

Fertilizers — Determination of chelating agents in fertilizers by chromatography —

Part 2: Determination of Fe chelated by o,o-EDDHA and o,o-EDDHMA by ion pair chromatography

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National foreword

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Düngemittel - Bestimmung von Chelatbildnern in Düngemitteln mit Chromatographie - Teil 2: Bestimmung von Fe chelatisiertem o,o-EDDHA und o,o-EDDHMA mit Ionen-Paarchromatographie

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Contents

Page

Foreword.....	3
1 Scope	4
2 Normative references	4
3 Principle	4
4 Interferences	5
5 Reagents	5
6 Apparatus	6
7 Preparation of the sample.....	7
8 Procedure	7
9 Expression of the results (Fe in Fe-chelates)	11
10 Precision	11
11 Test report	13
Annex A (informative) General procedure for the determination of the titrimetric purity of the chelating agents using a photometric automatic titrator	14
Annex B (informative) Results of the inter-laboratory test	15
Annex C (informative) Complete names of chelating agents	17
Bibliography	18

Foreword

This document (EN 13368-2:2007) 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of an identical text or by endorsement, at the latest by October 2007, and conflicting national standards shall be withdrawn at the latest by October 2007.

This document supersedes EN 13368-2:2001.

EN 13368:2001 consisted of two parts:

- Fertilizers — Determination of chelating agents in fertilizers by ion chromatography — Part 1: EDTA, HEDTA and DTPA
- Fertilizers — Determination of chelating agents in fertilizers by ion chromatography — Part 2: EDDHA and EDDHMA

For technical reasons, the second element in the title of this document has been modified (the word “ion” has been deleted). Consequently, the title of Part 1 of EN 13368 should be revised in the same way. There is agreement that the replacement of Part 1 by a new edition only for harmonization of the title should be avoided. Therefore, it is proposed to harmonize the title within the next revision procedure.

Following the revised title of Part 2, the title of EN 13368-1 should be revised as follows:

- Fertilizers — Determination of chelating agents in fertilizers by chromatography — Part 1: Determination of EDTA, HEDTA and DTPA

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: 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 United Kingdom.

1 Scope

This document specifies a method for the chromatographic determination of the iron chelated by each individual ortho(hydroxy)-ortho(hydroxy) isomer of the chelating agents o,o-EDDHA and o,o-EDDHMA in fertilizers containing one or both of these substances. The method allows the identification and the determination of the total concentration of water soluble iron chelates of these chelating agents. It does not determine the free form of the chelating agents.

NOTE 1 The substances EDDHA (ethylene diamine di(hydroxy phenyl) acetic acid) and EDDHMA (ethylene diamine di(hydroxy methyl phenyl)acetic acid) exist as several different isomeric forms. Positional isomers for the hydroxyl or methyl groups (in ortho, meta, and para positions) as well as stereo isomers (meso and dl-racemic forms) are known. Both meso and dl-racemic forms of the ortho,ortho-EDDHA and ortho,ortho-EDDHMA are positional isomers for the hydroxyl groups allowed by the Regulation (EC) No 2003/2003. Since para, meta and ortho methyl positional isomers of the EDDHMA present quite similar stability, they could be grouped: in the method here described the para, meta and ortho methyl positional isomers of the o,o-EDDHMA are considered together.

NOTE 2 At present, analytically pure standards only exist for ortho,ortho-EDDHA and ortho,ortho-EDDHMA. All other substances being unavailable as a standard, the influence of their eventual presence in the samples (with respect to the sensitivity and the selectivity of this method) has not been studied.

NOTE 3 The meso and the dl-racemic forms of o,o-EDDHA and o,o-EDDHMA can be determined separately by this method.

This procedure concerns EC fertilizers covered by Regulation (EC) No 2003/2003 [5]. It is applicable to a mass fraction of the metal chelated of at least 0,625 %.

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 ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Principle

The iron chelates are separated and determined by isocratic ion-pair high-performance liquid chromatography. When an iron chelate (anion) is added to a polar fluid (eluent), containing a large cation, an ion pair is formed. This ion pair is retained by an apolar solid phase (stationary phase). The strength of the retention depends on the molecular size and its acidity. Then, each iron chelate presents a characteristic retention time depending on the chelating agent, and it is separated from the other substances present in the sample. The separation is carried out on a reverse phase silica column and an aqueous solution of TBA⁺ (tetrabutylammonium) and acetonitrile as eluent. The detection is based on photometry at 280 nm.

NOTE For additional information see [3] and [4].

4 Interferences

No interferences have been detected. Iron chelates with HBED, HBEP, EDDHSA, EDTA, DTPA, CDTA, HEDTA, p,p-EDDHA, o,p-EDDHA, as well as the chelating agents do not interfere since they are separated from Fe-o,o-EDDHA and Fe-o,o-EDDHMA.

NOTE For the complete names of the abbreviations of chelating agents used in this document see Annex C.

5 Reagents

5.1 General

- a) All reagents shall be of recognized analytical grade;
- b) all water used for the preparation of eluent, standards, and sample solutions shall conform to EN ISO 3696, grade 1 and shall be degassed, and free of organic contaminants;
- c) if for the preparation of standard solutions products with a declared purity of less than 99 % are used, a correction should be made in order to obtain exactly the required concentration in the solution.

If there is any doubt of the purity of the standard, it is necessary to determine it.

NOTE For this determination a titrimetric method can be used. See Annex A for a general method using an automatic titrator. Manual titration could be also adequate.

5.2 Sodium hydroxide solution,

$c(\text{NaOH}) = 0,1 \text{ mol/l}$.

Dissolve 4 g of NaOH in pellet form in a 1 litre volumetric flask with water (see 5.1 b)). Dilute to the mark and homogenize.

NOTE The incorporation of CO_2 from the atmosphere should be carefully avoided. Otherwise dissolution of chelating agents (see 5.5) can be incomplete.

5.3 Hydrochloric acid solution,

$c(\text{HCl}) = 1,0 \text{ mol/l}$.

Dilute 88 ml of hydrochloric acid (mass fraction 35 % HCl) to 1 000 ml with water.

5.4 Hydrochloric acid solution,

$c(\text{HCl}) = 0,1 \text{ mol/l}$.

Dilute 50 ml of hydrochloric acid 1,0 mol/l (5.3) to 500 ml with water.