BRITISH STANDARD

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Fertilizers — Treatment with a cation exchange resin for the determination of the chelated micro-nutrient content and of the chelated fraction of micro-nutrients

The European Standard EN 13366:2001 has the status of a British Standard

ICS 65.080

Confirmed
August 2010

National foreword

This British Standard is the official English language version of EN 13366:2001.

The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilizers and related chemicals, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

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English version

Fertilizers — Treatment with a cation exchange resin for the determination of the chelated micro-nutrient content and of the chelated fraction of micro-nutrients

Engrais — Traitement avec une résine échangeuse d'ions cationique pour la détermination de la teneur en oligo-éléments chélatés et de la fraction chélatée des oligo-éléments

Düngemittel — Behandlung mit einem Kationenaustauscherharz zur Bestimmung des chelatisierten Spurennährstoffgehaltes und des chelatgebundenen Anteils von Spurennährstoffen

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Contents

Foreword

This European Standard 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of an identical text or by endorsement, at the latest by July 2001, and conflicting national standards shall be withdrawn at the latest by July 2001.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This standard defines a method for the treatment with a cation exchange resin for the determination of the chelated micro-nutrient content and the chelated fraction of the micro-nutrients (trace elements) cobalt, copper, iron, manganese, and zinc in fertilizers.

This method applies to fertilizers containing one or more of the micro-nutrients cobalt, copper, iron, manganese, and zinc, chelated by one or more chelating agents of the group of the polyamino polycarboxylic acids, previously determined according to EN 13368-1 and EN 13368-2, either alone or in combination with primary (N, P, K) and/or secondary (S, Na, Ca, Mg) nutrients.

The limit of determination of the chelated micro-nutrient content varies between 0,005 % in simple matrices with high amounts of chelated micro-nutrients, and 0,5 % in more complex cases (see 7.2).

2 Normative references

This European standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European standard only when incorporated in it by amendment or revision. For undated references, the latest edition of the publication referred to applies (including amendments).

EN 1482, *Sampling of solid fertilizers and liming materials*.

EN 13368-1, *Fertilizers — Determination of chelating agents in fertilizers by ion chromatography — Part 1:EDTA, HEDTA and DTPA.*

EN 13368-2, *Fertilizers — Determination of chelation agents in fertilizers by ion chromatography — Part 2:EDDHA and EDDHMA.*

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

3 Terms and definitions

For the purposes of this standard the following terms and definitions apply:

3.1
chelated fraction
chelated content of a micro-nutrient, divided by its total content, and expressed as a percentage

4 Principle

The sample is extracted with water and the extract adjusted to a neutral pH. The chelated forms of an element thus having a negative and/or neutral charge are not retained by an ion exchange resin of the strong sulfonated cationic type, and are separated from the non-chelated forms, having a cationic nature. The chelated forms are collected and their content determined by spectrometry, as well as the total element content.

5 Interferences

Any substance combining with a micro-nutrient to form a stable, negative or uncharged compound (chelate or complex) at neutral pH, will prevent the retention by the resin, and account for a certain degree of chelation. This is the case for many complexing agents, e.g. amino acids, citrate, and for chelating agents other than ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetetraacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediamine-di-(o-hydroxyphenyl)acetic acid (EDDHA) and ethylenediamine-di-(o-hydroxy-p-methylphenyl)acetic acid (EDDHMA).

NOTE In order to confirm the presence of the statutory chelating agents in the sample, EN 13368-1 and EN 13368-2 should be applied.

In some cases, especially where complex fertilizer matrices with high amounts of phosphate are handled, or where micro-nutrients with a low chelated fraction are present, slow precipitation reactions can occur during the contact with the resin, causing equilibrium shifts, adsorption, decreasing the exchange capacity and leading to inaccurate and imprecise results. It is advised to proceed as soon as possible with all steps. Highly unstable solutions cannot be considered.

