SLOVENSKI STANDARD
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Blato, obdelani biološki odpadki in tla - Določevanje živega srebra - 1. del: Metoda atomske absorpcijske spektrometrije s tehniko hladnih par (CV-AAS)

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

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

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

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English Version

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This Technical Specification (CEN/TS) was approved by CEN on 16 June 2012 for provisional application.

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Foreword

This document (CEN/TS 16175-1:2013) has been prepared by Technical Committee CEN/TC 400 “Project Committee - Horizontal standards in the fields of sludge, biowaste and soil”, the secretariat of which is held by DIN.

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 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).

The preparation of this document 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.

CEN/TS 16175, *Sludge, treated biowaste and soil — Determination of mercury*, is comprised of 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 organisations of the following countries are bound to announce this Technical Specification: 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 Technical Specification is validated for several types of matrices as indicated in Table 1 (see also Annex A for the results of validation).

Table 1 — Matrices for which this Technical Specification is applicable and validated

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

WARNING — Persons using this Technical Specification should be familiar with usual laboratory practice. This Technical Specification 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 Technical Specification be carried out by suitably trained staff.

1 Scope

This Technical Specification 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 Technical Specification, 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 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, $\rho(\text{HCl}) = 1{,}18$ g/ml, $c(\text{HCl}) = 12$ mol/l, $w(\text{HCl}) = 370$ 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, NaBH4, 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 stock mercury 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.