SLOVENSKI STANDARD
SIST EN 16963:2018

01-junij-2018

Gnojila - Določevanje bora, kobalta, bakra, železa, mangana, molibdena in cinka z atomsko emisijsko spektrometrijo z induktivno sklopljeno plazmo (ICP/AES)

Fertilizers - Determination of boron, cobalt, copper, iron, manganese, molybdenum and zinc using ICP-AES

Düngemittel - Bestimmung von Bor, Cobalt, Kupfer, Eisen, Mangan, Molybdän und Zink mit ICP-AES

Engrais - Dosage du bore, du cobalt, du cuivre, du fer, du manganèse, du molybdène et du zinc par ICP-AES

Ta slovenski standard je istoveten z: EN 16963:2018

ICS:

65.080	Gnojila	Fertilizers

SIST EN 16963:2018 **en,fr,de**

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English Version

Fertilizers - Determination of boron, cobalt, copper, iron, manganese, molybdenum and zinc using ICP-AES

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

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Contents

European foreword

This document (EN 16963:2018) 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of an identical text or by endorsement, at the latest by July 2018, and conflicting national standards shall be withdrawn at the latest by July 2018.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. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is nowadays widely used and well established in many laboratories. The European Standard can be used for determination of boron, cobalt, copper, iron, manganese, molybdenum and zinc in all extracts prepared according to EN 16962 and EN 16964. The method can be applied to mineral fertilizers with micro-nutrient contents of ≤ 10 % as well as contents 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 boron, cobalt, copper, iron, manganese, molybdenum and zinc in fertilizer extracts using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

This method is applicable to water and aqua regia fertilizer extracts prepared 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 ICP-AES 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 ICP-AES measurement of the concentration of boron, cobalt, copper, iron, manganese, molybdenum and zinc in fertilizer extracts prepared according to EN 16962 or EN 16964. The elements are determined after appropriate dilution of the extract. The solution is dispersed by a nebulizer of the ICP-AES instrument and the resulting aerosol is transported into the plasma. Element specific emission spectra are produced by a radio-frequency inductively coupled argon plasma where atoms or ions are excited at high temperature. The emission spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Multi-element determinations using sequential or simultaneous optical systems and axial or radial viewing of the plasma may be used.

5 Interferences

5.1 General

Interferences and matrix effects shall be recognized and appropriate measures to minimize them shall be made. There are several types of interferences – see 5.2 to 5.6.

5.2 Spectral interferences

Spectral interferences are due to incomplete isolation of the radiation emitted by the analyte from other detected radiation sources. Spectral interferences are caused by background emission from continuous or recombination phenomena, by stray light which causes background increase or overlap of a spectral line from another element, or unresolved overlap of molecular band spectra. Background emission and stray light can usually be compensated for by subtracting the background emission measured adjacent to the analyte wavelength peak. To correct a sloping background shift two background correction points on each side of the peak are used. Increase of background is more intensive with axial-view instruments. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. A spectral line overlap usually leads to the choice of an alternative line. If this is not possible, mathematical correction procedures (e.g. inter-element correction technique, multi-component spectral fitting) can be used to compensate for the interference. These correction procedures are usually a part of the instrument software.

5.3 Transport interferences

Transport interferences are caused by differences in the properties between the sample solutions and the calibration solutions (viscosity, surface tension, density, dissolved solid content, type and concentration of acids). As a consequence, the supply of solution to the nebulizer, the efficiency of nebulization and the droplet size distribution of the aerosol is altered, resulting in a change of sensitivity. Errors due to these interferences can be overcome by dilution of the solutions, by matrix matching, by standard addition or by internal standard.

5.4 Excitation interferences

Excitation interferences are attributed to a change in the excitation conditions in the plasma especially by the presence of easily ionisable elements. The interference depends on the operating conditions of the plasma (e.g. power, sample introduction, gas flow-rate, observation height) and differ from element to element. Improvement of the plasma conditions can therefore reduce excitation interferences. Other possibilities are dilution of the solutions, matrix matching or the standard addition technique.

