

**Fertilizers —
Determination of urea
condensates using
high-performance
liquid chromatography
(HPLC) —
Isobutylidenediurea
and
crotonylidenediurea
(method A) and
methylen-urea
oligomers (method B)**

ICS 65.080

National foreword

This Draft for Development is the UK implementation of CEN/TS 15705:2009.

This publication is not to be regarded as a British Standard.

It is being issued in the Draft for Development series of publications and is of a provisional nature. It should be applied on this provisional basis, so that information and experience of its practical application can be obtained.

Comments arising from the use of this Draft for Development are requested so that UK experience can be reported to the international organization responsible for its conversion to an international standard. A review of this publication will be initiated not later than 3 years after its publication by the international organization so that a decision can be taken on its status. Notification of the start of the review period will be made in an announcement in the appropriate issue of Update Standards.

According to the replies received by the end of the review period, the responsible BSI Committee will decide whether to support the conversion into an international Standard, to extend the life of the Technical Specification or to withdraw it. Comments should be sent to the Secretary of the responsible BSI Technical Committee at British Standards House, 389 Chiswick High Road, London W4 4AL.

The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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English Version

Fertilizers - Determination of urea condensates using high-performance liquid chromatography (HPLC) - Isobutylidenediurea and crotonylidenediurea (method A) and methylen-urea oligomers (method B)

Engrais - Dosage des condensats d'urée par chromatographie liquide haute performance (HPLC) - Isobutylidène diurée et crotonylidène diurée (méthode A) et oligomères de méthylène-urée (méthode B)

Düngemittel - Bestimmung von Harnstoffkondensaten mit Hochleistungs-Flüssigchromatographie (HPLC) - Isobutylidendiarnstoff und Crotonylidendiarnstoff (Verfahren A) und Methylenharnstoff-Oligomere (Verfahren B)

This Technical Specification (CEN/TS) was approved by CEN on 15 November 2008 for provisional application.

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Foreword

This document (CEN/TS 15705:2009) 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 document specifies methods for the determination of isobutylidenediurea (IBDU), crotonylidenediurea (CDU) (method A) and methylene-urea oligomers (MU) (method B) in fertilizers using high-performance liquid chromatography (HPLC).

The method is applicable for all fertilizers which do not contain interfering organic compounds.

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 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 [1].

Sample preparation shall be carried out in accordance with EN 1482-2.

5 Method A: Determination of CDU and IBDU

5.1 Principle

The sample is extracted with water and, after appropriate dilution, analyzed using a suitable HPLC system.

5.2 Reagents

5.2.1 General

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

5.2.2 Acetonitrile, p.a., HPLC-grade;

5.2.3 Isobutylidenediurea and crotonylidenediurea, in their pure form.

5.3 Apparatus

5.3.1 Laboratory equipment and glassware, for preparation of solutions and dilutions;

5.3.2 Analytical balance, capable for weighing to an accuracy of $\pm 0,1$ mg;

5.3.3 HPLC-system, with UV-detector;

5.3.4 Ultrasonic bath;

5.3.5 Magnetic stirrer;

5.3.6 Disposable filter, $0,45\ \mu\text{m}$.

5.4 Procedure

5.4.1 System parameters of HPLC

Analytical/separating column: silica column with C18 reverse phase ¹

Detection wavelength: 200 nm

Eluent: acetonitrile/water: 10/90 (volume fraction)

Flow rate: 1 ml/min

Temperature: ambient temperature

Injection volume: 20 μl

5.4.2 Calibration

5.4.2.1 Stock solution IBDU $\rho(\text{IBDU}) = 100\ \text{mg/l}$

Weigh $100/R$ mg of IBDU (5.2.3), where R is the purity of IBDU, into a 1 000 ml flask and add about 900 ml of water (5.2.1). Dissolve in an ultrasonic bath (5.3.4) for about 10 min, followed by stirring on a magnetic stirrer (5.3.5) for about 1 h. Make up to volume. Filtration is not necessary.

5.4.2.2 Stock solution CDU $\rho(\text{CDU}) = 100\ \text{mg/l}$

Weigh $100/R$ mg of CDU (5.2.3), where R is the purity of CDU, into a 1 000 ml flask and add about 900 ml of water (5.2.1). Dissolve in an ultrasonic bath (5.3.4) for about 10 min, followed by stirring on a magnetic stirrer (5.3.5) for about 1 h. Make up to volume. Filtration is not necessary.

¹ E.g. LiChrosorb RP-18 $7\ \mu\text{m}$ 250/4 mm or equivalent.

5.4.2.3 Calibration solution

For calibration, prepare three solutions according to Table 1 using one-mark (bulb) pipettes and dilute to the mark with water (5.2.1).

For the determination of the retention time, dilute 10 ml of the stock solution 5.4.2.1 or respectively 5.4.2.2 into two 100 ml flasks and make up to volume with water (5.2.1).

The evaluation of calibration is carried out manually or by means of a suitable PC-aided (computerized) calculation method.

Table 1 — Preparation of calibration solutions

Parameter	Amount of stock solution IBDU/CDU ml (to be added to the 100 ml flask)	Content of IBDU mg/l	Content of CDU mg/l
Standard1	10	10,0	10,0
Standard 2	25	25,0	25,0
Standard 3	50	50,0	50,0

5.4.3 Preparation of the test portion

Weigh 1 g of the sample grounded to < 0,2 mm to the nearest 0,1 mg and flush into a 1 000 ml volumetric flask with water (5.2.1). Fill the flask to an amount of approximately 900 ml and treat it for 10 min in the ultrasonic bath (5.3.4). Then make up to the mark and stir for 1 h at room temperature on a magnetic stirrer (5.3.5). Dilute 10 ml of the solution in a 100 ml volumetric flask and filter into the HPLC injection vial through a disposable filter (5.3.6).

5.4.4 Measurement

Measurement is performed manually or by means of an automatic sample loading system (autosampler).

5.4.5 Important annotations

IBDU is able to form urea in aqueous solution. Therefore, the measurement of the calibration and sample solutions shall be completed within one working day.

The concentrations of CDU and IBDU in the sample solutions shall be kept within the calibration limits (5.4.2) to ensure sufficient reproducibility.

5.5 Calculation

The calculation can be performed manually or by means of a PC using the calibration parameters in respect to the amount used.

In the case of PC-aided (computerized) calculation and application of Table 1 regarding the amounts of stock solution, the content of IBDU/CDU in milligrams per litre will be calculated by the system. The calculated values are equal to the percentage mass concentration of IBDU/CDU in the analysed sample of fertilizer.