TECHNICAL
SPECIFICATION

ISO/TS
16727

First edition
2013-09-15

Corrected version
2013-10-01

Soil quality — Determination of mercury — Cold vapour atomic fluorescence spectrometry (CVAFS)

Qualité du sol — Dosage du mercure — Spectrométrie de fluorescence atomique à vapeur froide (CVAFS)

Reference number
ISO/TS 16727:2013(E)

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Published in Switzerland

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

In this corrected version, the status of the document was amended to Technical Specification on the cover page. In addition, the page headings were changed to ISO/TS 16727:2013(E).

Introduction

ISO/TS 16727 is based upon CEN/TS 16175-2, *Sludge, treated biowaste and soil — Determination of mercury — Part 2: Cold vapour atomic fluorescence spectrometry (CV-AFS)*, which was developed by CEN/TC 400, *Project Committee — Horizontal standards in the fields of sludge, biowaste and soil*.

TECHNICAL SPECIFICATION **ISO/TS 16727:2013(E)**

Soil quality — Determination of mercury — Cold vapour atomic fluorescence spectrometry (CVAFS)

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 ISO 11466 or ISO 16729 using cold vapour atomic fluorescence spectrometry. The lower working range limit is 0,003 mg/kg (dry matter).

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.

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

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

ISO 16729, *Soil quality — Digestion of nitric acid soluble fractions of elements*

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

3 Principle

Monovalent 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 of 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.

Less 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 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 ISO 3696 for all sample preparations and dilutions.

5.2 **Hydrochloric acid,** HCl, $\rho(\mathrm{HCl}) \approx 1{,}17$ g/ml, $c(\mathrm{HCl}) \approx 12$ mol/l, $w(\mathrm{HCl}) \approx 370$ g/kg.

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

5.3 **Nitric acid,** $\mathrm{HNO_3}$, $\rho(\mathrm{HNO_3}) \approx 1{,}4$ g/ml, $c(\mathrm{HNO_3}) \approx 15$ mol/l $w(\mathrm{HNO_3}) \approx 650$ g/kg.

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

5.4 **Nitric acid,** diluted solution (1 + 9).

Add 100 ml of 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,** rinsing solution for glassware, ≈ 2 mol/l.

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 (1 + 9).

Add 21 ml of hydrochloric acid (5.2) and 7 ml of 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,** $\rho(\mathrm{SnCl_2 \cdot 2\ H_2\ O}) = 100$ g/l.

Dissolve 10 g of $\mathrm{SnCl_2 \cdot 2\ H_2O}$ 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, $NaBH_4$, 30 g/l.

1 g of sodium hydroxide, NaOH, is weighed into a 100 ml volumetric flask and dissolved in water. 3 g of sodium borohydride, $NaBH_4$, is weighed and dissolved in the sodium hydroxide solution, then diluted to the mark with water.

5.9 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.

5.10 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 of 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 of 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 of 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 Argon, with a purity of ≥ 99,99 %.

6 Apparatus

6.1 Usual laboratory apparatus

All glassware shall be carefully cleaned as usual 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 stream (5.13) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing 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 occurres continuously (FIA-System), the concentration of stannous 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 sample solution

The test sample solution is an aliquot of the particle free digest or extraction solution prepared according to ISO 11466 or ISO 16729.

7.2 Test blank solution

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

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 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.

7.5 Measurement of test sample

Transfer 10 ml of test blank solution (7.2) 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 sample solution (7.1), and record the signal.

If the mercury concentration of the test sample 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.

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

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the signal of the tenfold diluted test sample solution (7.1) and of the tenfold diluted blank test sample solution (7.2).

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

$$w_{(\mathrm{Hg})} = \frac{(\rho_1 - \rho_0)\times 10\times f\times V\times C}{m} \tag{1}$$

where

$w_{(\mathrm{Hg})}$ is the mass fraction of mercury in the solid sample, in milligrams per kilogram (mg/kg) corrected to dry matter at 105 °C;

ρ_1 is the mercury concentration in the diluted test sample solution (7.1), in micrograms per litre (µg/l);

ρ_0 is the mercury concentration in the diluted test blank solution (7.2), in micrograms per litre (µg/l);

f is the dilution factor of the test sample solution (7.1);

V is the volume of the test sample solution (digest solution), in litres (l);

m is the mass of the digested test portion, in grams (g);

C is the correction factor for dry matter.

The correction factor C is calculated by Equation (2):

$$C = \frac{100}{w_{dm}} \tag{2}$$

where w_{dm} is the dry matter fraction of the sample, obtained according to ISO 11465, in percent (%).

8.2 Expression of results

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

9 Test report

The test report shall contain at least the following information:

a) a reference to this Technical Specification (ISO/TS 16727);

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 Technical Specification or which are optional, as well as any factor which may have affected the results.

Bibliography

[1] ISO 16772, *Soil quality — Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry*

ICS 13.080.10

Price based on 6 pages