5.5 Chemical interferences

Chemical interferences are not significant with the ICP-AES technique, but if observed, they can be minimized by careful selection of operating conditions (e.g. radio frequency power, observation position, gas flow rate and so forth).

5.6 Memory interferences

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. The possibility of memory interferences should be recognized within an analytical run and suitable rinse steps and rinse times should be used. In particular, the memory effects caused by boron are well documented in the literature and this source of interference may be significant when samples containing high concentrations of boron are being analysed.

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, boron, cobalt, copper, iron, manganese, molybdenum 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. Multi-element stock solutions are usually available at the individual mass concentration ρ = 100 mg/l for each element. 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.

Use commercially available multi-element solution of this concentration for each element or pipette 10 ml of the appropriate element 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 Argon, purity 99,95 % or better.

7 Apparatus

7.1 Common laboratory glassware.

7.2 Inductively coupled plasma optical emission spectrometer.

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

The ICP atomic-emission spectrometer consists of a sample introduction system, the plasma as an excitation source, an optical system, a detector and a computer with suitable software. The sample is transported by the introduction system (rotation tube pump, nebulizer and a spray chamber) to the plasma torch. Around the torch a water cooled RF coil is placed. A frequency from 27 MHz to 56 MHz with a power of 600 W to 2 000 W is usually used. The emission from the plasma can be observed either from the side (radial) or from the torch central symmetrical axis (axial). Axial viewing gives more signal intensity due to the increased observation path length of the normal analytical zone of the plasma but an increase of interference is also commonly observed. Spectral lines are measured and registered either in a sequential or a simultaneous manner.

8 Procedure

8.1 Preparation of test and blank solution

Dilute an aliquot portion of the extract, obtained according to EN 16962 or EN 16964, in one or more steps so that the final concentration of the element to be determined is approximately in the middle of 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, fill to the mark with diluted nitric acid (6.2.2) and mix well.

Prepare a blank solution by pipetting only extracting solution diluted in the same way as the test solution.

For aqua regia extracts where further dilution is not suitable use these extracts directly for the measurement with calibration solutions of the same concentration of aqua regia. The aqua regia extracts can also be used for the determination of cadmium, chromium, lead and nickel according to EN 16319.

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 five 100 ml volumetric flasks respectively. Add the corresponding volumes of acid solution (6.2.1, 6.2.2 or 6.4) necessary to reach the same final concentration of those acids present in the test solution (8.1) 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, calibration solutions of higher or lower concentrations may be prepared in the same way.

NOTE 1 Small differences in acid concentration between sample extracts and calibration solutions do not usually affect the measurement.

For determination of boron it is necessary to avoid contamination of the extracts, blanks and calibration solutions with boron from borosilicate glass and/or detergents. Avoid or minimize contact of these solutions with borosilicate glass.

NOTE 2 It is possible to calibrate the instrument for higher concentrations of the micro-nutrients if the calibration curve is linear.

Where possible avoid nebulizing solutions with high concentration of boron. This can result in a very high memory effect in the instrument. In circumstances where it is not possible to avoid running samples with high boron concentration, extended rinse steps using diluted nitric acid shall be used to clear the system of boron after analysis. The effectiveness of the rinse steps shall be verified by measuring a blank sample: further analysis shall be delayed until the emission intensity obtained from the blank sample returns to that of the calibration blank.

8.3 Measurement

8.3.1 Instrument conditions

Due to differences between various kinds of instruments no detailed instructions can be given to operate the specific instrument. The instruction provided by the manufacturer for waiting time, instrument stability, gas flows, plasma conditions, nebulizer conditions, sample uptake rate, etc. should be followed.

Examples of conditions for two types of instruments (radial and axial view) are given in Table 1. Recommended wavelengths are given in Table 2.

The software of the instrument is used to calculate concentrations of the elements in the individual test solutions. All test solutions, blanks and calibration solutions are measured under the same optimized conditions using background correction and other suitable steps to eliminate or minimize interferences.

