SLOVENSKI STANDARD
kSIST-TS FprCEN/TS 17706:2021

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Rastlinski biostimulansi - Določevanje anorganskega arzena

Plant biostimulants - Determination of inorganic arsenic

Biostimulanzien für die pflanzliche Anwendung - Bestimmung von anorganischem Arsen

Biostimulants des végétaux - Dosage de l'arsenic inorganique

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ICS:

65.080	Gnojila	Fertilizers

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FprCEN/TS 17706

September 2021

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English Version

Plant biostimulants - Determination of inorganic arsenic

Biostimulants des végétaux - Dosage de l'arsenic inorganique

Biostimulanzien für die pflanzliche Anwendung - Bestimmung von anorganischem Arsen

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
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European foreword

This document (FprCEN/TS 17706:2021) 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 Vote on TS.

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

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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 describes procedure of extraction and measurement for the determination of inorganic arsenic in plant biostimulants. The standard is based on a mild acid oxidative extraction of the arsenic species followed by liquid chromatography (HPLC or IC) coupled to the element-specific detector ICP-MS for the determination of the mass fraction of iAs.

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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 apply.

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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.

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1 Scope

This document specifies a method for extraction, separation, and determination of inorganic arsenic (iAs) in plant biostimulants using anion-exchange HPLC or IC coupled to ICP-MS.

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 apply.

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 17704, *Plant biostimulants — Determination of dry matter*

3 Terms and definitions

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

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3.1
analyte
parameter to be determined

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

4 Principle

This document describes a method for the determination of inorganic arsenic in plant biostimulants. Inorganic arsenic consists of arsenite As (III) and arsenate, As(V). A representative test portion of the sample is treated with a diluted nitric acid and hydrogen peroxide solution in a heated water bath. By this means the sample is solubilised, arsenic species are extracted into solution and As (III) is oxidized to As(V). The inorganic arsenic is selectively separated from other arsenic compounds using anion exchange HPLC (High Performance Liquid Chromatography) coupled online to the element-specific detector ICP-

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MS (Inductively Coupled Plasma Mass Spectrometer) for the determination of the mass fraction of the inorganic arsenic. External calibration with solvent matrix-matched standards is used for the quantification of the amount of the inorganic arsenic. Alternatively, IC (ion chromatography) coupled to ICP-MS can be used.

A preliminary determination of the total arsenic in aqua regia extracts by ICP-AES (FprCEN/TS 17701-1 and FprCEN/TS 17701-2) could reduce the number of the samples where the determination of iAs is necessary because if the content of aqua regia (total) extractable arsenic is lower than the legislative limit for iAs then the determination of iAs is not necessary.

5 Reagents

When using a method of high sensitivity like ICP-MS and HPLC the control of the blank levels of water, acid and other reagents is very important. The reagents shall be of adequate purity and of recognized analytical grade. The concentration of arsenic species in the reagents and water used shall be negligible and low enough not to affect the results of the determination. Generally ultra-pure water from a purification system and nitric acid of minimum p.a. quality is recommended.

5.1 Water with an electrical conductivity not higher than 0,1 mS/m at 25 °C, having a resistivity greater than 18,2 MΩ·cm.

5.2 Nitric acid (HNO_3), concentrated, ≥ 65 % (mass fraction), mass concentration of approximately ρ (HNO_3) 1,4 g/ml.

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Use only nitric acid available with high purity (minimum p.a. quality) in order to avoid potential contamination.

5.3 Hydrogen peroxide, H_2O_2 not less than 30 % (mass fraction)

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High purity is essential to avoid potential contamination. Commercially available hydrogen peroxide for analysis should be tested for contamination of arsenic prior to use. It is necessary to prevent peroxide degradation and ensure the stability of the solution.

5.4 Extraction solution, 0,1 mol/l HNO_3 in 3 %(V/V) H_2O_2

Add 6,5 ml of HNO_3 (5.2) and thereafter 100 ml of hydrogen peroxide (5.3) into 800 ml water (5.1) in a 1 000 ml volumetric flask. Fill the flask to the mark with water (5.1.). This solution is prepared on the day of use.

It is recommended that the total volume needed for the analysis is estimated and only this amount is produced in the day of use.

5.5 Ammonium carbonate, $(NH_4)_2CO_3$, mass fraction w ≥ 99,999 %, for preparation of the mobile phase solution.

5.6 Aqueous ammonia, (NH_3(aq).) w ≥ 25 %, for adjustment of pH in the mobile phase.

5.7 Methanol, (CH_3OH), HPLC grade, for preparation of the mobile phase solution.

5.8 Mobile phase, e.g. 50 mmol/l ammonium carbonate in 3 % methanol at pH 10,3

Dissolve 4,80 g of ammonium carbonate (5.5) in approximately 800 ml water (5.1). Adjust the pH to 10,3 with aqueous ammonia (5.6) and add 30 ml of methanol (5.7) and then fill up to 1 000 ml with water (5.1). Prior to use filter the mobile phase solution through a 0,45 µm filter using a filtering device (6.4).

