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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

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

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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

Ta slovenski standard je istoveten z: EN 13366:2001

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65.080 Gnojila Fertilizers

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EUROPEAN STANDARD

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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

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This European Standard was approved by CEN on 1 January 2001.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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COMITÉ EUROPÉEN DE NORMALISATION
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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of an identical text or by endorsement, at the latest by July 2001, and conflicting national standards shall be withdrawn at the latest by July 2001.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.

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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*.

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

3 Terms and definitions

For the purposes of this European Standard, the following term and definition apply:

3.1

chelated fraction

the 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 resistant to aqueous solutions, with porosity of 0,45 µm.

7 Reagents

7.1 General

- all water used should conform to EN ISO 3696 and be degassed by boiling before use ;
- 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 Zn¹⁾.

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 hour 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 which 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, $c(\text{HCl}) \approx 6 \text{ mol/l}$

Hydrochloric acid, diluted 1 + 1 with water.

7.4 Hydrochloric acid solution, $c(\text{HCl}) = 1 \text{ mol/l}$

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

7.5 Sodium chloride solution, $c(\text{NaCl}) = 1 \text{ mol/l}$

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

7.6 Sodium hydroxide solution, $c(\text{NaOH}) = 2 \text{ mol/l}$

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

7.7 Sodium hydroxide solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$

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

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.

7.8 Nitric acid solution, $c(\text{HNO}_3) = 0,1 \text{ mol/l}$

Carefully dilute 6,9 ml of nitric acid (65 % HNO_3 , $\rho = 1,40 \text{ g/ml}$) to 1 litre.

7.9 Sodium hydroxide solution, $c(\text{NaOH}) = 0,01 \text{ mol/l}$

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

7.10 Nitric acid solution, $c(\text{HNO}_3) = 0,01 \text{ mol/l}$

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.