BS EN 16175-1:2016

BSI Standards Publication

Sludge, treated biowaste and soil — Determination of mercury

Part 1: Cold-vapour atomic absorption spectrometry (CV-AAS)

National foreword

This British Standard is the UK implementation of EN 16175-1:2016.

BSI, as a member of CEN, is obliged to publish EN 16175-1 as a British Standard. However, attention is drawn to the fact that during the development of this European Standard, the UK committee voted against its approval as a European Standard.

The UK committee is concerned that some of the conditions attached to the validation trials lack clarity.

It is also the opinion of the UK committee that validation trials for horizontal methods should include conditions for the preparation and extraction of the original sample.

The UK participation in its preparation was entrusted by Technical Committee H/-, Health and Environment Sector Policy and Strategy Committee, to Subcommittee H/-/4, Environmental Testing Programmes.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

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English Version

Sludge, treated biowaste and soil - Determination of mercury - Part 1: Cold-vapour atomic absorption spectrometry (CV-AAS)

Boues, bio-déchets traités et sols - Détermination du mercure - Partie 1: Spectrométrie d'absorption atomique de vapeur froide (SAA-VP)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von Quecksilber - Teil 1: Kaltdampf-Atomabsorptionsspektrometrie (CV-AAS)

This European Standard was approved by CEN on 19 March 2016.

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European foreword

This document (EN 16175-1:2016) has been prepared by Technical Committee CEN/TC 444 “Test methods for environmental characterization of solid matrices”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2017, and conflicting national standards shall be withdrawn at the latest by April 2017.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TS 16175-1:2013.

The preparation of the previous edition of this analytical method by CEN is based on a mandate by the European Commission (Mandate M/330), which assigned the development of standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants, aiming to make these standards applicable to sludge, treated biowaste and soil as far as this is technically feasible.

EN 16175, *Sludge, treated biowaste and soil — Determination of mercury* comprises the following parts:

— *Part 1: Cold-vapour atomic absorption spectrometry (CV-AAS)*;

— *Part 2: Cold-vapour atomic fluorescence spectrometry (CV-AFS)*.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

This European Standard is applicable and validated for several types of matrices as indicated in Table 1 (see Annex A for the results of validation).

Table 1 — Matrices for which this European Standard is applicable and validated

Matrix	Materials used for validation
Sludge	Municipal sludge
Biowaste	Compost
Soil	Soil

WARNING — Persons using this European Standard should be familiar with usual laboratory practice. This European Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this European Standard be carried out by suitably trained staff.

1 Scope

This European Standard specifies a method for the determination of mercury in *aqua regia* or nitric acid digests of sludge, treated biowaste and soil, obtained according to EN 16173 or EN 16174 using cold-vapour atomic absorption spectrometry (CV-AAS). The lower working range limit is 0,03 mg/kg (dry matter basis).

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

EN 16173, *Sludge, treated biowaste and soil — Digestion of nitric acid soluble fractions of elements*

EN 16174, *Sludge, treated biowaste and soil — Digestion of aqua regia soluble fractions of elements*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

3 Principle

Mono- and divalent mercury is reduced to the elemental form by tin(II) chloride or sodium borohydride in acid medium. Elemental mercury is stripped off from the solution in a closed system. 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.

NOTE 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 in this European 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 1 µg/l to 10 µg/l in the digested solution, corresponding to 0,03 µg/g to 0,3 µg/g of mercury when a 3,0 g sample has been digested, can be determined directly. Higher concentrations can be determined if the digested solution is diluted. Sensitivity can be increased by the amalgamation technique.

4 Interferences

Because the samples are digested with oxidizing, strong acids before determination of mercury starts, there are no interferences with organic substances in the gas phase that can absorb in the UV range. Neither are there any interferences with mercury compounds which cannot be fully reduced with tin(II) chloride alone. The interferences due to the presence of other elements in the matrix depend on their concentrations. Element concentrations exceeding those listed in Table 2 may cause negative bias.

Fewer interferences arise from heavy metals when tin(II) chloride is used rather than sodium borohydride. When flow systems are used, interference effects due to heavy metals may be less than indicated in Table 2.

Table 2 — Tolerable concentrations of some matrix elements

Element	**Acceptable concentration in the test solution** mg/l
Cu(II)	500
Ni(II)	500
Ag(I)	1

5 Reagents

For the determination of mercury at trace and ultra-trace level, the reagents shall be of adequate purity. The concentration of mercury or interfering substances in the reagents and the water should be negligible compared to the lowest concentration of mercury to be determined.

