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Fertilizers — Determination of the complexed micro-nutrient content and of the complexed fraction of micro-nutrients

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National foreword

This British Standard is the UK implementation of EN 15962:2011.

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

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Fertilizers - Determination of the complexed micro-nutrient content and of the complexed fraction of micro-nutrients

Engrais - Dosage de la teneur en oligo-élément complexé et de la fraction complexée des oligo-éléments

Düngemittel - Bestimmung des Gehalts an komplexgebundenen Spurennährstoffionen und der komplexgebundenen Fraktion von Spurennährstoffen

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Foreword

This document (EN 15962:2011) 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of an identical text or by endorsement, at the latest by July 2011, and conflicting national standards shall be withdrawn at the latest by July 2011.

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1 Scope

This European Standard specifies a general method for the determination of the micronutrients complexed by complexing agents in fertilizers. The method allows the determination of the total concentration of each complexed micronutrient in complexes after subtraction of the chelated micro-nutrients content, but it does not identify the individual complexing agents.

This procedure concerns EC-fertilizers which contain complexed micro-nutrients covered by Regulation (EC) No 2003/2003. The method is applicable to a mass fraction of the metal complexed of at least 0,07 %, 0,006 % and 0,035 % of Fe, Mn and Zn respectively (see [2]). A lower limit of quantification has not been established for Cu and Co.

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 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Principle

The method is based on the precipitation of the inorganic forms at pH 9. Then the complexed forms of an element remain in solution and are separated from the non complexed forms. The complexed forms are collected and their content determined by spectrometry, as well as the soluble element content.

NOTE For additional information see [2] and [3].

4 Interferences

Any substance combining with a micro-nutrient to form a stable soluble compound (chelate or complex) at pH 9, will prevent the precipitation of the metal, and account for a certain degree of complexation. This is the case for chelating agents. If the presence of chelates is suspected the appropriate analytical method should be used (see Bibliography) to identify and quantify the amount of element chelated, that should be subtracted from the amount of the element given by this method in order to obtain the actual amount of element complexed.

5 Apparatus

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, glassware and in particular the following:

5.1 Magnetic stirrer.

5.2 Balance, capable for weighing to an accuracy of 1 mg.

5.3 pH-meter, equipped with a glass electrode; the system shall be calibrated with pH 7 and pH 10 calibration buffers.

5.4 Membrane filters, micro-membrane filters resistant to aqueous solutions, with porosity of 0,45 µm.

5.5 Cellulose filters, fast filtration quantitative cellulose filters.

6 Reagents

All reagents shall be of recognized analytical grade.

6.1 Water used for the preparation of standard solutions.

Water used for the preparation of standard solutions, and sample solutions shall conform to EN ISO 3696:1995, grade 1 and be free of organic contaminants.

6.2 Hydrogen peroxide, H_2O_2, 30 % to 33 %.

6.3 Sodium hydroxide solution, c(NaOH) = 0,5 mol/l.

Carefully dissolve 20,0 g of NaOH in water and dilute to 1 l.

This solution is also available commercially.

6.4 Sodium hydroxide solution, c(NaOH) = 0,05 mol/l.

Carefully dissolve 2,0 g of NaOH in water and dilute to 1 l.

This solution is also available commercially.

6.5 Buffer solution, pH = 7,0.

6.6 Buffer solution, pH = 10,0.

7 Preparation of the sample

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.

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

8 Procedure

8.1 Preparation of the sample solution

Weigh, to the nearest 1 mg, a quantity of the fertilizer between 5 g and 10 g, depending on the declared content of the metal complex, into a 250 ml or 500 ml beaker. Add 200 ml or 400 ml of water. Stir using a magnetic stirrer (5.1) for 1 h. Transfer quantitatively into a 250 ml or 500 ml volumetric flask. Dilute to the mark with water and homogenize. The mass of the test sample and volume of extract should be taken according to Table 1.

