Rastlinski biostimulanti - Določevanje specifičnih 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 végétaux - 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: prEN 17701-2

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65.080	Gnojila	Fertilizers

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EUROPEAN STANDARD

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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

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

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

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

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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

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prEN 17701-2:2023 (E)

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European foreword

This document (prEN 17701-2:2023) has been prepared by Technical Committee CEN/TC 455 "Plant biostimulants", the secretariat of which is held by AFNOR.

This document is currently submitted to the CEN Enquiry.

This document will supersede CEN/TS 17701-2:2022.

This document has been prepared under a Standardization Request given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s) / Regulation(s).

For relationship with EU Directive(s) / Regulation(s), see informative Annex ZA, which is an integral part of this document.

EN 17701 series, *Plant biostimulants — Determination of specific elements*, consists of the following parts:

— *Part 1: Digestion by aqua regia for subsequent determination of elements*;

— *Part 2: Determination of total content of Cd, Pb, Ni, As, Cr, Cu and Zn*;

— *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 the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products ("FPR" or "Fertilising Products Regulation").

This standardization request, presented as M/564 and M/564/Amd1, also contributes to the Communication on "Innovating for Sustainable Growth: A Bio economy for Europe". Working Group 4 "Other safety parameters" was created to develop a work programme as part of this standardization request. Technical Committee CEN/TC 455 "Plant biostimulants" was established to carry out the work programme 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 boosting 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. Aqua regia digestion followed by inductively coupled plasma atomic emission spectrometry is widely used for determination of many elements. For example, a multi-matrix standard for aqua regia extraction of soils, sludges and biowaste was prepared by CEN/TC 444. A similar procedure was applied for determination of aqua regia extractable contents of arsenic, mercury, cadmium, chromium, nickel and lead in fertilizers and liming materials (standard prepared by CEN/TC 260). Inductively coupled plasma atomic emission spectrometry (ICP-AES) is nowadays widely used and a well-established method in many laboratories.

The inter-laboratory study reflects the final statistical characteristics of the method for the determination of the specific elements in aqua regia digests including both, the digestion and the measurement steps.

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 aqua regia plant biostimulant digests using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

This document is applicable to the fertilizing product blends belonging to PFC 7 where the EU fertilising product plant biostimulant contained in the blend represents the highest % by mass in the blend. In case of equal shares, the user can apply either this or the standard(s) applicable to the other component product(s).

This method is applicable to aqua regia digests prepared according to EN 17701-1:—[1]. The method can be used for the determination of other elements, provided the user has verified the applicability.

NOTE   Alternatively, inductively coupled plasma mass spectrometry (ICP-MS) can be used for the determination of the elements in the aqua regia digests if the user proves that the method gives the same results.

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.

EN 17701-1:—[1], *Plant biostimulants — Determination of specific elements — Part 1: Digestion by aqua regia for subsequent determination of elements*

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EN 17704:—[2], *Plant biostimulants — Determination of dry matter*

3 Terms and definitions

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

oSIST prEN 17701-2:2023
https://standards.iteh.ai/catalog/standards/sist/5a7f855c-0d64-4e58-b7a8-
2032f54f1e63/osist-pren-17701-2-2023

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

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[1] Under preparation

[2] Under preparation

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 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 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 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 interferences depend on the operating conditions of the plasma (e.g. power, sample introduction, gas flowrate or observation height) and differs 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

The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

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, $c(HNO_3) \approx 14,3$ mol/l, $\rho \approx 1,4$ 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).

6.3 Hydrochloric acid, $c(HCl) \approx 12$ 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 (6.4) consecutively to 600 ml of water (6.1) and fill up to 1 000 ml with 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, ρ = 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, ρ = 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, nebulizer and a spray chamber) to the plasma torch. Around the torch a water-cooled radio frequency (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 sample solution and blank test solution

Aqua regia digests prepared according to EN 17701-1:—[1] are usually measured using ICP-AES directly with calibration solutions of the same final concentration of aqua regia. The aqua regia digests may also be used for the determination of other elements.

A blank test solution is prepared for the measurement following the same procedure as for test sample solutions.

If dilution is necessary, dilute an aliquot portion of the test sample solution 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 test solution by pipetting a blank test solution and dilute in the same way as the test sample 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.

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

It is possible to calibrate the instrument for higher concentrations of the elements 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 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.