5.1 Water quality 2 according to EN ISO 3696 for all sample preparations and dilutions.

5.2 Carrier gas, argon or nitrogen, with a purity of ≥ 99,99 %.

5.3 Hydrochloric acid, HCl, $\rho(HCl) = 1,18$ g/ml, $c(HCl) = 12$ mol/l, $w(HCl) = 370$ g/kg.

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

5.4 Nitric acid, HNO_3, $\rho(HNO_3) = 1,4$ g/ml, $c(HNO_3) = 15$ mol/l, $w(HNO_3) = 650$ g/kg.

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

5.5 Nitric acid, diluted solution.

Add 10 ml nitric acid (5.4) to 500 ml of water in a 1 000 ml volumetric flask, mix and fill to the mark with water.

5.6 Nitric acid, $c(HNO_3) = 2$ mol/l, rinsing solution for glassware.

Add 150 ml of nitric acid (5.4) to about 500 ml of water, and dilute with water to 1 000 ml.

5.7 *Aqua regia*, diluted solution.

Add 21 ml hydrochloric acid (5.3) and 7 ml nitric acid (5.4) to 500 ml of water in a 1 000 ml volumetric flask, mix and fill to the mark with water.

5.8 Tin(II) chloride solution, $\rho(SnCl_2 \cdot 2\,H_2O) = 100$ g/l.

Dissolve 10 g of $SnCl_2 \cdot 2\,H_2O$ in 30 ml of hydrochloric acid (5.3), 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.

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

5.9 Sodium borohydride solution, $NaBH_4$, $\rho(NaBH_4)$ = 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 latter solution freshly on the day of use from the more concentrated solution by diluting with water. Follow the recommendations of the manufacturer of the spectrometer.

5.10 Mercury standard stock solution, 1 000 mg/l.

Use a commercially available quantitative stock solution with a mercury concentration of (1 000 ± 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.

5.11 Mercury, standard solution I, 100 mg/l.

Pipette 10 ml of the mercury standard stock solution (5.10) into a 100 ml volumetric flask, add 10 ml nitric acid (5.4), mix and fill to the mark with water.

This solution is stable for one month.

5.12 Mercury, standard solution II, 1 mg/l.

Pipette 1 ml of the mercury standard solution I (5.11) into a 100 ml volumetric flask, add 10 ml nitric acid (5.4), mix and fill to the mark with water.

This solution is stable for 7 days.

5.13 Mercury, standard solution III, 100 µg/l.

Pipette 10 ml of the mercury standard solution II (5.12) into a 100 ml volumetric flask, add 10 ml nitric acid (5.4), mix and fill to the mark with water.

This solution shall be freshly prepared on the day of use.

6 Apparatus

6.1 Usual laboratory apparatus

All glassware shall be carefully cleaned for low trace element determinations, e. g. by immersion in nitric acid rinsing solution (5.6) for a minimum of 6 h, followed by rinsing with water before use. The nitric acid shall be replaced each week.

6.2 Atomic absorption spectrometer (AAS)

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

6.3 Automated sample introduction system

Automated mercury flow systems (flow injection systems or continuous flow systems) are very common for atomic absorption 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.

6.4 Cold-vapour generator, batch system or an automated flow injection analysis system (FIA)

The system should be adaptable to the atomic absorption spectrometer (6.2). A flow-controlled nitrogen or argon stream (5.2) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II) chloride solution (5.8) 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 (6.2) are commercially available. In this case, the quartz cell shall be electrically heated to a temperature of 60 °C to 100 °C to avoid condensation of water.

If an automated system is used, where the reaction occurs in a continuously flowing system (e. g. FIA), the concentration of tin(II) chloride solution, reaction time and the gas-liquid separator configuration shall be optimised due to the slow reaction kinetics of the reducing system.

7 Procedure

7.1 Test solution

The test solution is an aliquot of the particle free digest or extraction solution prepared according to EN 16173 or EN 16174.

To dilute the test solution transfer 10 ml of the prepared digest solution to a 100 ml volumetric flask and fill to the mark with water.

7.2 Test blank solution

Prepare a test blank solution at the same time as the extraction of the test sample with *aqua regia* or nitric acid following the same procedure, using the same quantities of all reagents for the determination, but omitting the test solution.

Transfer 10 ml of the test blank solution to a 100 ml volumetric flask and fill to the mark with water.

7.3 Preparation of the calibration solutions

Before each batch of determinations, prepare a calibration blank solution and from the 100 µg/l mercury standard solution III (5.13) at least five calibration solutions covering the range of concentrations to be determined.

Pipette 0 ml, 1 ml, 2 ml, 5 ml, 10 ml and 20 ml of mercury standard solution III (5.13) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (5.5) or diluted *aqua regia* solution (5.7) 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.