6 Apparatus

NOTE All glassware, filters, and equipment parts coming in contact with samples and solutions, should be appropriate for micro-nutrient analysis, be very clean and free from contamination, especially by the elements Co, Cu, Fe, Mn and Zn.

Usual laboratory equipment and in particular:

6.1 Sieve, sieve having a plastic body and a nylon mesh of aperture size less than the minimum diameter of the resin particles. The mass of the dry sieve shall be determined to within 0,01 g.

6.2 Tumbling shaker, tumbling or rotary shaker operating at a rotational speed between 30 min^{-1} and 40 min^{-1}, at a temperature of 18 °C to 22 °C.

6.3 Conductivity meter, equipped with a conductivity cell and a temperature controller. The cell shall be rinsed and dried before immersion, and calibrated with a 0,01 mol/l potassium chloride solution, having a specific conductivity at 20 °C of 1,28 mS/cm.

6.4 Shaking flasks, polyethylene flasks, each having a capacity of 50 ml and a stopper.

6.5 Membrane filters, micromembrane filters resistent to aqueous solutions, with porosity of 0,45 µm.

7 Reagents

7.1 General

a) all water used should conform to EN ISO 3696 and be degassed by boiling before use;

b) all reagents should be of recognized analytical grade.

7.2 Sulfonated cationic exchange resin

7.2.1 General

Polystyrene divinylbenzene (PS-DVB) copolymer, slightly crosslinked (mass fraction of DVB less than or equal to 8 %), in sodic or protonic form, free from Co, Cu, Fe, Mn, and Zn[1)].

7.2.2 Preparation and determination of exchange capacity

Protonate the resin prior to use, transform to the sodic form, to eliminate any contamination and measure the cationic exchange capacity (CEC) of the sodic resin in wet form as follows:

— Transfer 50 g of resin to a 500 ml beaker and add 250 ml of hydrochloric acid solution (7.4).

— Place on a magnetic stirrer.

— After 1 h of moderate stirring, the suspension is transferred onto the sieve (6.1).

— The resin is recovered and transferred back to the beaker.

— The acidification and separation operations are repeated as described.

— At the end of the second operation, the protonated resin present on the sieve is washed thoroughly with water until the rinsing water is free from chloride when tested with silver nitrate.

— Transfer the wet protonated resin into a 500 ml beaker and add 250 ml of sodium chloride solution (7.5).

— While stirring on a magnetic stirrer and using a pH meter, titrate the resin using the sodium hydroxide solution (7.6) until a stable pH of 7,0 is obtained.

— Let V_0 be the required volume of NaOH (7.6), in millilitres.

— Transfer quantitatively the resin that is now in sodic form onto the sieve (6.1).

— Rinse thoroughly with water until the rinsing water is free from chloride (silver nitrate test).

— Once rinsing is complete, allow the resin to drain.

— Weigh the drained wet resin to within 0,01 g. Let P be the mass in grams.

— The wet sodic resin can be stored in a stoppered opaque flask at ambient temperature for 2 years.

The cationic exchange capacity of the resin is given by the following formula:

$$CEC = 2 \cdot V_0 / P$$

where:

CEC is the cationic exchange capacity, in millimoles per gram of wet resin

7.3 Hydrochloric acid, *c*(HCl) ≈ 6 mol/l

Hydrochloric acid, diluted 1 + 1 with water.

7.4 Hydrochloric acid solution, *c*(HCl) = 1 mol/l

Dilute 165 ml of hydrochloric acid solution (7.3) to 1 l.

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1) Dowex 50 x 4-400, Amberlite IR 120 or equivalent are examples of suitable products available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products.

7.5 Sodium chloride solution, *c*(NaCl) = 1 mol/l

Dissolve 58,4 g of NaCl in water and dilute to 1 l.

7.6 Sodium hydroxide solution, *c*(NaOH) = 2 mol/l

Carefully dissolve 80,0 g of NaOH in water and dilute to 1 l.

