SLOVENSKI STANDARD
SIST EN 16965:2018

01-junij-2018

Gnojila - Določevanje kobalta, bakra, železa, mangana in cinka s plamensko atomsko absorpcijsko spektrometrijo (FAAS)

Fertilizers - Determination of cobalt, copper, iron, manganese and zinc using flame atomic absorption spectrometry (FAAS)

Düngemittel - Bestimmung von Cobalt, Kupfer, Eisen, Mangan und Zink mit Flammen-Atomabsorptionsspektrometrie (FAAS)

Engrais - Dosage du cobalt, du cuivre, du fer, du manganèse et du zinc par spectrométrie d'absorption atomique de flamme (FAAS)

Ta slovenski standard je istoveten z: EN 16965:2018

ICS:

65.080	Gnojila	Fertilizers

SIST EN 16965:2018 **en,fr,de**

EUROPEAN STANDARD
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EN 16965

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English Version

Fertilizers - Determination of cobalt, copper, iron, manganese and zinc using flame atomic absorption spectrometry (FAAS)

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (EN 16965:2018) 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of an identical text or by endorsement, at the latest by July 2018, and conflicting national standards shall be withdrawn at the latest by July 2018.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

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, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

The preparation of this document is based on a mandate given to CEN by the European Commission and the European Free Trade Association (Mandate M/335) concerning the modernization of methods of analysis of fertilizers in the framework of Regulation (EC) No 2003/2003 [1].

This document is part of a modular approach and concerns the analytical measurement step. “Modular” means that a test standard concerns a specific step in assessing a property and not the whole chain of measurements. Flame atomic absorption spectrometry (FAAS) is widely used and well established in most laboratories. The European Standard can be used for the determination of cobalt, copper, iron, manganese and zinc in all extracts prepared according to EN 16962 and EN 16964. The method can be applied to mineral fertilizers with micro-nutrient content of ≤ 10 % as well as of > 10 %.

The inter-laboratory study reflects the final properties of the method for determination of individual micro-nutrients in water and aqua regia extracts including extraction steps.

WARNING — Persons using this European Standard should be familiar with normal laboratory practice. This European Standard does not purport to address all of the safety issues, if any, associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this European Standard are carried out by suitably trained staff.

1 Scope

This European Standard specifies a method for the determination of cobalt, copper, iron, manganese and zinc in fertilizer extracts using flame atomic absorption spectrometry (FAAS).

This method is applicable to water and aqua regia fertilizer extracts obtained according to EN 16962 and/or EN 16964.

NOTE In most cases, the presence of small quantities of organic matter will not affect determinations by FAAS and it is not necessary to apply organic matter removal.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12944-1, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 1: General terms*

EN 12944-2, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 2: Terms relating to fertilizers*

EN 16962, *Fertilizers — Extraction of water soluble micro-nutrients in fertilizers and removal of organic compounds from fertilizer extracts*

EN 16964, *Fertilizers — Extraction of total micro-nutrients in fertilizers using aqua regia*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 apply.

4 Principle

The method is based on the FAAS measurement of the concentration of the elements in fertilizer extracts prepared according to EN 16962 and/or EN 16964. The elements are determined after appropriate dilution of the extracts. Background correction, matrix matching and lanthanum addition are applied to remove possible interferences.

5 Interferences

Matrix matching can avoid interferences from different physical behaviour of the standards and samples (in particular, different viscosity can influence aspiration of the solution). Light scattering is eliminated by background correction. Ionization of cobalt, copper, iron, manganese and zinc in air-acetylene flame may be neglected. The formation of refractory compounds is prevented or reduced by adding a releasing agent (lanthanum).

6 Reagents

All reagents shall be of recognized analytical grade and they shall have negligible concentration of the element to be determined if compared to the lowest concentration of that element in the sample solution.

6.1 Water, grade 2 according to EN ISO 3696, free from micro-nutrients.

6.2 Nitric acid, $c(HNO_3)$ = 14,3 mol/l; ρ = 1,4 g/ml.

6.2.1 Diluted nitric acid solution, $c(HNO_3)$ = 5 mol/l.

Add 350 ml of nitric acid (6.2) to 650 ml of water (6.1).

