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Rastlinski biostimulanti - Določevanje specifičnih elementov - 3. del: Določevanje živega srebra

Plant biostimulants - Determination of specific elements - Part 3: Determination of mercury

Pflanzen-Biostimulanzien - Bestimmung spezifischer Elemente - Teil 3: Bestimmung von Quecksilber

Biostimulants des végétaux - Détermination des éléments spécifiques - Partie 3 : Détermination du mercure

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Plant biostimulants - Determination of specific elements - Part 3: Determination of mercury

Biostimulants des végétaux - Détermination des
éléments spécifiques - Partie 3 : Détermination du
mercure

Pflanzen-Biostimulanzien - Bestimmung spezifischer
Elemente - Teil 3: Bestimmung von Quecksilber

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

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European foreword

This document (prEN 17701-3:2023) 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 17701-3:2022.

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.*

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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 fertilizing 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”. The Working Group 4 “Other safety parameters” was created to develop a work programme as part of this request. The 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 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 and M/564/Amd1) 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 concerns the analytical measurement step for the determination of mercury in plant biostimulants after digestion by aqua regia according to EN 17701-1:—¹. It covers cold vapour generation followed by mercury determination using atomic absorption spectrophotometry (AAS). Different cold vapour generation techniques can be used (flow injection, segmented flow, batch). This document also includes a method based on a direct amalgamation technique which is widely used in many analytical laboratories. It is also possible to use other suitable methods of mercury determination described in Annex A if users prove that the methods give the same results as the methods described in this document.

The inter-laboratory study reflects the final statistical characteristics of the method for the determination of mercury 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 determination of the content of mercury (Hg) in plant biostimulants using (cold) vapour generation apparatus coupled to an atomic absorption spectrophotometer and a method using a direct amalgamation technique. It is applicable to aqua regia digests prepared according to EN 17701-1:—¹.

NOTE It is also possible to use other suitable methods for the determination of mercury described in Annex A if users prove that the method gives the same results as the methods described in this document.

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

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

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

EN 17704:—³, *Plant biostimulants — Determination of dry matter*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 17701-2:—² apply.

4 Principle

4.1 Vapour generation atomic absorption spectrophotometry (VG-AAS)

Mono- and divalent mercury is reduced to the elemental form by tin(II) chloride or sodium borohydride in an acid medium. Elemental mercury is stripped off from the solution and determined in the form of an atomic gas by an atomic absorption spectrophotometer.

4.2 Direct amalgamation (DA)

The sample is thermally decomposed in an oxygen rich environment. The decomposition products are carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapour. Flowing oxygen carries the mercury vapour through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at 253,7 nm as a function of mercury concentration.

¹ Under preparation

² Under preparation

³ Under preparation

5 Interferences

5.1 Vapour generation atomic absorption spectrophotometry (VG-AAS)

The matrix of the solution analysed is dominated by the acids used in the digestion step. Tin (II) chloride as a reduction substance is recommended, because sodium borohydride reduces many elements commonly found in plant biostimulant digests to the elemental state, which may cause matrix problems under particular circumstances. However, it is still possible to use sodium borohydride as a reduction agent. The interferences due to the presence of other elements in the matrix depend on its concentrations. Copper and nickel exceeding a concentration of 500 mg/l can cause a negative bias.

5.2 Direct amalgamation (DA)

Instruments with an amalgamation technique are very often used for a direct determination of mercury in samples without a digestion step. Nevertheless, some solid samples (e.g. silicates or phosphates) might not be fully thermally decomposed and therefore in this case or if an unknown sample is analysed, the analysis of aqua regia digests is preferable. For plant biostimulants usually no difference is observed between the direct determination of mercury and the determination of mercury after digestion in aqua regia.

6 Reagents

The concentration of mercury 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 mercury.

6.2 Carrier gas.

Argon or nitrogen for VG-AAS, oxygen for DA, purity according to the recommendation of the manufacturer.

6.3 Hydrochloric acid, $c(\text{HCl}) \approx 12 \text{ mol/l}$, 37 % volume fraction, ρ approximately 1,18 g/ml.

6.4 Nitric acid, $c(\text{HNO}_3) \approx 16 \text{ mol/l}$, not less than 65 % volume fraction, ρ approximately 1,42 g/ml.

6.5 Mixed acid solution of 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).

6.6 Reducing agents

Tin(II) chloride or sodium borohydride may be used as the reducing agent, but it is not advisable to use the two reagents alternately. Follow the instructions of the manufacturers of the apparatus. The concentration by mass of the reducing agent solutions may be varied to suit the system, and the relevant information provided by the manufacturer of the apparatus shall be observed.

6.6.1 Tin(II) chloride solution, $\rho(\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}) = 100 \text{ g/l}$.

Dissolve 10 g of $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ in 30 ml of hydrochloric acid (6.3), transfer to a 100 ml volumetric flask and fill to the mark with water (6.1). The blank concentration of mercury can be reduced by bubbling a stream of nitrogen through the solution for 30 min, if necessary. Prepare this solution on the day of use.

