SLOVENSKI STANDARD
kSIST-TS FprCEN/TS 17701-2:2021

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Rastlinski biostimulansi - Določevanje določenih elementov - 2. del: Določevanje celotnega Cd, Pb, Ni, As, Cr, Cu in Zn

Plant biostimulants - Determination of specific elements - Part 2: Determination of total content of Cd, Pb, Ni, As, Cr, Cu and Zn

Biostimulanzien für die pflanzliche Anwendung - Bestimmung spezifischer Elemente - Teil 2: Bestimmung des Gesamtgehaltes an Cd, Pb, Ni, As, Cr, Cu und Zn

Biostimulants des plantes - Détermination des éléments spécifiques - Partie 2 : Détermination du contenu total en Cd, Pb, Ni, As, Cr, Cu et Zn

Ta slovenski standard je istoveten z: FprCEN/TS 17701-2

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English Version

Plant biostimulants - Determination of specific elements - Part 2: Determination of total content of Cd, Pb, Ni, As, Cr, Cu and Zn

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Biostimulanzien für die pflanzliche Anwendung - Bestimmung spezifischer Elemente - Teil 2: Bestimmung des Gesamtgehaltes an Cd, Pb, Ni, As, Cr, Cu und Zn

This draft Technical Specification is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 455.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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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 (FprCEN/TS 17701-2:2021) has been prepared by the Technical Committee CEN/TC 455 "Plant Biostimulants", the secretariat of which is held by AFNOR.

This document is currently submitted to the Vote on TS.

The CEN/TS 17701 series, *Plant biostimulants - Determination of specific elements*, consists of the following parts:

— CEN/TS 17701-1, *Plant biostimulants - Determination of specific elements - Part 1: Digestion by aqua regia for subsequent determination of elements*;

— CEN/TS 17701-2, *Plant biostimulants - Determination of specific elements - Part 2: Determination of total content of Cd, Pb, Ni, As, Cr, Cu and Zn*;

— CEN/TS 17701-3, *Plant biostimulants - Determination of specific elements - Part 3: Determination of mercury*.

Introduction

This document was prepared by the experts of CEN/TC 455 ‘Plant Biostimulants’. The European Committee for Standardization (CEN) was requested by the European Commission (EC) to draft European standards or European standardization deliverables to support the implementation of Regulation (EU) 2019/1009 of 5 June 2019 laying down rules on the making available on the market of EU fertilising products (“FPR” or “Fertilising Products Regulation”).

This request, presented as SR M/564, also contributes to the Communication on “Innovating for Sustainable Growth: A Bio economy for Europe”. The Working Group 4 “Other safety parameters” was created to develop a work program as part of this Request. The technical committee CEN/TC 455 ‘Plant Biostimulants’ was established to carry out the work program that will prepare a series of standards. The interest in biostimulants has increased significantly in Europe as a valuable tool to use in agriculture. Standardization was identified as having an important role in order to promote the use of biostimulants. The work of CEN/TC 455 seeks to improve the reliability of the supply chain, thereby improving the confidence of farmers, industry, and consumers in biostimulants, and will promote and support commercialisation of the European biostimulant industry.

The preparation of this document is based on a standardization request to CEN by the European Commission and the European Free Trade Association (Mandate M/564) concerning the modernization of methods of analysis of fertilizers in the framework of Regulation (EU) 2019/1009 of the European Parliament and of the Council.

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.

WARNING – Persons using this document should be familiar with usual laboratory practice. This document 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 document are carried out by suitably trained staff.

1 Scope

This document specifies a method for the determination of arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn) in plant biostimulant digests using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

This document is also applicable to the blends of fertilizing products where plant biostimulants are the main part of the blend. Otherwise, the Technical Specification for the main part of the blend applies.

This method is applicable to aqua regia digests prepared according to CEN/TS 17701-1. 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.

