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

**ICS:**

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## European foreword

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

This is a working document.

This document will supersede CEN/TS 17769:2022. In comparison with the previous edition the following main changes have been made:

Introduction revised according to the recommended wording from FprEN 17701-3.

Analysis of blends added into the Scope

Normative references to the digestion procedure added and deleted from Bibliography

Normative reference to dry matter content determination added and deleted from Bibliography

Normative reference to sampling added and deleted from Bibliography

Terms and definitions revised and completed

Editorial changes and changes demanded for FprEN 17701-3 were included

Chapter 9. 3. 5 Measurement by DA revised and completed

Test report revised

Bibliography revised

Annex B (informative) Results of the inter-laboratory study, text prepared to be added after the validation

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 and supports essential requirements of EU Directive(s) / Regulation(s).

## Introduction

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 [1] laying down rules on the making available on the market of EU fertilizing products (“FPR” or “Fertilising Products Regulation”).

The interest in organic and organo-mineral fertilizers has increased significantly in Europe as they are a valuable tool to use in agriculture. Standardization was identified as having an important role in order to promote the use of organic and organo-mineral fertilizers. The work of CEN/TC 260 seeks to improve the reliability of the supply chain, thereby boosting the confidence of farmers, industry, and consumers in organic and organo-mineral fertilizers, and will promote and support commercialisation of the European fertilizer 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 relevant amendments) concerning the modernization of methods of analysis of fertilizers within the framework of Regulation (EU) 2019/1009 of the European Parliament and of the Council [1]. This standardization request, presented as M/564, also contributes to the Communication on “Innovating for Sustainable Growth: A Bio economy for Europe”.

This document specifies the analytical measurement step for the determination of mercury in organic fertilizers and organo-mineral fertilizers after digestion by aqua regia according to prEN 17768<sup>1</sup>. The document covers cold vapour generation followed by mercury determination using atomic absorption spectrophotometry (VG-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.

The other standards developed for determination of mercury content in soils, sludges, treated biowaste, fertilizers and liming materials, plant biostimulants were studied and considered as a basis of the described method [2], [3] [4], [5], [6].

The inter-laboratory study reflects the final statistical characteristics of the method for the determination of mercury content in organic and organo-mineral fertilizers including both, the digestion in aqua regia 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.

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<sup>1</sup> Under preparation

## 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 prEN 17768<sup>2</sup>.

This document is applicable to the fertilizing product blends where the EU fertilising product organic and organo-mineral fertilizer contained in the blend represents the highest % by mass in the blend. In case of equal shares, the user may apply either this or the standard(s) applicable to the other component product(s).

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 1482-1 (2007), *Fertilizers and liming materials – Sampling and sample preparation – Part 1: Sampling*

EN 1482-2 (2007), *Fertilizers and liming materials – Sampling and sample preparation – Part 2: Sample preparation*

prEN 17768<sup>3</sup>, *Organic and organo-mineral fertilizers – Digestion by aqua regia for subsequent determination of elements*

prEN 17773<sup>4</sup>, *Organic and organo-mineral fertilizers — Determination of the dry matter content*

## 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>

### 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

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<sup>2,3,4</sup> Under preparation

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### **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

### **3.6**

#### **test sample solution**

solution prepared after extraction or digestion of the test sample according to appropriate specifications

### **3.7**

#### **digest**

solution received after mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacting with a reagent mixture

## **4 Principle**

### **4.1 Cold 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 Sampling**

Sampling and preparation of the test sample is not part of this procedure. Sampling and sample preparation method given in EN 1482 (all parts) with appropriate adaptations required account for specificities of organic and organo-mineral fertilizers shall be used.

## **6 Interferences**

### **6.1 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 can 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.

## 6.2 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) 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 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.

## 7 Reagents

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 mercury in the reagents and water used shall be negligible and low enough not to affect the results of the determination. Generally, ultra-pure water and acids of minimum p.a. quality are recommended. 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 7.2, 7.6 are used only for the VG-AAS method.

**7.1 Water** with a specific conductivity not higher than 0,2 mS/m at 25 °C, free from mercury

**7.2 Carrier gas**, argon or nitrogen for VG-AAS, oxygen for DA, purity according to the recommendation of the manufacturer.