Table 1 — Preparation of sample solution

Parameter	Declared content of complexed micro-nutrient in the fertilizer	
	< 0,5 %	≥ 0,5 %
Mass of test portion (g)	10	5
Mass of element in the sample (mg)	< 50	≥ 25
Volume of the extract (ml)	250	500
Concentration of the element in the extract after precipitation (mg/l)	< 40	≥ 10

If insoluble matter is observed, filter immediately after the final volume has been reached using cellulose filters (5.5).

8.2 Precipitation

Pipette 20 ml of the solution (8.1) into a 50 ml beaker. Add two drops of H_2O_2 (6.2), stir and rise pH, with NaOH 0,5 mol/l (6.3) or 0,05 mol/l (6.4), to 9,0 as fast as possible in order to avoid reaction with atmospheric carbon dioxide. Cover the beaker. Rise pH again to 9,0 after 30 min and cover the beaker again. Let the solution stand for a minimum of 18 h and a maximum of 24 h in the dark. Readjust the pH to 9,0, transfer the sample to a 100 ml volumetric flask and dilute to the mark with water (6.1). Filtrate the solution through the membrane filter (5.4). If precipitation is observed and filtration is difficult then samples may be centrifuged at 7 500 min^{-1} at 20 ºC to 25 ºC for 10 min before filtration.

The acidification of the solution required for the spectrometric determination (8.3) should be made as soon as possible after the precipitation process, in order to stabilize the solution.

8.3 Spectrometric determination

Determine the micro-nutrient concentration in the filtrate after precipitation procedure (8.2) by atomic absorption spectrometry (AAS) or by inductively coupled plasma emission spectrometry (ICP-ES). The AAS determination may be carried out in accordance with the appropriate methods (see Regulation (EC) No 2003/2003). If flame AAS is used, removal of the organic compounds is required, and should be made in accordance with method 9.3 ([1]) using H_2O_2 (6.2) and HCl 0,5 mol/l for the digestion of the samples and 0,5 % La as $La(NO_3)_3$, 0,2 % Cs as CsCl and 5 % HCl as matrix modifier.

Let $d_{(i)}$ be the micro-nutrient concentration of the filtrate, in milligrams per litre.

8.4 Water-soluble micro-nutrient content determination

Extract following method 9.2 ([1]). The same sample solutions 8.1 may be used in some cases. Determine the water-soluble 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 [1]. If flame AAS is used, removal of the organic compounds is required and should be made in accordance with method 9.3 ([1]) using H_2O_2 (6.2) and HCl 0,5 mol/l for the digestion of the samples and 0,5 % La as $La(NO_3)_3$, 0,2 % Cs as CsCl and 5 % HCl as matrix modifier.

Let $S_{(i)}$ be the water-soluble micro-nutrient content in the sample, expressed as mass fraction in percent.

9 Expression of results

9.1 Complexed micro-nutrient content in the fertilizer

The content of a complexed micro-nutrient (i) in the fertilizer, $C_{(\mathrm{i})}$, expressed as mass fraction in percent, is given by the following equation:

$$C_{(\mathrm{i})} = \frac{d_{(\mathrm{i})} \times V}{2\,000 \times W} \tag{1}$$

where

$d_{(\mathrm{i})}$ is the micro-nutrient (i) concentration of the filtrate solution, in milligrams per litre;

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

V is the volume of the extract in millilitres.

9.2 Complexed fraction of a micro-nutrient in the fertilizer

The complexed fraction $F_{(\mathrm{i})}$ of a micro-nutrient (i) is the ratio of the complexed micro-nutrient content $C_{(\mathrm{i})}$ to the water-soluble micro-nutrient content $S_{(\mathrm{i})}$ in the fertilizer, expressed as a percentage, and is given by the following equation:

$$F_{(\mathrm{i})} = 100 \times \frac{C_{(\mathrm{i})}}{S_{(\mathrm{i})}} \tag{2}$$

where

$C_{(\mathrm{i})}$ is the complexed micro-nutrient (i) content in percent (mass fraction);

$S_{(\mathrm{i})}$ is the water-soluble micro-nutrient (i) content in percent (mass fraction).

