SLOVENSKI STANDARD

kSIST-TS FprCEN/TS 17774:2021

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Organska in organsko-mineralna gnojila - Določevanje določenih elementov z atomsko emisijsko spektrometrijo z induktivno sklopljeno plazmo (ICP/AES) po ekstrakciji z vodo

Organic and organo-mineral fertilizers - Determination of the content of specific elements by ICP-AES after extraction by water

Organische und organisch-mineralische Düngemittel - Bestimmung des Gehalts spezifischer Elemente mittels ICP-AES nach Extraktion mit Wasser

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Organic and organo-mineral fertilizers - Determination of the content of specific elements by ICP-AES after extraction by water

Organische und organisch-mineralische Düngemittel - Bestimmung des Gehalts spezifischer Elemente mittels ICP-AES nach Extraktion mit Wasser

This draft Technical Specification is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 260.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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European foreword

This document (FprCEN/TS 17774:2021) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN

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Introduction

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 a well-established method in many laboratories.

1 Scope

This document specifies a method for the determination of boron (B), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn) in organic fertilizers and organo-mineral fertilizers extracts using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

NOTE Alternatively, inductively coupled plasma mass spectrometry (ICP-MS) can be used for the measurement if the user proves that the method gives the same results.

This method is applicable to water extracts prepared according to FprCEN/TS 17766. The method can be used for the determination of other elements, provided the user has verified the applicability.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

FprCEN/TS 17766, *Organic and organo-mineral fertilizers — Extraction by water for subsequent determination of elements*

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

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

The method is based on the ICP-AES measurement of the concentration of boron (B), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn) in fertilizer extracts prepared according to FprCEN/TS 17766. 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.

The method may be used for the determination of other elements, provided the user has verified the applicability.

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 nebuliser, the efficiency of nebulisation 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 flowrate or 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 a 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. This type of interference can be caused by sample deposits or the accumulation in pump tubing, nebulizer, spray chamber or plasma torch. The possibility of memory interferences should be recognized within an analytical run and suitable rinse steps and rinse times should be used.

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 3696:1995 free from micronutrients.

6.2 Standard stock solutions, boron, cobalt, copper, iron, manganese, molybdenum and zinc, mass concentration 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.

6.3 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 (6.2) into a 100 ml volumetric flask, add 5 ml of diluted nitric acid (6.5.1),fill to the mark with water and mix well. This solution is used to prepare spiked test solutions and calibration solutions.

6.4 Argon, purity 99,995 % or higher

6.5 Nitric acid, substance concentration c(HNO3) ≈ 14,3 mol/l; ρ ≈ 1,4 g/ml.

6.5.1 Diluted nitric acid solution, $c(\text{HNO}_3)$ = 5 mol/l.

Add 350 ml of nitric acid (6.5) to 650 ml of water.

7 Apparatus

7.1 Common laboratory glassware.

7.2 Inductively coupled plasma atomic 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 FprCEN/TS 17766:2021 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, add 5 ml diluted nitric acid (6.5.1), 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.

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 (6.3) and 5 ml diluted nitric acid (6.5.1) into five 100 ml volumetric flasks respectively. 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 It is possible to calibrate the instrument for higher concentrations of the micronutrients if the calibration curve is linear.

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 and alternative wavelengths may be used according to the instrument and recommendations of the producer.

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 nebuliser 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 (see 8.3.5).