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The optimal concentration of ammonium carbonate in the mobile phase depends on the analytical column used (e.g. brand, particle size and dimensions) and should be verified in advance. The appropriate concentration of ammonium carbonate (usually between 10 and 50 mmol/l) is highly dependent on the column used and is up to the discretion of the analyst. It should fulfil the criteria for sufficient resolution of the arsenate peak.

Methanol is added to the mobile phase in order to enhance the signal intensity for arsenic. The concentration of methanol to achieve the highest signal to noise ratio depends on the instrument used and should be identified by the analyst.

Different mobile phase may be also used according to the instructions of the manufacturer of the column but it is necessary to verify optimal separation conditions.

For example, Agilent column G3154-65001 with a guard column G3154-65002 and a recommended mobile phase for this column (dihydrogen potassium carbonate 2 mmol, EDTA 0,2 mmol, pH 6,0 adjusted with sodium hydroxide solution 1 mol) were successfully used for the analysis.

5.9 Arsenic (V) standard stock solution, with an arsenic (V) mass concentration of 1 000 mg/l

The use of commercial standards of arsenic As (V), with a mass concentration of 1 000 mg/l is recommended.

5.10 Arsenic (V) standard solution I, with an arsenic (V) mass concentration of 10 mg/l in 2 % (V/V) HNO_3

Pipette 1 ml of arsenic standard stock solution (5.9) into a 100 ml volumetric flask. Add 2 ml of nitric acid (5.2), fill to the mark with water (5.1) and mix well. This solution is stable in a refrigerator at least one week.

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5.11 Arsenic (V) standard solution II, with an arsenic (V) mass concentration of 1 mg/l

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Pipette 10 ml of arsenic standard solution I (5.10) into a 100 ml volumetric flask, fill to the mark with water (5.1) and mix well. This solution should be prepared on the same day of use.

5.12 Solution for checking chromatographic separation, containing organic arsenic compounds (e.g. 10 µg/l) monomethylarsenous acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AB), as well as arsenate (e.g. 10 µg/l) and chloride (e.g. 100 mg/l).

6 Apparatus

6.1 Common laboratory glass (plastic) ware.

Plastic volumetric flasks are recommended for the preparation of the mobile phase and calibration solutions. All glassware and plastic ware shall be adequately cleaned and stored to avoid any contamination.

6.2 Laboratory grinder, capable of grinding to a particle size less than 0,5 mm.

6.3 Analytical balance, accuracy ≤ 1 mg.

6.4 Filtering device, for filtration of mobile phase with a filter, pore size 0,45 µm.

6.5 Shaking heated water bath, capable of maintaining 90 °C.

6.6 Centrifuge, for minimum 4 000 min^{-1} (approx. 2 000 g).

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6.7 Single use syringe filters (0,45 µm) or HPLC vials with filters, compatible with acidic solutions for filtering of test solutions prior to analysis.

6.8 High Pressure Liquid Chromatograph (HPLC).

6.9 Anion exchange column, suitable for the selective separation of arsenate from other arsenic compounds present in the sample extracts.

It is highly recommended to use a guard column to prolong the life-time of the analytical column.

Use of a different column and a different mobile phase is possible. The other columns may be used in combination with the suitable type of mobile phase depending on the recommendations of the manufacturer (see 5.8).

6.10 Inductively coupled plasma mass spectrometer (ICP-MS).

6.11 Argon gas, purity ≥ 99,99 %.

7 Sampling

Sampling and preparation of the test sample is not part of this procedure. A recommended sampling method is given in FprCEN/TS 17702-1 Plant biostimulants – Sampling and method for sample preparation is given in FprCEN/TS 17702-2 Plant biostimulants – Sample preparation.

8 Procedure

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8.1 Sample preparation

Solid samples are milled using a laboratory grinder (6.2) and homogenized. Excessive heating during the sample pre-treatment should be avoided. Liquid samples are homogenized by thorough mixing before weighing the test portion.

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8.2 Water bath extraction

Weigh a test portion of approximately 0,2 g to 0,6 g sample to the nearest milligram into an extraction tube and add to 10,00 ml of the extraction solution (5.4). The tubes shall be securely closed with a tight lid. Shake the tubes thoroughly in order to ensure that the sample is wetted sufficiently in the extraction solution (5.4) prior to placing it in the water bath in order to ensure a satisfactory extraction of the analyte.

The solutions are then placed into a heated shaking water bath (6.5) at 90 °C ± 2 °C and extracted for 60 min ± 5 min.

Include also a reagent blank sample. A blank test solution is prepared following the same procedure as for samples.

After extraction and cooling to room temperature the tubes are centrifuged for 10 min at 4 000 min^{-1} (approx. 2 000 g)). The supernatant is transferred to clean plastic (PE or PP) tubes. Sample extracts should be filtered by a syringe filter (6.7) to clean HPLC vials prior to analysis. The sample extracts can be stored in a refrigerator (at approximately 4 °C) for a maximum of one week.

8.3 Preparation of the calibration solutions

The external calibration is used for quantification. Prepare a blank calibration solution and at least three calibration standard solutions in the linear range of calibration for inorganic arsenic (As V) by diluting the arsenic standard solution II of As (V) concentration 1 mg/l (5.11) with mobile phase solution (5.8).