10 Precision

10.1 Inter-laboratory test

An inter-laboratory test has been carried out in 2008 with twelve participating laboratories and four different commercial samples. The results of this inter-laboratory test are summarized in Annex A. The results of one of the samples (LS-2) were not statistically analyzed because soluble element content was very low and few laboratories were able to measure it.

Repeatability and reproducibility were calculated according to ISO 5725-2.

A second inter laboratory test was performed later in 2008 with ten participating laboratories and three different samples. In this test the method was modified, but it did not improve the reproducibility, so the modifications were ruled out. One of the samples was a non-commercial sample with less than 80 % complexed element and the repeatability and reproducibility results were poor.

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 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 2.

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 2.

Table 2 — Mean values, repeatability and reproducibility limits. Complexed element
(g element/100 g sample)

Sample	**Mean value**	**Repeatability limit r**	**Reproducibility limit R**
LS-1 Fe	7,11	0,20	1,46
LS-1 Zn	1,19	0,04	0,20
LS-1 Mn	2,72	0,03	0,50
LS-1 Cu	0,43	0,02	0,11
LS-3 Fe	10,92	0,37	2,29
LS-4 Fe	5,04	0,21	0,83
LS-5 Zn	7,43	0,21	1,45
Complexed fraction (%)			
Sample	**Mean value**	**Repeatability limit r**	**Reproducibility limit R**
LS-1 Fe	98,3	8,1	12,5
LS-1 Zn	95,0	3,7	13,4
LS-1 Mn	96,7	2,6	14,0
LS-1 Cu	99,1	5,2	8,2
LS-3 Fe	97,7	2,3	13,0
LS-4 Fe	98,7	11,6	12,3
LS-5 Zn	97,6	8,4	10,3

11 Test report

The test report shall contain at least the following information:

a) reference to this European Standard;

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

c) results of the determination;

d) date of the 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 might have influenced the test result(s).

Annex A
(informative)

Results of the inter-laboratory test

A.1 Test samples

Five different samples were provided to all the participants, three solid fertilizers and two liquid solutions. The solid products were one mixed micronutrient fertilizer, one NPK product with Zn lignosulfonate and one Fe lignosulfonate. The liquid products were one Fe lignosulfonate and one Zn lignosulfonate. The results of the NPK product were not statistically analyzed because soluble Zn content was very low and few laboratories were able to measure it.

A.2 Inter-laboratory test procedure

The test samples were sent to thirteen laboratories from five countries, and twelve laboratories presented results.

The participating laboratories were requested to perform two replicates of each sample. The parameters measured were the complexed element and the soluble element in the samples, expressed as grams of element per 100 g of product, and the complexed fraction, expressed as percentage. Two decimals were specified for each determination.

Test results, observations and remarks were reported.

A.3 Results and statistical interpretation

Statistical calculations were run on all the results, according to ISO 5725-2.

Parameters of repeatability and reproducibility were evaluated for each sample (mean value, standard deviation of repeatability, standard deviation of reproducibility, repeatability, reproducibility, relative standard deviation of repeatability and relative standard deviation of reproducibility). Tables A.1, A.2 and A.3 show the statistical results of the inter-laboratory test.

