001 45	0,001 74	0,002 05
RSD_r (%)	1,52	2,02	2,74	2,92
Repeatability limit r (2,77 s_r) (%)	0,002 4	0,004 0	0,004 83	0,005 68
Reproducibility standard deviation, s_R (%)	0,002 68	0,007 61	0,007 55	0,007 02
RSD_R (%)	4,66	10,60	11,87	10,02
Reproducibility limit R (2,77 s_R) (%)	0,007 4	0,021 1	0,020 9	0,019 5

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[3] EN 15905, *Fertilizers — Determination of 3-methylpyrazole (MP) using high-performance liquid chromatography (HPLC)*

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[5] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[6] Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers, Official Journal L 304, 21/11/2003 P. 0001-0194

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