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Plant biostimulants - Determination of inorganic arsenic

Biostimulants des végétaux - Dosage de l'arsenic inorganique

Biostimulanzien für die pflanzliche Anwendung - Bestimmung von anorganischem Arsen

This Technical Specification (CEN/TS) was approved by CEN on 3 January 2022 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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

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European foreword

This document (CEN/TS 17706:2022) has been prepared by Technical Committee CEN/TC 455 “Plant biostimulants”, the secretariat of which is held by AFNOR.

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 Standardization Request given to CEN by the European Commission and the European Free Trade Association.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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 fertilizing products (“FPR” or “Fertilising Products Regulation”).

This standardization request, presented as 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.

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 extraction, separation, and determination of inorganic arsenic (iAs) in plant biostimulants using anion-exchange high performance liquid chromatography (HPLC) or ion chromatography (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 applies.

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 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
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-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 (CEN/TS 17701-1 and CEN/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.

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).

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).

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 mmol/l 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.