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

Soluble element							
Parameter	**Sample**						
	LS-1 Fe	LS-1 Zn	LS-1 Mn	LS-1 Cu	LS-3 Fe	LS-4 Fe	LS-5 Zn
Number of laboratories	12	12	12	12	12	12	12
Number of outliers	0	0	1	0	2	0	0
Number of laboratories after elimination of outliers	12	12	11	12	10	11	11
Mean value g/100 g	7,23	1,25	2,80	0,44	11,43	5,15	7,61
Repeatability standard deviation (s_r) g/100 g	0,13	0,02	0,03	0,01	0,30	0,15	0,19
Repeatability limit, r g/100 g	0,36	0,05	0,09	0,04	0,22	0,42	0,53
Relative Standard Deviation of repeatability RSD_r %	1,77	1,47	1,14	2,91	0,68	2,91	2,51
Reproducibility standard deviation (s_R) g/100 g	0,49	0,07	0,14	0,04	0,30	0,37	0,65
Reproducibility limit, R g/100 g	1,37	0,21	0,39	0,10	0,84	1,03	1,82
Relative Standard Deviation of reproducibility RSD_R %	6,75	5,97	5,02	8,43	2,64	7,12	8,57

Table A.2 — Statistical results of the inter-laboratory test for complexed element

Complexed element							
	Sample						
Parameter	LS-1 Fe	LS-1 Zn	LS-1 Mn	LS-1 Cu	LS-3 Fe	LS-4 Fe	LS-5 Zn
Number of laboratories	12	12	12	12	12	12	12
Number of outliers	1	1	0	1	1	1	1
Number of laboratories after elimination of outliers	11	11	12	11	11	11	11
Mean value g/100 g	7,11	1,19	2,72	0,43	10,92	5,04	7,43
Repeatability standard deviation (s_r) g/100 g	0,07	0,02	0,18	0,006	0,13	0,08	0,08
Repeatability limit, r g/100 g	0,20	0,04	0,03	0,02	0,37	0,21	0,21
Relative Standard Deviation of repeatability RSD_r %	1,01	1,30	1,25	1,42	1,22	1,51	1,03
Reproducibility standard deviation (s_R) g/100 g	0,52	0,07	0,18	0,04	0,82	0,30	0,52
Reproducibility limit, R g/100 g	1,46	0,20	0,50	0,11	2,29	0,83	1,45
Relative Standard Deviation of reproducibility RSD_R %	7,32	5,94	6,54	8,84	7,49	5,91	6,99

Table A.3 — Statistical results of the interlaboratory test for complexed fraction

Complexed fraction							
Parameter	**Sample**						
	LS-1 Fe	LS-1 Zn	LS-1 Mn	LS-1 Cu	LS-3 Fe	LS-4 Fe	LS-5 Zn
Number of laboratories	12	12	12	12	12	12	12
Number of outliers	0	1	1	0	2	1	1
Number of laboratories after elimination of outliers	12	11	11	12	10	11	11
Mean value %	98,3	95,0	96,7	99,1	97,7	98,7	97,6
Repeatability standard deviation (s_r) %	2,9	1,3	0,9	1,9	0,8	4,2	3,0
Repeatability limit, r %	8,1	3,7	2,6	5,2	2,3	11,6	8,4
Relative Standard Deviation of repeatability RSD_r %	2,9	1,4	0,9	1,9	0,8	4,2	3,1
Reproducibility standard deviation (s_R) %	4,5	4,8	5,0	2,9	4,7	4,4	3,7
Reproducibility limit, R %	12,5	13,4	14,0	8,2	13,0	12,3	10,3
Relative Standard Deviation of reproducibility RSD_R %	4,5	5,1	5,2	3,0	4,8	4,4	3,8

Bibliography

[1] *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, Pp. 0001-0194 and amendments

[2] Villén, M.; Lucena, J. J.; Cartagena, M. C.; Bravo, R.; García-Mina, J.; de la Hinojosa, M. I. M., 2007: *Comparison of two analytical methods for the evaluation of the complexed metal in fertilizers and the complexing capacity of complexing agents*. J. Agric. Food Chem. 55, 5746-5753

[3] AOAC Official Method 983.03. *Iron (Chelated) in iron chelates concentrates. Atomic Absorption spectrophotometric method*. 1983

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

[5] 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*

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