6.2.2 Diluted nitric acid solution, $c(HNO_3)$ = 0,5 mol/l.

Dilute 35 ml nitric acid (6.2.) to 1 l with water (6.1).

6.3 Hydrochloric acid, $c(HCl)$ = 12 mol/l; ρ = 1,18 g/ml.

6.4 Mixed solution, 0,8 mol/l nitric acid and 1,8 mol/l hydrochloric acid.

Add 150 ml of hydrochloric acid (6.3) and 56 ml nitric acid (6.2) to 800 ml of water (6.1).

6.5 Standard stock solutions, cobalt, copper, iron, manganese and zinc standard stock solutions, ρ = 1 000 mg/l for each element.

Both single-element stock solutions and multi-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered. Alternatively, the stock solutions may be prepared by dissolution of high purity metals.

6.5.1 Standard solution, ρ = 100 mg/l of element.

Pipette 10 ml of the appropriate standard stock solution (6.5) into a 100 ml volumetric flask. Add 10 ml of diluted nitric acid (6.2.1), fill to the mark with water and mix well. This solution is used to prepare spiked test solutions and calibration solutions.

6.6 Lanthanum solution, ρ = 10 g/l lanthanum.

Place 11,73 g of lanthanum oxide (La_2O_3) in a 500 ml beaker, add 150 ml of water and slowly add 140 ml of diluted nitric acid (6.2.1). After complete dissolution transfer the solution quantitatively into a 1 000 ml volumetric flask and then make up to 1 l with water (6.1) and mix thoroughly. The substance concentration of this solution amounts to approximately 0,5 mol/l nitric acid.

Alternatively, lanthanum chloride, lanthanum sulfate or lanthanum nitrate may be used.

Alternative procedures: Dissolve 26,7 g of lanthanum chloride heptahydrate ($LaCl_3 .7 H_2O$) or 31,2 g of lanthanum nitrate hexahydrate [$La(NO_3)_3 .6 H_2O$] or 26,2 g of lanthanum sulfate nonahydrate [$La_2(SO_4)_3 .9 H_2O$] in 150 ml of water (6.1), then add 100 ml of diluted nitric acid (6.2.1). Allow to dissolve and then make up to 1 l with water (6.1). Mix thoroughly. The substance concentration of this solution amounts to approximately 0,5 mol/l nitric acid.

7 Apparatus

7.1 Atomic absorption spectrometer, equipped with:

- a hollow cathode lamp or other suitable light emission source;
- background correction;
- a burner, suitable for an air-acetylene flame.

WARNING — It is essential that the manufacturer's safety instructions are strictly observed when using this apparatus.

8 Procedure

8.1 Preparation of test and blank solutions

Dilute an aliquot portion of the water or aqua regia extract obtained according to EN 16962 or EN 16964 in one or more steps so that a final concentration of the element to be determined is in the given calibration range (8.2). In the final diluting step add a suitable volume of the extract or diluted extract to a 100 ml volumetric flask, add 10 ml of diluted nitric acid (6.2.1), 10 ml of lanthanum solution (6.6), fill to the mark with water and mix well. Prepare a blank solution by pipetting only extracting solution diluted in the same way as the test solution. For extracts where further dilution is not suitable pipette 20 ml of the sample extract into a 25 ml volumetric flask, add 2,5 ml of lanthanum solution (6.6) and fill to the mark with water (6.1). Mix well and use for the measurement.

8.2 Preparation of the calibration solutions

Pipette volumes of: 0 ml; 0,5 ml; 1 ml; 2 ml and 5 ml of the standard solution (6.5.1) into 100 ml volumetric flasks and add 10 ml of lanthanum solution (6.6). Add acid solution (6.2.1, 6.2.2 or 6.4) in a volume necessary to reach the same final acid concentration in the test (8.1) and calibration solutions, and fill to the mark with water. The mass concentrations of each element in the calibration solutions are: 0 mg/l; 0,5 mg/l; 1 mg/l; 2 mg/l and 5 mg/l. Mixed calibration solutions for all elements or individual sets of calibration solutions for each element may be used. If necessary, higher or lower concentrations of calibration solutions may be prepared in the same way.

