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Organic and organo-mineral fertilizers - Determination of the mercury content

Organische und organisch-mineralische Düngemittel -
Bestimmung des Quecksilbergehaltes

This draft Technical Specification is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 260.

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

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FprCEN/TS 17769:2021 (E)

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European foreword

This document (FprCEN/TS 17769:2021) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This document is currently submitted on the Vote on TS.

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FprCEN/TS 17769:2021 (E)**Introduction**

This document concerns the analytical measurement step for the determination of mercury in organic fertilizers and organo-mineral fertilizers after digestion by aqua regia according to FprCEN/TS 17768. The document 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). The 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.

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1 Scope

This document specifies a method for determination of the content of mercury (Hg) in organic fertilizers and organo-mineral fertilizers 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 FprCEN/TS 17768.

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 standard.

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 17773, *Organic and organo-mineral fertilizers — Determination of the dry matter content*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

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.

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 organic fertilizers and organo-mineral fertilizers 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

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the matrix depend on its concentrations. Copper and nickel exceeding a concentration of 500 mg/l may 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. samples with a very high silicates or phosphate content) may 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 organic fertilizers and organo-mineral fertilizers usually no difference is observed between the direct determination of mercury and the determination of mercury after digestion in aqua regia.

6 Reagents

6.1 General

The concentration of mercury in the reagents and in water shall be negligible compared to the lowest concentration of mercury to be determined. Reagents in 6.2, 6.6 and 6.7 are used only for the VG-AAS method.

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, substance concentration $c(\text{HCl}) \approx 12 \text{ mol/l}$; 37 % volume fraction; mass concentration 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, 0,8 mol/l nitric acid and 1,8 mol/l hydrochloric acid.

Mix 150 ml of hydrochloric acid (6.3) and 50 ml nitric acid (6.4) to 800 ml of water (6.1).

WARNING - For safety reasons the acid has to be poured into the water.

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. 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. 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. 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) solutions

6.7.1 Standard stock solution, $\rho = 1\,000$ 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.

6.7.2 Standard solution I, $\rho = 100$ mg/l.

Pipette 10 ml of the mercury standard stock solution (6.7.1) into a 100 ml volumetric flask. Add 10 ml of nitric acid (6.4), fill to the mark with water and mix well. This solution is stable for one month.

6.7.3 Standard solution II, $\rho = 1$ mg/l.

Pipette 1 ml of mercury standard solution I (6.7.2) into a 100 ml volumetric flask. Add 10 ml of nitric acid (6.4) fill to the mark with water and mix well. This solution is stable for 7 days.

6.7.4 Standard solution III, $\rho = 100$ μ g/l.

Pipette 10 ml of mercury standard solution II (6.7.3) into a 100 ml volumetric flask. Add 10 ml of nitric acid (6.4) fill to the mark with water 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 are measured after a suitable dilution. Calibration solutions with the same final concentration of aqua regia as in the tested samples are used. Blank tests are prepared for the measurement following the same procedure as for samples.

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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 solution by pipetting blank solution and dilute it in the same way as the test solutions.

8.2 Preparation of the calibration solutions

Prepare a calibration blank solution and calibration solutions from the 100 µg/l mercury standard solution III (6.7.4). 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 (6.7.4) 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

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Calibration blank and calibration solutions, calibration verification solution (one of the calibration standard solutions used to check calibration of the instrument), blank test, sample solutions and quality control solutions are measured after the stabilisation 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 spike sample;
- matrix effects by running a fivefold diluted sample.

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

8.3.3 Spiking

Add a known amount of a standard solution and an equal amount of a blank solution to two separate but equal portions of the sample solution (or its dilution). The spike shall be between 0,4 and 2 times the expected sample mass concentration. Measure both solutions as sample solutions. Determine the 'measured spike concentration' as the difference in mass concentration between the two spiked sample portions.

If the spike recovery is between 90 % and 110 % and/or the difference between the results for the original sample and the fivefold-diluted sample is less than 10 %, then the external calibration method may be applied. If the spike recovery or the difference for the diluted sample exceeds the given limit, the standard addition method shall be used. The standard addition method, spike recovery and dilution are