7.7 Sodium hydroxide solution, *c*(NaOH) = 0,1 mol/l

Dilute 25 ml of the sodium hydroxide solution (7.6) to 500 ml.

7.8 Nitric acid solution, *c*(HNO_3) = 0,1 mol/l

Carefully dilute 6,9 ml of nitric acid (65 % HNO_3 , ρ = 1,40 g/ml) to 1 l.

7.9 Sodium hydroxide solution, *c*(NaOH) = 0,01 mol/l

Dilute 50 ml of the sodium hydroxide solution (7.7) to 500 ml.

7.10 Nitric acid solution, *c*(HNO_3) = 0,01 mol/l

Dilute 50 ml of the nitric acid solution (7.8) to 500 ml.

8 Procedure

8.1 Preparation of the sample

Prepare the sample according to EN 1482.

NOTE 1 Sample may also be prepared according to method 1 (see [1] of bibliography).

NOTE 2 For the size reduction of samples with a high amount of chelating agents, it is not recommended to use a high speed laboratory mill. It is more convenient to grind the sample in a mortar to a particle size less than 1 mm.

8.2 Extraction of the sample

— Weigh an amount of sample, depending on the declared content of water soluble micro-nutrient, to within 1 mg, into a volumetric flask of 250 ml or 500 ml, according to Table 1:

Table 1 — Sample mass/volume ratios

Micro-nutrient content (%)	< 0,01	0,01 - < 5	> 5
Mass of sample E (g)	10	5	2
Volume of the extract V (ml)	250	500	500

— Add about 200 ml of water for a 250 ml flask, or about 400 ml for a 500 ml flask.

— Stopper the flask, shake well to disperse the matter, and put on the tumbling shaker (6.2) for 30 min.

— Adjust to the mark with water, homogenize, and filter.

— By means of a conductivity meter (6.3), measure the specific conductivity at 20 °C of the filtrate. This shall not exceed 1,5 mS/cm. Otherwise dilute the filtrate, in order to obtain a solution with a specific conductivity at 20 °C not higher than 1,5 mS/cm. Let D be the dilution factor.

NOTE 1 Aqueous sample extracts cannot be stabilized by acidifying since in acid conditions, chelates can dissociate or precipitate, and the resin can be protonated. It is essential to proceed immediately with the analysis from the extraction (8.2) until the contact solution (8.4) has been obtained.

NOTE 2 The maximum specific conductivity of 1,5 mS/cm corresponds to an ionic concentration of about 0,01 mol/l or less, depending on the intrinsic conductance of each ion present in the solution, and accounts for about a 10 fold excess of resin capacity, compared to the ionic concentration of the sample.

NOTE 3 The determination limit of the chelated element content depends on its water soluble content, its chelated fraction, and the matrix complexity. Cations present in the sample (e.g. ammonium, potassium, sodium, calcium, magnesium) can, varying with their type and concentration at neutral pH, compete for exchange sites on the resin with the non-chelated fraction of the micro-nutrient. For a high concentration of a chelated micro-nutrient in a simple matrix, a determination limit of 0,005 % can be reached. For a low concentration in a complex matrix, the highly conductive solution should be diluted and the micro-nutrient concentration can drop below the limit of the spectrometric analysis. In such cases, the determination limit can increase to about 0,5 %.

8.3 pH adjustment

— Pipette 50 ml of the filtrate (8.2) into a 100 ml beaker.

— Adjust to pH 7,0. Initially, use the sodium hydroxide solution (7.7) or the nitric acid solution (7.8).

— At the approach of the desired pH, use the more diluted solution (7.9 or 7.10).

— The adjustment of the pH is reached if the measurement is stable within 0,05 pH units for 5 min.

— Transfer quantitatively into a 100 ml volumetric flask, adjust to the mark with water, and homogenize. If a precipitation occurs, filter before proceeding.

NOTE The pH adjustment may take a considerable time, especially where slow precipitation reactions occur.