CEN/TS 17701-1, *Plant biostimulants - Determination of specific elements - Part 1: Digestion by aqua regia for subsequent determination of elements*

CEN/TS 17704, *Plant biostimulants - Determination of dry matter*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
analyte
parameter to be determined

3.2
blank calibration solution
solution prepared in the same way as the calibration solution but leaving out the analytes

3.3
blank test solution
solution prepared in the same way as the test sample solution but omitting the test portion

3.4
calibration solution
solution used to calibrate the instrument, prepared from stock solutions by adding acids, buffer, reference element and salts as needed

3.5
digest
solution received after mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacting with a reagent mixture

3.6
stock solution
solution with accurately known analyte concentration(s), prepared from pure chemicals (6.5)

3.7
test sample solution
solution prepared after extraction or digestion of the test sample according to appropriate specifications

4 Principle

The method is based on the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement of the concentration of arsenic, cadmium, copper, chromium, lead, nickel and zinc in plant biostimulant aqua regia digests. The elements are determined after an appropriate dilution of the digest, if necessary. The solution is dispersed by a suitable nebulizer of the ICP-AES instrument and the resulting aerosol is transported into the plasma torch. Element specific emission spectra are produced by a radiofrequency 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, radial or dual 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 – 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 the background emission from continuous or recombination phenomena, by stray light which causes background increase or overlap of a spectral line from another element, or by the 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 background correction points on each side of the peak are used. The 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 or 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 may 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

6.1 Water with a specific conductivity not higher than 0,2 mS/m at 25 °C, free from the elements to be determined.

6.2 Nitric acid, *c*(HNO3) ≈ 14,3 mol/l; $\rho \approx 1,4$ g/ml.

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

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

6.3 Hydrochloric acid, *c*(HCl) ≈ 12 mol/l; $\rho \approx 1,18$ g/ml.

6.4 Mixed acid 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, arsenic, cadmium, copper, chromium, lead, nickel and zinc standard stock solutions, $\rho = 1\,000$ 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 $\rho = 100$ 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 the dissolution of high purity metals.

6.5.1 Standard solution, $\rho = 100$ mg/l of element.

Use commercially available 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 (6.1) and mix well. This solution is used to prepare spiked test solutions and calibration solutions.

6.5.2 Standard solution, $\rho = 10$ mg/l of cadmium.

Pipette 10 ml of cadmium standard solution (6.5.1) into a 100 ml volumetric flask. Add 10 ml of diluted nitric acid (6.2.1), fill to the mark with water (6.1) and mix well. This solution is used to prepare calibration solutions for cadmium.

6.6 Argon, purity 99,995 % or better.

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 inductively coupled plasma 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, nebuliser and a spray chamber) to the plasma torch. Around the torch a water-cooled RF coil is placed. A frequency of 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

Aqua regia digests prepared according to CEN/TS 17701-1 are usually measured using ICP-AES directly with calibration solutions of the same final concentration of aqua regia. The aqua regia extracts may also be used for the determination of other elements.

A blank test is prepared for the measurement following the same procedure as for samples.

If dilution is necessary, dilute an aliquot portion of the extract 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 fill to the mark with the mixed acid solution (6.4) and mix well. Prepare a diluted blank solution by pipetting a blank solution and dilute in the same way as the test solution.

8.2 Preparation of the calibration solutions

Individual calibration series for each element or mixed series may be used. For cadmium calibration standards, pipette volumes of 0 ml; 0,5 ml; 1 ml; 2 ml and 5 ml of the standard solution (6.5.2) into five 100 ml volumetric flasks respectively. For arsenic, copper, chromium, lead, nickel and zinc calibration standards pipette volumes of 0 ml; 1 ml; 2 ml; 5 ml and 10 ml of the standard solution (6.5.1) into the same five 100 ml volumetric flasks respectively.

Fill the volumetric flasks to the mark with the mixed acid solution (6.4).

The mass concentrations of cadmium in the calibration solutions are: 0 mg/l; 0,05 mg/l; 0,1 mg/l; 0,2 mg/l and 0,5 mg/l. The mass concentrations of arsenic, copper, chromium, lead, nickel and zinc in the calibration solutions are: 0 mg/l; 1 mg/l; 2 mg/l; 5 mg/l and 10 mg/l respectively.

Individual sets of calibration solutions for each element may be used instead of the mixed calibration solutions for all elements. 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 digests and calibration solutions do not affect the measurement.