NOTE Small differences in acid concentration between sample extracts and calibration solutions do not usually affect the measurement.

The calibration range may be extended for Fe and Mn up to 10 mg/l.

Although it has been demonstrated that lanthanum addition and background correction is not necessary for some elements and/or matrices, it is strongly recommended to apply background correction and lanthanum addition for all elements and matrices.

8.3 Measurement

Set up the atomic absorption spectrometer (7.1) according to the manufacturer's instructions at the appropriate wavelength (see Table 1). Aspirate a calibration solution (8.2) and optimize the aspiration conditions, burner height and flame conditions. Aspirate the set of calibration solutions in ascending order. Set the delay and the integration time according to the manufacturer's instructions (usually 3 s of delay and 3 s to 5 s of integration are sufficient). Care shall be taken to ensure that, when using more concentrated standards, the absorbance is < 1, and preferably not more than 0,7. The software of the instrument is used to plot the calibration graph and to calculate concentrations of the elements in the individual test solutions. All test solutions, blanks and calibration solutions are measured under the same conditions using background correction and lanthanum addition to eliminate or minimize interferences.

Standard addition method or spike recovery is recommended to test the efficiency of interference reduction especially in complicated matrices and for unknown samples.

A suitable burner rotation is usually needed for determination of Zn.

Table 1 — Recommended wavelengths

Element	Co	Cu	Fe	Mn	Zn
Wavelength (nm)	240,7	324,8	248,3	279,6	213,8

9 Calculation and expression of the results

Calculate the content of an element in the fertilizer, w_X, as a mass fraction in percent according to Formula (1).

$$w_X = \frac{V_{extr} \times (X_S - X_b) \times D \times 100}{1\,000 \times 1\,000 \times M} \qquad (1)$$

where

w_X is the mass fraction of the individual element, in percent;

V_{extr} is the volume of the extract after extraction (according to EN 16962 or EN 16964), in ml;

X_S is the concentration of the test solution as recorded on the calibration curve, in mg/l;

X_b is the concentration of the blank solution as recorded on the calibration curve, in mg/l;

M is the mass of the test portion, in g;

D is the dilution factor calculated as:

$$D = \frac{V_1}{V_{p1}} \times \frac{V_2}{V_{p2}} \times \ldots \frac{V_n}{V_{pn}} \qquad (2)$$

where

$V_{1,2..n}$ are the volumes of the volumetric flasks, in ml;

$V_{p1,2\ldots n}$ are the volumes of the pipetted solutions used for an individual diluting step, in ml.

10 Precision

10.1 Inter-laboratory test

An inter-laboratory test has been carried out in 2015 with 23 participating laboratories from 11 European countries and 8 different samples of fertilizer extracts prepared according to EN 16962 and EN 16964. This inter-laboratory test yielded the precision data given in Annex A.

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 single 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 be in no more than 5 % of the cases exceed the values of the repeatability limit, *r* given in Table 2 to Table 6.

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 no more than 5 % of the cases exceed values of the reproducibility limit, *R* given in Table 2 to Table 6.

Table 2 — Cobalt — Mean values, repeatability limits and reproducibility limits in percent

Sample	**Aqua regia extraction according to EN 16962**		
	Co ≤ 10 %		
	$\bar{x}$	r	R
No 2	0,440	0,031	0,123
Sample	**Water extraction according to EN 16964**		
	Co ≤ 10 %		
	$\bar{x}$	r	R
No 2	0,440	0,011	0,063

Table 3 — Copper — Mean values, repeatability limits and reproducibility limits in percent

Sample	**Aqua regia extraction according to EN 16962**					
	Cu ≤ 10 %			Cu > 10 %		
	$\bar{x}$	r	R	$\bar{x}$	r	R
No 1	0,515	0,016	0,065	-	-	-
No 4	0,075	0,004 8	0,027	-	-	-
No 6	-	-	-	14,51	0,48	1,43
Sample	**Water extraction according to EN 16964**					
	Cu ≤ 10 %			Cu > 10 %		
	$\bar{x}$	r	R	$\bar{x}$	r	R
No 1	0,490	0,023	0,102	-	-	-
No 4	0,037	0,005	0,018	-	-	-
No 6	-	-	-	14,02	0,46	3,49