

Sludge, treated biowaste and soil – Determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry and cold vapour atomic fluorescence spectrometry.

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

Descriptors:

Foreword

This document is a working document.

This document TF WI has been prepared by CEN/BT/Task Force 151 – Horizontal Standards in the Field of Sludge, Biowaste and Soil, the secretariat of which is held by Danish Standards.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex A, B, C or D, which is an integral part of this document.

This standard is applicable and validated for several types of matrices. The table below indicates which ones.

[table to be filled and amended by the standards writer]

Material	Validated for (type of sample, e.g. municipal sludge, compost)	Reference
Sludge		(reference)
Soil		
Biowaste	Not validated yet	
Sediment		
Waste		

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Introduction

NOTE: This is a draft version; the introduction will need to be adjusted.

This document is developed in the project 'Horizontal'. It is the result of a desk study "Horizontal no 20 AAS" and aims at evaluation of the latest developments in assessing mercury in sludge, soil, treated biowaste and neighbouring fields. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study the standard has been developed further as an modular horizontal method and has been validated within in the project 'Horizontal' .

A horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in a test procedure and not the whole test procedure (from sampling to analyses).

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The other horizontal modules that will be available in due time are to be found in the informative annex [xxx] which contains a brief overview of the modules that will be worked out in the project 'Horizontal.'

The texts of the chapters 1 to 12 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

1 Scope

This horizontal standard specifies a method for the determination of mercury in nitric acid digest or aqua regia extract of soil, sludge and waste, obtained in accordance with ISO 11466 with cold-vapour atomic absorption spectrometric method. Alternatively a cold vapour atomic fluorescence spectrometric method may be used. The matrix of the solution analyzed is dominated by the acids used in the digestion step. Tin(II)-chloride as a reduction substance is recommended in this standard, because sodium borohydride reduces many elements commonly found in soil, sludge and waste extract solutions, to the elemental state, which may cause matrix problems under particular circumstances. However, it is still possible to use sodium borohydride as reduction agent. The concentration range 0,1 – 10 µg/l in the digested solution, corresponding to 0,005 – 0,5 µg/g of mercury when a 2,0 g sample has been digested, can be determined directly. Higher concentrations can be determined if the digested solution is diluted.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO 3696: 1997, Water for analytical laboratory use - Specification and test methods.

ISO 5725-1: 1994 Accuracy (trueness and precision) of measurement methods and results – Part 1: general principles and definitions.

EN xxx: 200y (Hor.) Chemical analyses - Digestion of soil, sludge, biowaste and waste for the extraction of *aqua regia* soluble elements.

EN xxx: 200y (Hor.) Chemical analyses - Digestion of soil, sludge, biowaste and waste for the extraction of nitric acid soluble fraction of trace elements.

3 Terms and definitions

For the purpose of this European Standard, the following definition applies:

3.1

4 Safety remarks

5 Principle

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 nitrogen or mercury-free air. The mercury vapour, in the form of an atomic gas, passes through a cell positioned in the light path of an atomic absorption spectrometer. 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.

Alternatively, after the reduction step, the mercury vapour is injected into the cell of an atomic fluorescence spectrometer 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, and are linear over 10^6 to 10^7 orders of concentration.

6 Interferences and sources of errors

As the samples are digested before determination of mercury, there is no problem with organic substances that can absorb in the UV range. Neither are there any problems with mercury compounds which cannot be fully reduced with tin(II) chloride alone. The interference due to the presence of other elements in the matrix are dependent on their concentrations. Element concentrations in excess of those listed in Table 1 may cause negative bias. Iodide in concentrations $> 0,1$ mg/l causes interferences in the determination due to the formation of mercury complexes. In this case the other reduction agent, sodium tetrahydroborate, may be used.

The presence of water vapour or aerosol in the fluorescence cell may cause suppression due to quenching. Water vapour should be removed from the carrier gas stream using a hygroscopic membrane before entering the detector. The noble metals, such as gold and silver, amalgamate with mercury and, therefore, may cause suppression. Also anions, for instance sulphide, iodide and bromide, which complex strongly with mercury, can cause suppression.

Less interferences arises from heavy metals when tin(II) chloride is used rather than sodium tetrahydroborate. When flow systems are used, interference effects due to heavy metals may be less than indicated in Table 1.

