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Description

Please find enclosed the 1st working draft on WI 00223123, Soil improvers and growing media – Determination of the mercury content for your information.

As agreed during the last meeting of WG 4 on 2021-11-09, the enclosed 1st working draft and the forms for the activation of the work item will be circulated to CEN/TC 223 as soon as the call for tender for the project leaders is completed and the project leaders are known.

CEN/TC 223

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Soil improvers and growing media – Determination of the mercury content

ICS:

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European foreword

This document (prEN WI 00223123:2021) has been prepared by Technical Committee CEN/TC 223 “Soil improvers and growing media”, the secretariat of which is held by NEN.

This document is a working document.

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

Introduction

This document concerns the analytical measurement step for the determination of mercury in soil improvers and growing media after digestion by aqua regia according to EN 13650:—[1]. 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.

[1] Under preparation. Stage at the time of publication: EN 13650:20**.

1 Scope

This document specifies a method for determination of the content of mercury (Hg) in soil improvers and growing media 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 13650:— .

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.

EN 13650:—, *Soil improvers and growing media – Digestion by aqua regia for subsequent determination of elements*

EN 13040-1 :—[2], *Soil improvers and growing media – Sample preparation – Part 1: Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory bulk density*

3 Terms and definitions

For the purposes of this document the terms and definitions given in CEN/TS 00223137:—[3] and EN 13040-1:— 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.

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

[2] Under preparation. Stage at the time of publication: EN 13040-1:20**.

[3] Under preparation. Stage at the time of publication: prCEN/TS 00223137:20**.

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 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

The concentration of mercury in the reagents and in water shall be negligible compared to the lowest concentration of mercury to be determined.

6.1 Water with a specific conductivity not higher than 0,2 mS/m at 25 °C

6.2 Carrier gas

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

6.3 Hydrochloric acid, substance concentration c(HCl) ≈ 12 mol/l; 37 % volume fraction; mass concentration ρ approximately 1,18 g/ml.

6.4 Nitric acid, c(HNO_3) ≈ 16 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 1,0 l of 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, ρ ($SnCl_2 \cdot 2\ H_2O$) = 100 g/l

Dissolve 10 g of $SnCl_2 \cdot 2\ H_2O$ 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, $NaBH_4$, ρ ($NaBH_4$) = 30 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 solution, ρ = 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.

6.7.1 Standard solution I, ρ = 100 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 and mix well. This solution is stable for one month.

6.7.2 Standard solution II, ρ = 1 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 and mix well. This solution is stable for 7 days.

6.7.3 Standard solution III, ρ = 100 µg/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 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 according to EN 13650:— 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.

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 (6.7.3) and the 1 mg/l mercury standard solution II (6.7.2). Select suitable calibration standards covering the linear range of the calibration. Suggested calibration standards are in the concentration range 0 µg/l to 20 µg/l.

Pipette 0 ml, 1 ml, 2 ml and 5 ml of mercury standard solution III (6.7.3) and 1 ml and 2 ml of mercury standard solution II (6.7.2) 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 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 recommended to check the efficiency of interference reduction especially in complicated matrices and for unknown samples.

EXAMPLE Spiking procedure: pipette 10 ml of organic fertilizers and organo-mineral fertilizers digest or diluted digest into two test tubes, add 0,1 ml of standard solution (6.7.2) into the first test tube and 0,1 ml of blank into the second test tube. Mix well and measure.

8.3.4 Measurement by VG-AAS

Adjust the apparatus as specified in the operating manual of the manufacturer. Then optimize the settings, paying particular attention to gas flow, times and the amounts of tin(II) chloride or sodium borohydride introduced.

Absorbance is measured at 253.7 nm. The calibration solutions are measured first, followed by the blank and test solutions. Check the linear range of the calibration function. If the concentration of the test solution is outside the linear range, dilute the test solution with the mixed acid solution (6.5).

As an analytical control, one or more internal reference samples (IRM) having reliable known mercury contents could be analysed in parallel with the samples. IRM should be subjected to all steps in the method starting from the digestion.

8.3.5 Measurement by DA

100 µl of calibration standard solution, blank or sample digestate is transferred to a sample boat of liquid sample is weighed onto a tared sample boat. Instead of liquid samples, solid samples may be used as well.