7.4 Calibration

Set up the atomic absorption spectrometer (6.2) and the cold-vapour generator (6.4) 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 (5.8) or sodium borohydride solution (5.9) to get acceptable sensitivity and peak shape. Start the measurements with the test blank solution. The signal of the blank calibration solution should be negligible compared to the lowest calibration solution.

7.5 Measurement of test sample

Connect the cold-vapour generator to the atomic absorption spectrometer and start the time-controlled measurement programme. Analyse the test blank solution (7.2) and then each test solution (7.1), and record the signals.

If the mercury concentration of the test solution exceeds the range of calibration, the test sample solution shall be diluted with diluted nitric acid solution (5.5), or diluted *aqua regia* solution (5.7) 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.

8 Calculation and expression of results

8.1 Calculation

Calculate the mercury contents of solid samples, corrected to dry matter, according to Formula (1):

$$w_{\mathrm{Hg}} = \frac{(\rho_1 - \rho_0) \cdot f \cdot V \cdot C}{m} \qquad (1)$$

with

$$C = 100/w_{\mathrm{dm}} \qquad (2)$$

where

w_{Hg}	is the mass fraction of mercury in the solid sample, expressed in milligrams per kilogram (mg/kg) corrected to dry matter at 105 °C;
ρ_1	is the concentration of the element in the test solution (7.1), expressed in milligrams per liter (mg/l);
ρ_0	is the concentration of the element in the test blank solution (7.2), expressed in milligrams per liter (mg/l);
f	is the dilution factor of the test solution (7.1);
V	is the volume of the digest solution prepared according to EN 16173 or EN 16174, expressed in liters (l);
m	is the mass of the digested test portion, expressed in kilograms (kg);
C	is the correction factor for dry mass;
w_{dm}	is the dry matter fraction of the sample, determined according to EN 15934, in per cent (%).

8.2 Expression of results

Report as many significant figures as are acceptable according to the precision of the measuring values but not more than three significant figures.

9 Performance data

The performance characteristics of the method data have been evaluated (see Annex A).

10 Test report

The test report shall contain at least the following information:

a) a reference to this European Standard (EN 16175-1);

b) all information necessary for identification of the sample;

c) information about the pretreatment and method of digestion of the sample;

d) results of the determination as indicated in 8.2;

e) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Repeatability and reproducibility data

A.1 Materials used in the interlaboratory comparison study

The interlaboratory comparison on determination of mercury in *aqua regia* and nitric acid digests of sludge, treated biowaste and soil by cold-vapour atomic absorption spectrometry was carried out by 7 to 8 European laboratories on 5 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broadly as possible, because the method will find general application across different types of soil and soil related materials.

Table A.1 lists the types of materials tested.

Table A.1 — Materials tested in the interlaboratory comparison on the determination of mercury in *aqua regia* and nitric acid digests of sludge, treated biowaste and soil using CV-AAS

Grain size	Sample	Material
Sludge (< 0,5 mm)	Sludge 1	Mix 1 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany
	Sludge 2	Mix 2 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany
Fine grained (< 2,0 mm)	Compost 2	Compost from Germany
	Soil 1	A sludge amended soil from Pavia, Italy
	Soil 2	A sludge amended soil from Düsseldorf, Germany

A.2 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table A.2).

Table A.2 — Results of the interlaboratory comparison study on the determination of mercury in *aqua regia* and nitric acid digests – Cold-vapour atomic absorption spectrometry

Matrix	l	n	n_0	$\bar{\bar{x}}$	s_R	$C_{V,R}$	s_r	$C_{V,r}$
Sludge 1	7	27	2	1,120	0,253	22,6	0,052	4,61
Sludge 2	8	41	0	0,660	0,156	23,6	0,053	8,05
Compost 2	7	32	1	0,118	0,014	12,0	0,005	3,88
Soil 1	7	38	0	0,070	0,021	29,7	0,008	11,8
Soil 2	7	38	0	0,052	0,008	14,7	0,005	8,71

Explanation of symbols

l	number of participating laboratories
n	number of analytical results
n_0	number of rejected laboratories
$\bar{\bar{x}}$	total mean of results (without outliers) in milligram per kilogram (mg/kg)
s_R	reproducibility standard deviation in milligram per kilogram (mg/kg)
$C_{V,R}$	coefficient of variation of reproducibility in percent (%)
s_r	repeatability standard deviation in milligram per kilogram (mg/kg)
$C_{V,r}$	coefficient of variation of repeatability in percent (%)

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[1] Umweltbundesamt, Texte 42/2015: Validierung von Analyseverfahren, die im Rahmen des Projektes HORIZONTAL entwickelt, jedoch nicht validiert wurden.
Download: http://www.umweltbundesamt.de/publikationen

[2] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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