Table 1 – Acceptable concentrations of some matrix elements in a measurement solution, in milligrams per litre.

Element	Atomic absorbance
Cu(II)	500
Ni(II)	500
Ag(I)	1
I	0,1
As(V)	0,5
Bi(III)	0,5
Sb(III)	0,5
Se(IV)	0,05

7 Reagents

All reagents shall be of recognised analytical grade with particularly low mercury content. Use deionized water or water distilled from an all-glass apparatus, complying with grade 2 as defined in ISO 3696. The water used for blank determinations, and for preparing reagents and standard

solutions shall have a mercury concentration that is negligible compared with the lowest concentration to be determined in the sample solutions.

Purity of argon or nitrogen should be $\geq 99,99\%$.

Note: For atomic fluorescence measurements argon should always be used, as nitrogen results in a significant signal reduction due to quenching of excited mercury atoms.

7.1 Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml

The same batch of hydrochloric acid shall be used throughout the procedure.

7.2 Nitric acid, 65 %; $\rho \sim 1,40$ g/ml

The same batch of nitric acid shall be used throughout the procedure.

7.2.1 Nitric acid, diluted solution

Pour 250 ml of water into a 500 ml volumetric flask. Add 50 ml of nitric acid (7.2) with caution, mix and fill to the mark with water. The acid concentration is corresponding to the digested sample when it has been diluted to a 100 ml solution.

7.2.2 Nitric acid, rinsing solution for glassware, ~ 2 mol/l

Add 150 ml of nitric acid (7.2) to about 500 ml of water, and dilute with water to 1000 ml.

7.3 Aqua regia, diluted solution

Add 105 ml hydrochloric acid (7.1) and 35 ml nitric acid (7.2) to 250 ml of water in a 500 ml volumetric flask, mix and fill to the mark with water. The acid concentration is corresponding to the digested sample when it has been diluted to a 100 ml solution.

7.4 Tin(II)-chloride solution, 10 % (m/v)

Dissolve 10 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 ml of hydrochloric acid (7.1), 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 minutes, if necessary. Prepare this solution on the day of use.

A solution of lower concentration, e.g. 0,5 g in 100 ml, may be used with flow systems. Prepare this latter solution freshly the day of use from the more concentrated solution by diluting with water.

7.5 Sodium borohydride solution, 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 , is weighed and dissolved in the sodium hydroxide solution, then diluted to the mark with water.

7.6 Mercury stock solution, 1000 mg/l

Use a commercially available quantitative stock solution with a mercury concentration of (1000 ± 2) mg/l. This solution is considered to be stable for at least one year, but in reference to guaranteed stability, see the recommendations of the manufacturer.

7.7 Mercury, standard solution I, 100 mg/l

Pipette 10 ml of the stock mercury solution (7.6) into a 100 ml volumetric flask, add 10 ml nitric acid (7.2.1), or 10 ml aqua regia (7.4), mix and fill to the mark with water.

7.8 Mercury, standard solution II, 1 mg/l

Pipette 1 ml of the standard mercury solution I (7.7) into a 100 ml volumetric flask, add 10 ml nitric acid (7.2.1), or 10 ml aqua regia (7.4), mix and fill to the mark with water.

7.9 Mercury, standard solution III, 100 µg/l

Pipette 10 ml of the standard mercury solution II (7.8) into a 100 ml volumetric flask, add 10 ml nitric acid (7.2.1), or 10 ml aqua regia (7.4), mix and fill to the mark with water.

8 Apparatus

All glassware shall be carefully cleaned for low trace element determinations, e.g. by immersion in nitric acid rinsing solution (7.2.2) for a minimum of six hours, followed by rinsing with water before use. The nitric acid shall be replaced each week.

8.2 Atomic absorption spectrometer (AAS)

Instrument equipped with an appropriate monitoring system, with a cold vapour generation system and a quartz or glass tube atomizer. As radiation source use a hollow cathode lamp or, preferably, an electrodeless discharge lamp (which give a greater and more stable light intensity) operated at a current recommended by the lamp and instrument manufacturer. An AAS system with background correction device is recommended.