NOTE If solid samples are used for the direct determination, an additional homogenisation of the sample may be necessary according to the lower sample intake used (e.g. 20 mg to 100 mg).

The sample boat is made from a non-amalgamating thermally stable material (e.g. nickel, quartz etc.). The sample boat with the sample is inserted into the instrument. The analytical parameters for drying, decomposition, waiting and analysis based on the weight, moisture content, and organic matter content of the sample are chosen. For most instruments the time of 70 s is used for drying 100 µl of liquid sample followed by 120 s of decomposition (appr. 650 °C) and 60 s of waiting to allow the gases to be purged out of the instrument. For samples with high organic matter content, which is typical for some organic fertilizers and organo-mineral fertilizers, the decomposition time should be increased to 180 s to 210 s and the waiting time to 90 s. Mercury trapped in the amalgamator is released and measured by a single wavelength AAS at 253.7 nm. The signal is evaluated by the software of the instrument.

9 Calculation and expression of the results

9.1 Content of mercury

Calculate the content of mercury in 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, w_X, as a mass fraction in mg/kg according to Formula (1).

$$m_X = \frac{V_{\mathrm{dig}} \times (X_S - X_b) \times D \times 100}{m \times DM} \tag{1}$$

where

m_X is a mass fraction of the individual element, in mg/kg; expressed on dry matter basis, according to EN 00223123:—

V_{dig} is the final volume after digestion in ml;

X_S is the concentration of the test solution, in mg/l;

X_b is the concentration of the blank solution, in mg/l;

m is the mass of the test sample, in g;

DM is the dry matter content in percent in the test sample according to EN 13040-1;

D is the dilution factor calculated according to Formula (2):

$$D = \frac{V_1}{V_{p1}} \times \frac{V_2}{V_{p2}} \times \ldots \frac{V_n}{V_{pn}} \quad (2)$$

where

$V_{1,2...n}$ are the volumes of the volumetric flasks, in ml;

$V_{p1,2...n}$ are the volumes of the pipetted solutions used for an individual diluting step, in ml.

10 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) the test method used with reference to this document (EN 00223123:—);

c) the method used for preparation of the digestion solution;

d) the test results obtained;

e) date of sampling and sampling procedure (if known);

f) date when the analysis was finished;

g) whether the requirement of the repeatability limit has been fulfilled; - optional

h) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

Annex A
(informative)

Methods for mercury determination

A.1 General

In Figure 1, possibilities for the mercury determination are displayed.

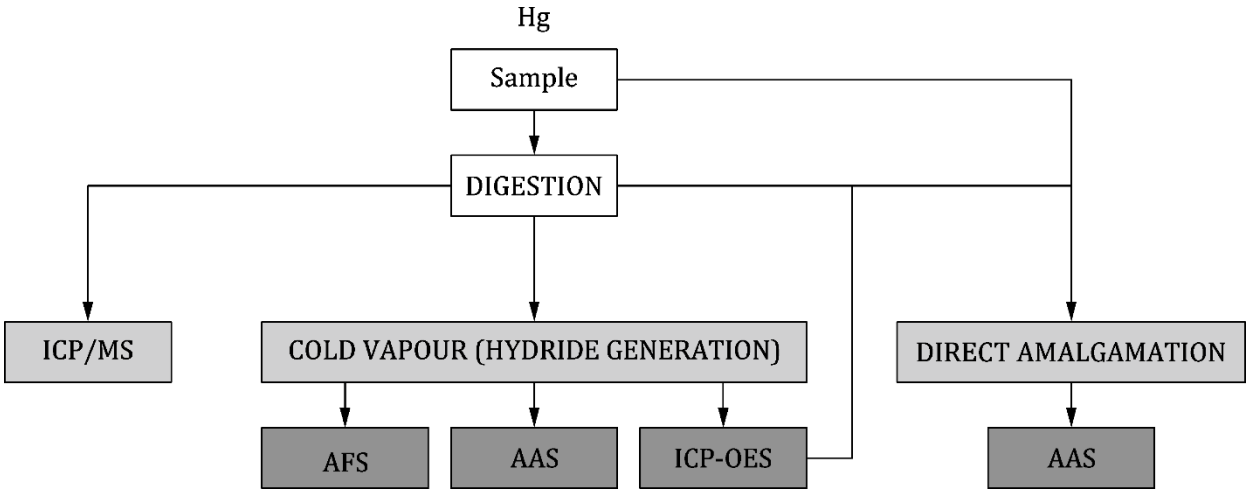

Figure 1: Methods for mercury determination

Parts of the EN 16175-1, EN 16175-2 and publication of Anja Jungnickel (Analytik Jena AG): *Mercury in the environment* [6] were used in this part of the Annex.