8.4 Ion exchange separation

— Weigh a mass R (g) of wet sodic resin (7.2) corresponding to 2,5 mmol (R = 2,5 / CEC) to within 0,01 g.

— Place the resin in a shaking flask (6.4) together with a pipetted volume of 25 ml of the sample solution (8.3).

— Close hermetically.

— Shake on the tumbling shaker at a temperature of 18 °C to 22 °C (6.2) for 4 h. During this operation protect the flask from exposure to light by use of a dark chamber or by covering the walls of the flask with an aluminium foil.

— When shaking is complete, filter the contents of the flask into a 100 ml volumetric flask, in one operation.

— Rinse the resin with 3 portions of approximately 20 ml of water and transfer the rinsing water to the flask.

— Add 5 ml of hydrochloric acid solution (7.3), make up to the mark with water, and homogenize. The solution obtained at the end of this filtration phase is called the "contact solution".

— If the contents of the flask are turbid, filter over a 0,45 µm membrane filter (6.5).

— The concentration of the separated micro-nutrients may be determined to enable the calculation of the chelated fraction as follows in 8.5, 8.6 and clause 9.

8.5 Spectrometric determination

Determine the micro-nutrient concentration in the contact solution by atomic absorption spectrometry (AAS) or by inductively coupled plasma emission spectrometry (ICP). The AAS determination may be carried out in accordance with the appropriate EC methods, referred to in the bibliography. Let d_i be the micro-nutrient concentration of the contact solution, in milligrammes per litre.

8.6 Total micro-nutrient content determination

Determine the total micro-nutrient content in the sample by AAS or by ICP. The AAS determination may be carried out in accordance with the appropriate EC methods, referred to in the bibliography. Let T be the total micro-nutrient content in the sample, expressed as mass fraction in percent.

9 Expression of results

9.1 Chelated micro-nutrient content in the fertilizer

The content of a chelated micro-nutrient (i) in the fertilizer, $Ch(i)$, expressed as mass fraction in percent, is given by the following formula:

$$Ch(i)\,(\%) = \frac{8 \cdot d(i) \cdot V \cdot D}{10^4 \cdot E}$$

where:

E is the mass of the test portion, in grams;

V is the volume of the extract, in millilitres;

$d(i)$ is the micro-nutrient (i) concentration of the contact solution, in milligrams per litre;

D is the dilution factor (see 8.2).

9.2 Chelated fraction of a micro-nutrient in the fertilizer

The chelated fraction $F(i)$ of a micro-nutrient (i) is the ratio of the chelated micro-nutrient (i) content to the total micro-nutrient (i) content in the fertilizer, expressed as a percentage, and is given by the following formula:

$$F(i)\,(\%) = \frac{Ch(i) \cdot 100}{T(i)}$$

where:

$Ch(i)$ is the chelated micro-nutrient (i) content (mass fraction in percent);

$T(i)$ is the total micro-nutrient (i) content (mass fraction in percent).

10 Precision

Results are based on 3 different ring tests involving between 9 and 10 laboratories with only 5 having completed the full range of testing (see [2] of bibliography).

Regarding both series of results, at the 95 % confidence level, repeatability and reproducibility are:

repeatability r = 10 %

and

reproducibility R = 18 %

11 Test report

The test report shall contain the following information:

a) a reference to this European Standard;

b) all information necessary for complete identification of the sample;

c) the results of the determination;

d) details of any operations not specified in the European Standard or regarded as optional, as well as any factor that may have affected the results.

Bibliography

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[2] 260 N 268 Technical report — Mandate M/051. Study and standardization remit assigned to CEN concerning the analytical method for chelated trace element content in fertilizers.

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Commission Directive 93/1/EEC of 21 January 1993. OJ N° L 113/17 of 7 May 1993 amending Directive 77/535/EEC on the approximation of the laws of the Member States relating to methods of sampling and analysis for fertilizers (Analysis methods for trace elements).

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