
Blato, obdelani biološki odpadki in tla - Določevanje živega srebra - 2. del: Metoda atomske fluorescenčne spektrometrije s tehniko hladnih par (CV-AFS)

Sludge, treated biowaste and soil - Determination of mercury - Part 2: Cold vapour atomic fluorescence spectrometry (CV-AFS)

Schlamm, behandelte Bioabfall und Boden - Bestimmung von Quecksilber - Teil 2: Kaldampf-Atomfluoreszenzspektrometrie (CV-AFS)

Boues, biodéchets traités et sols - Détermination du mercure - Partie 2: Spectrométrie de fluorescence atomique de vapeur froide (CV-AFS)

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**Sludge, treated biowaste and soil - Determination of mercury -
Part 2: Cold-vapour atomic fluorescence spectrometry (CV-AFS)**

Boues, bio-déchets traités et sols - Détermination du
mercure - Partie 2: Spectrométrie de fluorescence
atomique de vapeur froide (SFA-VP)

Schlamm, behandelter Bioabfall und Boden - Bestimmung
von Quecksilber - Teil 2: Kaltdampf-
Atomfluoreszenzspektrometrie (CV-AFS)

This Technical Specification (CEN/TS) was approved by CEN on 23 July 2012 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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Foreword

This document (CEN/TS 16175-2:2013) 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.

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.

CEN/TS 16175-2:2013 (E)

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 fluorescence spectrometry (CV-AVS). The lower working range limit is 0,003 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 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. 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. 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 0,1 µg/l to 10 µg/l in the digested solution, corresponding to 0,003 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

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 sulfide, iodide and bromide, which complex strongly with mercury, can cause suppression.

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 1.

Table 1 — 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 Hydrochloric acid, HCl, $\rho(\text{HCl}) = 1,18 \text{ g/ml}$, $c(\text{HCl}) = 12 \text{ mol/l}$, $w(\text{HCl}) = 370 \text{ g/kg}$.

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

5.3 Nitric acid, HNO_3 , $\rho(\text{HNO}_3) = 1,4 \text{ g/ml}$, $c(\text{HNO}_3) = 15 \text{ mol/l}$, $w(\text{HNO}_3) = 650 \text{ g/kg}$.

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

5.4 Nitric acid, diluted solution, <https://standards.iteh.ai/catalog/standards/sist/44d18dd2-79e2-4daf-a8c5-bb19a2e6c4cc/sist-ts-cen-ts-16175-2-2013>

Add 10 ml nitric acid (5.3) to 500 ml of water in a 1 000 ml volumetric flask, mix and fill to the mark with water.

5.5 Nitric acid, $c(\text{HNO}_3) = 2 \text{ mol/l}$, rinsing solution for glassware.

Add 150 ml of nitric acid (5.3) to about 500 ml of water, and dilute with water to 1 000 ml.

5.6 Aqua regia, diluted solution.

Add 21 ml hydrochloric acid (5.2) and 7 ml nitric acid (5.3) to 500 ml of water in a 1 000 ml volumetric flask, mix and fill to the mark with water.

5.7 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 (5.2), 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.

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

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.

CEN/TS 16175-2:2013 (E)**5.9 Mercury standard stock solution, 1 000 mg/l**

Use a commercially available quantitative stock solution with a mercury concentration of $(1\ 000 \pm 2)$ 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.

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

Pipette 10 ml of the stock mercury solution (5.9) into a 100 ml volumetric flask, add 10 ml nitric acid (5.3), mix and fill to the mark with water.

This solution is stable for one month.

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

Pipette 1 ml of the mercury standard solution I (5.10) into a 100 ml volumetric flask, add 10 ml nitric acid (5.3), mix and fill to the mark with water.

This solution is stable for 7 days.

5.12 Mercury, standard solution III, 100 µg/l

Pipette 10 ml of the mercury standard solution II (5.11) into a 100 ml volumetric flask, add 10 ml nitric acid (5.3), mix and fill to the mark with water.

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

5.13 Carrier gas, argon or nitrogen, with a purity of $\geq 99.99\%$ **6 Apparatus**

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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 (5.5) for a minimum of 6 h, followed by rinsing with water before use. The nitric acid shall be replaced each week.

6.2 Atomic fluorescence spectrometer (AFS)

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 gas supply (argon or nitrogen) should be equipped with a two stage regulator. The use of a gas purifier consisting of activated carbon is recommended. Nitrogen gas will cause reduced sensitivity compared to argon.

6.3 Automated sample introduction system

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

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

The system should be adaptable to the atomic fluorescence spectrometer (6.2). A flow-controlled argon or nitrogen stream (5.13) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II) chloride solution (5.7) in combination with automatic start of the read signal of the spectrometer is required. For the atomic fluorescence spectrometer (6.2), condensation in the cell is avoided by the inclusion of a drying tube in the detection system.

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 (5.12) 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 (5.12) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (5.4) or diluted *aqua regia* solution (5.6) 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 fluorescence spectrometer (6.2) and the cold-vapour generator (6.4) according to the manufacturer's instructions. Adjust the measuring cell, the gas flow and the flow rate of tin(II) chloride solution (5.7) or sodium borohydride solution (5.8). Wait until the system is in equilibrium. Aspirate a blank and start the measurement procedure. The signal should be negligible.

7.5 Measurement of test sample

Connect the cold-vapour generator to the atomic fluorescence 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 (5.4), or diluted *aqua regia* solution (5.6) accordingly.