**7.3 Hydrochloric acid**,  $c(\text{HCl}) \approx 12 \text{ mol/l}$ ;  $\rho$  approximately 1,18 g/ml.

**7.4 Nitric acid**,  $c(\text{HNO}_3) \approx 14,3 \text{ mol/l}$ ;  $\rho$  approximately 1,42 g/ml.

**7.5 Mixed acid solution**, 0,8 mol/l nitric acid and 1,8 mol/l hydrochloric acid.

Mix 150 ml of hydrochloric acid (7.3) and 50 ml nitric acid (7.4) to 800 ml of water (7.1).

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

### 7.6 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.

**7.6.1 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 (7.3), transfer to a 100 ml volumetric flask and fill to the mark with water (7.1). 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.

**7.6.2 Sodium borohydride solution**,  $\text{NaBH}_4$ ,  $\rho (\text{NaBH}_4) = 30 \text{ g/l}$

1 g sodium hydroxide,  $\text{NaOH}$ , is weighed into a 100 ml volumetric flask and dissolved in water (7.1). 3 g sodium borohydride,  $\text{NaBH}_4$ , are weighed into a 100 ml volumetric flask, dissolved and diluted to the mark with the sodium hydroxide solution.

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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 10 times with water (7.1). 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.

### 7.7 Standard (stock) solutions

#### 7.7.1 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.

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

Pipette 10 ml of the mercury standard stock solution (7.7.1) into a 100 ml volumetric flask. Add 10 ml of nitric acid (7.4), fill to the mark with water (7.1) and mix well. This solution is stable for one month.

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

Pipette 1 ml of mercury standard solution I (7.7.2) into a 100 ml volumetric flask. Add 10 ml of nitric acid (7.4) fill to the mark with water (7.1) and mix well. This solution is stable for 7 days.

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

Pipette 10 ml of mercury standard solution II (7.7.3) into a 100 ml volumetric flask. Add 10 ml of nitric acid (7.4) fill to the mark with water (7.1) and mix well. This solution shall be freshly prepared on the day of use.

## 8 Apparatus

The instruments in 8.2 and 8.3 are used for VG-AAS method.

### 8.1 Common laboratory glassware.

NOTE Due to memory effects of mercury, only glassware for preparation of stock/standard solutions of mercury, not plastic ware, should be used.

**8.2 Atomic absorption spectrophotometer (AAS)**, equipped with a heated quartz cell and an element specific lamp for mercury.

### 8.3 Vapour generation system

The system should be adaptable to the atomic absorption spectrophotometer (8.2). 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.

**8.4 Mercury analyser**, with combustion, amalgamation and measurement capabilities.



## 9 Procedure

### 9.1 Preparation of the test and blank solutions

Aqua regia digests of the samples and blanks shall be prepared according to prEN 17768<sup>5</sup>. The digests are measured after a suitable dilution. Calibration solutions (9.2) 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 (9.2). For all diluting steps, the volumetric flask is filled to the mark with diluted aqua regia (7.5). Prepare a diluted blank test solution by pipetting blank test solution and dilute it in the same way as the test sample solutions.

### 9.2 Preparation of the calibration solutions

Prepare a blank calibration solution and set of calibration solutions from the 100 µg/l mercury standard solution III (7.7.4). Suitable calibration standards covering the linear range of the calibration should be selected. Suggested calibration solution 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 (7.7.4) into a series of 100 ml volumetric flasks. Fill to the mark with diluted aqua regia solution (7.5) and mix well. These calibration 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 range of calibration depends on the type of the instrument and on the instructions provided by the manufacturer.

### 9.3 Measurement

#### 9.3.1 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.

#### 9.3.2 Matrix effects

Blank calibration solution and calibration solutions, calibration verification 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 solution 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.

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

### 9.3.3 Spiking

Add a known amount of a standard solution and an equal amount of a blank test solution to two separate but equal portions of the test sample solution (or its dilution). The spike shall be between 0,4 and 2 times the expected sample mass concentration. Measure both solutions as test 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 test sample solution or diluted test sample solution into two test tubes, add 0,1 ml of standard solution II (7.7.3) into the first test tube and 0,1 ml of blank test solution into the second test tube. Mix well and measure. Calculate the difference in mass concentration between the two spiked test solutions.

