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BRITISH STANDARD

BS EN 15905:2010

Fertilizers — Determination of 3-methylpyrazole (MP) using high-performance liquid chromatography (HPLC)

ICS 65.080

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EN 15905

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English Version

Fertilizers - Determination of 3-methylpyrazole (MP) using high-performance liquid chromatography (HPLC)

Engrais - Dosage du 3-méthylpyrazole (MP) par chromatographie liquide à haute performance (HPLC)

Düngemittel - Bestimmung von 3-Methylpyrazol (MP) mit Hochleistungs-Flüssigchromatographie (HPLC)

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Foreword

This document (EN 15905:2010) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

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1 Scope

This European Standard specifies a method for the determination of the 3-methylpyrazole (MP) content in fertilizers, in particular in urea and materials containing urea 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*[1)] (including corrigendum AC:2000)

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 3-methlypyrazole is determined in the solution using reversed phase high-performance liquid chromatography with an UV detector.

5 Reagents

Use only reagents of recognized analytical grade and distilled or demineralized water (grade 3 according to EN ISO 3696:1995).

5.1 Acetonitrile, HPLC purity.

5.2 De-ionized water, conductivity less than 0,5 mS/m according to ISO 3696, grade 3.

5.3 3-methylpyrazole.

6 Apparatus

6.1 Analytical balance, measuring accuracy 0,1 mg or better.

1) See corrigendum EN 12944-2:1999/AC:2000 which corrects EN 12944-2:1999.

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6.2 Ultrasonic bath.

6.3 Filtration equipment, (manual or pressure filtration).

6.4 Membrane filter, pore size 0,45 µm or smaller.

NOTE For samples which are difficult to filter, to the purpose a pressure filtration can be used.

6.5 Volumetric flasks,100 ml, 1 000 ml.

6.6 HPLC device, for isocratic working procedure.

6.7 Sample issuing system.

6.8 UV detector.

6.9 Evaluation unit, e.g. electronic integrator.

6.10 Reversed phase HPLC separator column, e.g. C18 10 µm, 250 mm × 4 mm.

NOTE With suitable separation performance, it is also possible to use a shorter separation column. Instead of a C18 column, a separation column with hydroxyl phase can be used.

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 a test portion corresponding to approximately 8 mg of 3-methlypyrazole into a 1 000 ml volumetric flask. Add approximately 750 ml of water (5.2) and dissolve in the ultrasonic bath (6.2). Make up to the mark with water (5.2) and filter a part of the sample solution through a membrane filter (6.3, 6.4) in order to remove any un-dissolved substances which may still be present. This solution is used for the determination.

NOTE The amount of ammonium nitrate-urea solution weighed in is 10 g, precise to 10 mg. For solid fertilizers, for reasons of homogeneity, an amount weighed in should be used of 100 g, precise to 0,1 g. In this case, the dilution of the filtrate by 1+9 is necessary; this is to be taken into account during the calculation.

8.2 Preparation of the calibration solutions

Weigh 1 g of 3-methylpyrazole (5.3) to the nearest of 0,1 mg into a 1 000 ml volumetric flask. Dissolve with water (5.2), make up to the mark with water (5.2) and mix well. Pipette 10 ml of this solution into a 100 ml volumetric flask, make up to the mark with water (5.2) and mix well. Pipette 5 ml, 10 ml, and 15 ml of this solution into three 100 ml volumetric flasks. Make up each flask to the mark with water (5.2) and mix well. Take the solutions to create the calibration curve.

8.3 HPLC conditions

Separation column: filling for reversed phase HPLC

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Column temperature:	room temperature
Elution agent:	water/acetonitrile (5.1) mixture 80+20 (volume fraction)
Flow rate:	0,8 ml/min to 1,2 ml/min
Injection volume:	20 µl
Wavelength:	214 nm

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 20 µl of each calibration solution (see 8.2) three times. The calibration curve can be used to for the content determination if the correlation coefficient ≥ 0,99.

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

Inject the test solution two times in succession.

9 Calculation and expression of the results

9.1 Calculation

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

Calculate the mass fraction of 3-methylpyrazole, w_{MP}, in percent according to the following equation:

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

where

A_{pk} is the peak height or peak area;

b is the ordinate section of calibration curve;

a is the rise 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 %.

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10 Precision

10.1 Inter-laboratory test

An inter-laboratory test has been carried out in 2008 with 9 participating laboratories and 2 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 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 values, repeatability and reproducibility limits

Sample	$\bar{x}$	r	R
Liquid sample 1	0,030 4	0,000 3	0,003 9
Liquid sample 2	0,034 5	0,000 9	0,003 9

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).

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Annex A
(informative)

Results of the inter-laboratory test

The precision of the method has been determined in the year 2008 in an inter-laboratory trial with 9 laboratories participating and carried out on 2 different liquid samples of fertilizer. The statistical results are given in Table A.1.

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

Parameter	Liquid sample 1	Liquid sample 2
Year of the test	2008	2008
Number of participating laboratories	9	9
Number of laboratories after eliminating outliers	8	9
mean value, $\bar{x}$, (%) (mass fraction)	0,030 4	0,034 5
Repeatability standard deviation s_r, (%) (mass fraction)	0,000 1	0,000 3
RSD_r (%) (mass fraction)	0,30	0,93
Repeatability limit r (2,83 s_r) (%) (mass fraction)	0,000 3	0,000 9
Reproducibility standard deviation, s_R (%) (mass fraction)	0,001 4	0,001 4
RSD_R (%) (mass fraction)	4,63	4,03
Reproducibility limit R (2,83 s_R) (%) (mass fraction)	0,003 9	0,003 9

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

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

[3] 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*

[4] *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. 1-194

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