8.3 Atomic fluorescence spectrometer (AAS)

It is equipped with a specific Hg lamp, a fixed 254 nm filter, a photomultiplier tube for the detection of fluorescence radiation and a suitable software for processing the output signal. Operate at a current recommended by the lamp or the instrument manufacturer. The argon gas supply should be with a two stage regulator. The use of a gas purifier consisting of activated carbon is recommended. Nitrogen gas will have reduced sensitivity.

8.4 Automated sample introduction system

Automated mercury flow systems (flow injection systems or continuous flow systems) are very common both for cold vapour atomic absorption spectrometry and atomic fluorescence spectrometry. They allow a concentration range lower by about one order of magnitude. Manually operated systems or semi-automated batch systems are adequate as well.

8.5 Cold-vapour generator, batch system or an automated flow injection analysis system (FIAS)

The system should be adaptable to the atomic absorption spectrometer (8.2) or to the atomic fluorescence spectrometer (8.3), according to the detection technique used for the determination of mercury. A flow-controlled nitrogen (7) or argon stream (7) is used as an inert carrier to transport

mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing solution (7.4) in combination with automatic start of the read signal of the spectrometer is required. Systems with a 10 cm quartz cell with quartz windows adapted for atomic absorption spectrometry (8.2) are commercially available. In this case, the quartz cell is electrically heated to a temperature of 60 - 100 °C to avoid condensation of water. For the atomic fluorescence spectrometer (8.3), condensation in the cell is avoided by the inclusion of a drying tube in the detection system.

NOTE If an automated system is used, where the reaction occurred continuously (FIA-System), the concentration of stannous chloride solution, reaction time and the gas-liquid separator configuration must be optimised due to the slow reaction kinetics of the reducing system.

Warning - It is essential that the manufacturer's safety recommendations are strictly observed.

9 Sampling and sample pre-treatment

9.1 Sampling

Sampling should be carried out in accordance with EN yyyy:2003 (Horizontal standard module(s) for sampling of sludge, soil and waste).

Samples should be stored in suitable containers with an appropriate closure material such as PTFE. Samples to be frozen may be stored in aluminium containers pre-cleaned by heating to 450°C for minimum 4 hours or by rinsing with a non-chlorinated solvent.

Samples should be kept cold ($< 8^{\circ}\text{C}$) and in the dark. The sample pre-treatment should take place within 24 hours of sampling. Alternatively, samples may be frozen (-18°C) directly after sampling and kept frozen for a maximum of one month before sample pre-treatment.

Transfer a sub-sample, homogenized according to EN www:2003 (Horizontal standard module(s) for pre-treatment of solid materials) of approximately 100 g to a porcelain dish.

Store the ground material in a desiccators or a tightly closed glass container.

9.2 Sample pre-treatment

Transfer a sub-sample, homogenized according to EN www:2003 (Horizontal standard module(s) for pre-treatment of solid materials) of approximately 100 g to a porcelain dish.

Store the ground material in a desiccators or a tightly closed glass container.

10 Procedure

10.1 Test solution

The nitric acid or aqua regia digested samples are transferred to 100 ml volumetric flasks and filled to the mark with water. The digested samples are prepared according to the Horizontal standards for digestion of soil, sludge and waste with nitric acid or aqua regia, respectively.

10.2 Blank test solution

Carry out a blank test at the same time as the extraction with nitric acid or aqua regia following the sample procedure, using the same quantities of all reagents for the determination, but omitting the test sample. Transfer 10 ml of the blank test solution to a 100 ml volumetric flask and fill to the mark with water.

10.3 Preparation of the calibration solutions

Before each batch of determinations, prepare a blank calibration solution and from the 100 µg/l mercury standard solution III (7.8) at least five calibration solutions covering the range of concentrations to be determined.

Pipette 1 ml, 2 ml, 5 ml, 10 ml and 20 ml of mercury standard solution (7.8) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (7.2.1) or diluted aqua regia solution (7.3) and mix well. These solutions correspond to mercury concentrations of 1 µg/l, 2 µg/l, 5 µg/l, 10 µg/l and 20 µg/l, respectively. Using 10 ml of each solution for the cold-vapour generator these solutions correspond to 10 ng, 20 ng, 50 ng, 100 ng and 200 ng of mercury, respectively.