### 9.3.4 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 (7.6.1) or sodium borohydride (7.6.2) introduced.

Absorbance is measured at 253,7 nm. The set of calibration solutions (9.2) are measured first, followed by the blank test solution and sample test solutions. Check the linear range of the calibration function. If the concentration of the test sample solution is outside the linear range, dilute the test sample solution with the mixed acid solution (7.5).

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.

### 9.3.5 Measurement by DA

100 µl of calibration standard solution (9.2), blank test solution or test sample solution is transferred to a sample boat or (20 ± 0,1) mg to (100 ± 0,1) mg of solid or liquid sample is weighed onto a tared sample boat. The sample boat is made from a non-amalgamating thermally stable material (e.g. nickel, quartz,). The sample boat with the sample is inserted into the instrument. The analytical parameters for drying, decomposition, waiting and analysis based on the mass, 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 (approximately 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.

Note 1 The instrument is calibrated for a suitable range of calibration solutions based on the instructions provided by the manufacturer.

Note 2 Once the instrument is calibrated for the whole calibration range, only the everyday verification of the calibration is performed. During normal operating conditions, the calibration is verified using one of the calibration solutions. If the recovery is between 95 % and 105 % then the calibration is considered to be acceptable and then the measurement of the samples can be performed. The whole calibration range of the instrument is measured only if the result of recovery verification is unsatisfactory.

Note 3 Calibration is necessary to be performed whenever the catalytic tube or amalgamator is replaced or the oxygen flow rate is changed.

## 10 Calculation and expression of the results

Calculate the content of mercury in organic fertilizers and organo-mineral fertilizers,  $w_X$ , is a mass fraction in mg/kg according to Formula (1).

$$w_X = \frac{V_{\text{dig}} \times (X_S - X_b) \times D \times 100}{m \times w_{DM}} \quad (1)$$

where

$w_X$  is a mass fraction of mercury, in mg/kg; expressed on dry matter basis;

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

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

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

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

$w_{DM}$  is the dry matter content of the test sample expressed as a mass fraction in percent determined according to prEN 17773<sup>6</sup>;

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

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

where

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

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

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## **11 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 for preparation of the digest;
- c) the Standard used (including its year of publication);
- d) the test method used with reference to this document (prEN 17769<sup>7</sup>);
- e) the test results obtained;
- f) date of sampling and sampling procedure (if known);
- g) date when the analysis was finished;
- h) whether the requirement of the repeatability limit has been fulfilled (optional);
- i) all operating details not specified in this document, or regarded as optional, together with details of any deviations from the procedure, any incidents occurred or any unusual features observed when performing the method, which might have influenced the test result(s).

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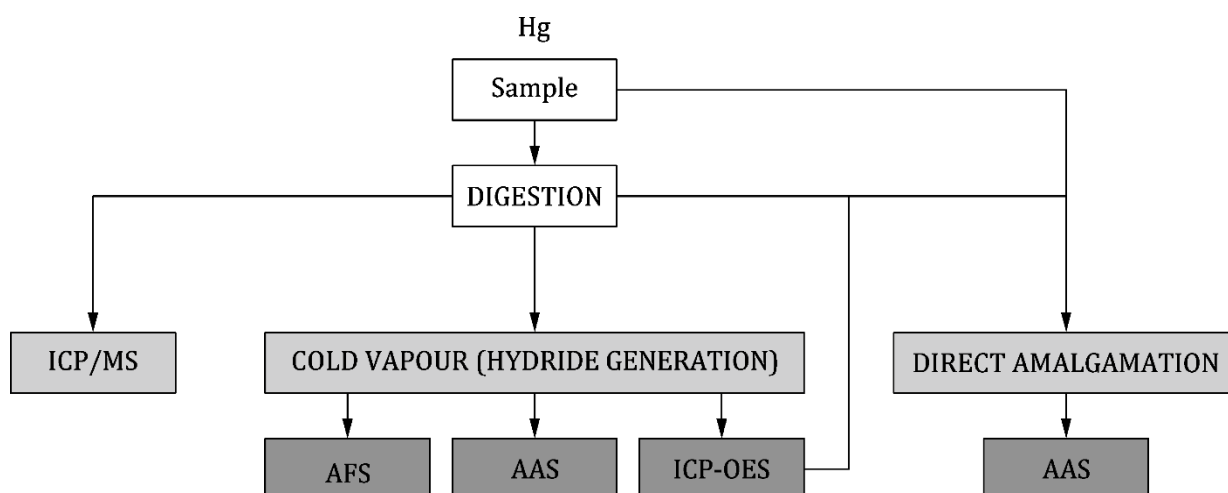
<sup>7</sup> Under preparation

## Annex A (informative)

### Overview of the methods for mercury determination

#### A.1 General

Figure A.1 presents possibilities for the mercury determination.