8.3.2 Optimization of the instrument conditions

The aim is to find the best sensitivity and precision and to minimize interferences for the set of lines to be used. Emission efficiency is related, amongst other parameters, to the plasma temperature, which is a function of RF power, argon gas flows and observation height (for radially viewed plasmas). Also the type of nebulizer and sample uptake rate will have an impact on the signal and the background.

8.3.3 Interferences

Background shall be measured adjacent to analyte lines on sample during analysis. The position selected for the background intensity measurement, on one or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analytical line. When working with an unknown matrix it is necessary to check the signal of every element to be measured for possible interferences by studying the region of the line. If spectral interferences (partial line overlap, line coincidence) occur, the measurement shall be carried out at another wavelength. If this is not possible, correction of the interference by mathematical correction procedures shall be carried out. High plasma power can minimize the matrix influence. Examples of suitable instrument conditions are given in Table 1.

Spectral lines which are free of interference by other elements shall be selected. Recommended wavelengths are given in Table 2. As the spectral interferences depend on the instrument resolution they shall be identified for each type of instrument in practical trials using mixtures of standard solutions containing the elements typically contained in fertilizer samples in varying concentrations.

NOTE For high concentrations of analytes and/or for high dilution of the extracts, that are typical for determination of micro-elements in fertilizers, the spectral interferences are usually negligible if instruments with adequate spectral resolution are used.

8.3.4 Matrix effects

The calibration blank and calibration solutions, calibration verification solution (one of the calibration standard solutions used to check calibration of the instrument), blank test, sample solutions and quality control solutions are measured after stabilization of the instrument and verification of stable conditions. Read the emission intensity of the solution at least twice and average the values. Every 20 samples or less and at the end, run a calibration blank and a calibration check solution.

Whenever an unknown matrix is encountered, check the following:

- matrix effects by running the spike sample;
- matrix effects by running a fivefold diluted sample (diluted nitric acid 6.2.1 is used for dilution);
- matrix effects by analysing at a different wavelength.

Spike recovery shall be between 90 % and 110 %. The difference between the results for the original sample and the fivefold-diluted sample shall be less than 10 %. If the spike recovery or difference for the diluted sample exceeds the given limit, standard addition method or matrix matching calibration shall be used.

8.3.5 Spiking

Add a known amount of standard solution of the analyte and an equal amount of blank solution to two separate but equal portions of the sample solution (or its dilution). The spike shall be between 0,4 and 2 times the expected sample mass concentration. Measure both solutions as sample solutions. Determine the ‘measured spike concentration' as the difference in mass concentration between the two spiked sample portions.

EXAMPLE Spiking procedure: pipette 10 ml of fertilizer extract or diluted extract into two test tubes, add 0,1 ml of multi-element standard solution (6.5.1) into the first test tube and 0,1 ml of blank into the second test tube. Mix well and measure. To achieve a higher concentration of an element by spiking, stock solutions of higher concentration can be used.

If the analytical results according to the standard addition method and the standard calibration method are equal, the calibration curve method can be applied.

The standard addition method, spike recovery and dilution are recommended to check the efficiency of interference reduction especially in complicated matrices and for unknown samples.

Table 1 — Example of instrument parameters
(Radial instrument – Spectro Blue, Axial instrument iCAP 6000[1])

Plasma view	Radial	Axial
Plasma power	1 550 W	1 250 W
Coolant flow	14,50 l·min^{-1}	12,00 l·min^{-1}
Auxiliary flow	1,00 l·min^{-1}	0,50 l·min^{-1}
Nebulizer flow	1,00 l·min^{-1}	0,65 l·min^{-1}
Peristaltic pump	30 rpm	30 rpm

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[1] Radial instrument – Spectro Blue and Axial instrument iCAP 6000 are examples of suitable instruments 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. Equivalent products may be used if they can be shown to lead to the same results.