6.6.2 Sodium borohydride solution, NaBH_4 , $\rho(\text{NaBH}_4) = 30 \text{ g/l}$.

1 g sodium hydroxide, NaOH , is weighed into a 100 ml volumetric flask and dissolved in water (6.1). 3 g sodium borohydride, NaBH_4 , are weighed into a 100 ml volumetric flask, dissolved and diluted to the mark with the sodium hydroxide solution.

A solution of lower concentration, e.g. 3 g/l may be used with flow systems. Prepare this solution freshly on the day of use from the more concentrated solution by diluting with water (6.1). Follow the recommendations of the manufacturer of the instrument.

WARNING — It is essential to observe the safety instructions for working with sodium borohydride. Sodium borohydride forms hydrogen with acids and this can result in an explosive air/hydrogen mixture. A permanent fume extraction system shall be provided at the point where measurements are carried out.

6.7 Standard stock solution, $\rho = 1\,000 \text{ mg/l}$.

Use commercially available mercury stock solution with adequate specification, stating the acid used and the preparation technique. The solution is considered to be stable for more than one year, but in reference to guaranteed stability, see the recommendations of the manufacturer. Alternatively, the stock solutions may be prepared by the dissolution of high purity metal mercury or its salts.

6.7.1 Standard solution I, $\rho = 100 \text{ mg/l}$.

Pipette 10 ml of the mercury standard stock solution (6.7) into a 100 ml volumetric flask. Add 10 ml of nitric acid (6.4), fill to the mark with water (6.1) and mix well. This solution is stable for one month.

6.7.2 Standard solution II, $\rho = 1 \text{ mg/l}$.

Pipette 1 ml of mercury standard solution I (6.7.1) into a 100 ml volumetric flask. Add 10 ml of nitric acid (6.4) fill to the mark with water (6.1) and mix well. This solution is stable for 7 days.

6.7.3 Standard solution III, $\rho = 100 \mu\text{g/l}$.

Pipette 10 ml of mercury standard solution II (6.7.2) into a 100 ml volumetric flask. Add 10 ml of nitric acid (6.4) fill to the mark with water (6.1) and mix well. This solution shall be freshly prepared on the day of use.

7 Apparatus

The instruments in 7.2 and 7.3 are used for VG-AAS method.

7.1 Common laboratory glassware.

7.2 Atomic absorption spectrophotometer, equipped with a heated quartz cell and an element specific lamp for mercury.

7.3 Vapour generation system.

The system should be adaptable to the atomic absorption spectrophotometer (7.2). Batch or continuous systems (segmented flow or flow-injection) may be used. The settings of the working conditions shall be optimized according to the manufacturer's instructions.

7.4 Mercury analyser, with combustion, amalgamation and measurement capabilities.

8 Procedure

8.1 Preparation of the test and blank solutions

Aqua regia digests of the samples and blanks prepared according to EN 17701-1:—¹ are measured after a suitable dilution. Calibration solutions with the same final concentration of aqua regia as in the tested samples are used. Blank test solutions are prepared for the measurement following the same procedure as for the test sample solutions.

If necessary, dilute the digest so that the final concentration of mercury to be determined is in the given calibration range (8.2). For all diluting steps, the volumetric flask is filled to the mark with diluted aqua regia (6.5). Prepare a diluted blank test solution by pipetting blank test solution and dilute it in the same way as the test sample solutions.

8.2 Preparation of the calibration solutions

Prepare a blank calibration solution and calibration solutions from the 100 µg/l mercury standard solution III (6.7.3). Suitable calibration standards covering the linear range of the calibration should be selected. Suggested calibration standards are in the concentration range 0 µg/l to 20 µg/l.

Pipette 0 ml, 1 ml, 2 ml, 5 ml, 10 ml and 20 ml of mercury standard solution III (6.7.3) into a series of 100 ml volumetric flasks. Fill to the mark with diluted aqua regia solution (6.5) and mix well. These solutions correspond to mercury concentrations of 0 µg/l, 1 µg/l, 2 µg/l, 5 µg/l, 10 µg/l and 20 µg/l, respectively.

NOTE It is possible to calibrate the instrument for higher concentrations of mercury if the calibration curve is linear or if a double range instrument is used. A suitable calibration depends on the type of the instrument and on the instructions provided by the manufacturer.

8.3 Measurement

8.3.1 Instrument conditions

Due to differences between various kinds of instruments, no detailed instructions for the operation of the specific instrument can be given. The instructions provided by the manufacturer should be followed.

The software of the instrument is used to calculate concentrations of mercury in the individual test solutions. All test solutions, blanks and calibration solutions are measured under the same optimized conditions.

8.3.2 Matrix effects

Calibration blank and calibration solutions, calibration check solution (one of the calibration standard solutions used to check stability of the calibration during the measurement), blank test solutions, test sample solutions and quality control solutions are measured after the stabilization of the instrument and verification of stable conditions. Run a calibration blank and a calibration check solution every 20 samples or less and at the end of the measurement.

Whenever an unknown matrix is encountered, check the following:

- matrix effects by running the spiked test sample solution;
- matrix effects by running a fivefold diluted test sample solution.

NOTE VG-AAS needs more attention regarding matrix effects than the direct amalgamation technique.