A.2 Cold vapour generation (hydride generation)

Mono- and divalent mercury is reduced to the elemental form by tin(II) chloride solution or sodium borohydride in acid medium. Elemental mercury is stripped off from the solution in a closed system, by means of a stream of argon or nitrogen, and the content of mercury is measured in gaseous form by one of the following analytical methods.

a) **Atomic absorption measurement (AAS)**: The mercury vapour, in the form of an atomic gas, passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Its absorbance at a wavelength of 253,7 nm is measured. The absorbance signal is a function of mercury concentration, and the concentrations are calculated using a calibration curve. The typical detection limit of mercury for this method is at 20 ng/l. The linear, dynamic measurement range extends over three orders of magnitude. The advantage of this technique is that other elements can also be determined.

b) **Atomic fluorescence measurement (AFS)**: The mercury vapour is injected into the cell of an atomic fluorescence spectrophotometer where the mercury atoms are excited by radiation of a specific wavelength, usually about 254 nm. The intensity of the fluorescence radiation is a function of mercury concentration. The concentrations are calculated using a calibration curve. A large measurement range of over five orders of magnitude is covered. With an additionally integrated amalgamation unit for mercury collection, typical detection limits below 1 ng/l are achieved.

c) **Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurement**: It is also possible to combine hydride technology with ICP-OES.

Mercury is determined in the gaseous form generated by an accessory to the ICP-OES instrument. The gaseous mercury is transported into the plasma torch. Element specific emission spectra are produced, and the intensities of the emission lines are monitored by photosensitive devices. This method gives a large linear dynamic range of more than six orders of magnitude for the determination of mercury and typically achieves very low detection limits of 100 ng/l.

Direct mercury determination using ICP-OES without upstream cold vapour technology can be used only for higher mercury concentrations.

A.3 Direct amalgamation technique

The sample is heated in an oxygen rich furnace, to release all the decomposition products, including mercury. These products are then carried in a stream of oxygen to the catalytic section of the furnace. The vapour is then carried to an amalgamation cell that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamation cell is rapidly heated, releasing mercury vapour. Flowing oxygen carries the mercury vapour through an absorbance cell positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at the 253.7 nm wavelength as a function of the mercury concentration in the sample (principle taken from booklet of Perkin Elmer to SMS 100 Mercury analyser [7]). More instruments using this principle are available on the market (LECO, Milestone, Altec, Perkin-Elmer etc.). Some instruments can measure mercury in two consecutive cells with different optical paths to achieve wider concentration range in one run.

A.4 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) can be used for direct ultra-trace analysis as a multi-element method for determining up to 75 elements, including mercury. For mercury, the maximum linear measurement range extends over ten orders of magnitude and a typical detection limit of 0.3 ng/l is achieved. The challenge lies in the carry-over and memory effects. The method is preferably used for speciation analysis after coupling ICP-MS with a suitable chromatograph.

Bibliography

[1] Regulation (EC) No 1009/2019 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilizing products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. Official Journal of the EU, L 170.

[2] U.S. EPA. 1998. "Method 7473 (SW-846): *Mercury in Solids and Solutions by Thermal Decomposition,* Amalgamation*, and Atomic Absorption Spectrophotometry*", *Washington, DC*.

[3] EN 16175-1:2016 *Sludge, treated biowaste and soil – Determination of mercury — Part 1: Cold-vapour atomic absorption spectrometry (CV – AAS)*

[4] EN 16175-2:2016 *Sludge, treated biowaste and soil – Determination of mercury — Part 2: Cold-vapour atomic fluorescence spectrometry (CV – AFS)*

[5] EN 16320:2013 *Fertilizers — Determination of trace elements — Determination of mercury by vapour generation (VG) after aqua regia dissolution*

[6] Anja Jungnickel: *Mercury in the environment*. Analytik Jena AG.

[7] SMS 100 Mercury analyser — principle description. Perkin Elmer, Inc., U.S.A.

[8] CEN/TS 00223137, *Soil improvers and growing media — Terminology*