10.4 Calibration

10.4.1 Cold vapour atomic absorption spectrometer (CV-AAS)

Set up the atomic absorption spectrometer (8.2) and the cold-vapour generator (8.4) according to the manufacturer's instructions, select a wavelength of 253,7 nm and adjust the quartz cell, the gas flow and the reaction time and flow rate of tin(II)-chloride solution (7.4) or sodium borohydride solution (7.5) to get maximum transmission intensity. Transfer 10 ml of blank calibration solution (10.3) into the cold-vapour generation bottle, connect the bottle to the system and start the time-controlled programme. The signal of the blank calibration solution should be negligible compared to with the lowest standard solution.

10.4.2 Cold vapour atomic fluorescence spectrometer (CV-AFS)

Set up the atomic fluorescence spectrometer (8.3) and the cold-vapour generator (8.4) according to the manufacturer's instructions. Adjust the quartz cell (if the instrument is equipped with one), the gas flow and the flow rate of stannous chloride or sodium borohydride. Wait until the system is in equilibrium. Aspirate a blank and start the measurement procedure. The signal should be negligible.

10.5 Plotting the calibration graph

Plot a graph having the mercury concentrations of the calibration solutions (10.3), from which the blank calibration solution reading has been subtracted, as abscissa, and the corresponding signal values as ordinate.

10.6 Measurement of test sample

Transfer 10 ml of blank test solution (10.2) into the cold-vapour generator bottle, connect the bottle to the system and start the time-controlled programme and record the signal. Repeat the measurement with each test solution (10.1), and record the signal.

If the mercury concentration of the test solution exceeds the range of calibration, the test solution shall be diluted with diluted nitric acid solution (7.2.1), or diluted aqua regia solution (7.3) accordingly.

NOTE The standard addition method can be used to check the absence of matrix effects. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied.

10.7 Quality Assurance of the overall procedure

10.7.1 Analysis of CRM

Analyse a test sample of a certified reference material with matrix comparable to the samples to be analysed.

10.7.1 Analysis of spiked natural samples

Analyse at least one spiked natural sample for each 20 samples in each series of samples:

Spike 50 µl or 100 µl of the metal stock solution (7.6) to an aliquot of a test sample. Establish a control limit for recovery of the spike based for example on precision data in Annex ? or on laboratory precision data.

NOTE If the recovery is outside the control limits, the whole series of analyses should be repeated.

10.7.2 Duplicate determination

Analyse two individual test samples of each dried, homogenised sample submitted for analysis. Establish a control limit for the difference between results for the two sub-samples based for example on precision data in Annex A or on laboratory precision data.

11 Expression of results

11.1 Method of calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the signal of the test solution (7.1) and of the blank test solution (7.2). Calculate the mercury content (w) of the sample, expressed as µg/g per dried matter using the equation:

$$w = (\rho - \rho_0) \times f \times V / m$$

where

w is the mass fraction of mercury in the sample, in µg/g dry matter,

ρ is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the test portion (7.1),

ρ_0 is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the same blank (7.2),

f is the dilution factor if the test solution (7.1) is diluted before the determination step,

V is the volume, in l, of the digested solution after dilution to the mark (usually 100 ml),

m is the mass of the sample in kg.

11.2 Expression of results

The result shall be expressed in mg/kg dry matter and reported to two significant figures. Values shall be rounded to 0,01 $\mu\text{g/g}$, but only significant figures should be expressed.

Example: $w(\text{Hg}) = 0,45 \mu\text{g/g}$

$w(\text{Hg}) = 12,5 \mu\text{g/g}$

12 Test report

The test report shall contain the following information:

- a) a reference to this European Standard including its date of publication;
- b) precise identification of the sample;
- c) expression of results, according to 11.2;
- d) any deviation from this standard, and any facts which may have influenced the result. Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx:2003 in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reason for deviation.

13 Performance characteristics

An interlaboratory test has to be performed to yield precision data.

Annex A
(informative)

Validation of methods

Annex B
(informative)

The modular horizontal system

Annex C
(informative)

Information on WP xx and the project Horizontal

Bibliography

ISO 16772, Soil quality, Determination of mercury in aqua regia soil extracts with cold-vapour atomic absorption spectrometry or cold-vapour atomic fluorescence spectrometry.

ISO 11466, Soil quality, Extraction of trace elements soluble in aqua regia.