**Figure A.1 — Diagram of possibilities for the mercury determination**

Parts of the EN 16175-1[3], EN 16175-2[4] and publication of Anja Jungnickel (Analytik Jena AG): *Mercury in the environment* [7] 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.

**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.

**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 of up to 0,1 ng/l are achieved.

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

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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 3 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 [8]). More instruments using this principle are available on the market (LECO, Milestone, Altec, Perkin-Elmer, etc.<sup>1</sup>). 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.

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<sup>1</sup> These are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of these products.

## **Annex B** (informative)

### **Results of the inter-laboratory study**

#### **To be included after validation**

##### **B.1 Inter-laboratory tests**

The precision of the method has been determined in an inter-laboratory study (ILS) with xx participating laboratories from xx EU countries using xx different samples. Further details regarding the outcome of the inter-laboratory study are available in the final validation report [x].

The samples were chosen to represent all typical organic and organo-mineral fertilizers available on the market. The concentrations of mercury in the samples were very low (usually below LOQ). Therefore, spiking was necessary to achieve measurable concentrations of mercury.

xx different sample materials (x solid and x liquid, x of them blends) were included in the ILS.

A detailed description of the materials is given in Table B1.

**Table B.1 – Samples selected for the inter-laboratory study**

<b>Sample ID</b>	<b>Sample type</b>

##### **B.2 Statistical results for the determination of mercury**

Statistical evaluation was carried out based on the mathematical algorithms prescribed by ISO 5725-2 [9]. The ILS reflects the final statistical characteristics of the method for the determination of the mercury in aqua regia digests including both, the digestion and the measurement steps. The results are summarized in Table B.2.

Based on the statistical evaluation of the results from the collaborative trial, it is concluded that the proposed method is suitable for the determination of mercury (Hg) in aqua regia digests by (cold) vapour generation atomic absorption spectrophotometry or a method using a direct amalgamation technique after digestion of the samples by hot aqua regia in organic and organo-mineral fertilizers and their blends.

**Table B.2- Determination of mercury**

Sample	Hg-S-1	Hg-S-2	Hg-S-3	Hg-S-4	Hg-S-5	Hg-S-6	Hg-S-7	Hg-S-8
<b>L</b>								
<b>L<sub>A</sub></b>								
<b>N</b>								
<b>N<sub>A</sub></b>								
<b>O</b>								
$\bar{\bar{x}}$								
<b>s<sub>R</sub></b>								
<b>s<sub>r</sub></b>								
<b>RSD<sub>R</sub></b>								
<b>RSD<sub>r</sub></b>								
<b>R</b>								
<b>r</b>								
<b>HorRat</b>								
<b>L</b>	Number of participating laboratories							
<b>L<sub>A</sub></b>	Number of laboratories after elimination of outliers							
<b>N</b>	Number of all analytical values							
<b>N<sub>A</sub></b>	Number of analytical values after rejection of outliers							
<b>O</b>	Percentage of outliers (%)							
$\bar{\bar{x}}$	Total mean of results (without outliers) (mg/kg)							
<b>s<sub>R</sub></b>	Reproducibility standard deviation (mg/kg)							
<b>s<sub>r</sub></b>	Repeatability standard deviation (mg/kg)							
<b>RSD<sub>R</sub></b>	Relative reproducibility standard deviation (%)							
<b>RSD<sub>r</sub></b>	Relative repeatability standard deviation (%)							
<b>R</b>	Reproducibility limit (2,77 s <sub>R</sub> ) (mg/kg)							
<b>r</b>	Repeatability limit (2,77 s <sub>r</sub> ) (mg/kg)							
<b>HorRat</b>	HorRat index							



## Bibliography

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