
**Soil quality — Determination of mercury
in aqua regia soil extracts with cold-
vapour atomic spectrometry or cold-
vapour atomic fluorescence spectrometry**

*Qualité du sol — Dosage du mercure dans les extraits de sol à l'eau
régale par spectrométrie d'absorption atomique de vapeur froide ou par
spectrométrie de fluorescence atomique de vapeur froide*

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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Soil quality — Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry

WARNING — Mercury is highly toxic. Safety measures shall be taken in handling mercury and mercury solutions. Mercury compounds should not be introduced into the environment. The laboratory handling these compounds should be aware of the relevant international and national legislation regulating the handling of mercury and its compounds.

1 Scope

This International Standard specifies a method for the determination of mercury in an aqua regia extract of soil, obtained in accordance with ISO 11464 and ISO 11466, using cold-vapour atomic absorption spectrometry or cold-vapour atomic fluorescence spectrometry. The limit of determination of the method is at least 0,1 mg/kg.

2 Normative references

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

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 11464:1994, *Soil quality — Pretreatment of samples for physico-chemical analysis*

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 11466:1995, *Soil quality — Extraction of trace elements soluble in aqua regia*

3 Principle

Mercury is reduced to the elemental state by tin(II) chloride solution and liberated from solution in a closed system. The mercury vapour 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.

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. The intensity of the fluorescence radiation is a function of mercury concentration.

NOTE Tin(II) chloride as a reduction substance is specified in this International Standard because sodium borohydride reduces many elements common in soil extract solutions to the elemental state, which cause matrix problems under particular circumstances.

4 Reagents and gases

All reagents shall be of recognized analytical grade. 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 calibration concentration, e.g. 10 times of the determination limit of the method.

4.1 Hydrochloric acid, $w(\text{HCl}) = 37\%$; $c(\text{HCl}) \approx 12 \text{ mol/l}$, $\rho(\text{HCl}) \approx 1,18 \text{ g/ml}$.

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

4.2 Nitric acid, $w(\text{HNO}_3) = 65\%$, $c(\text{HNO}_3) \approx 14,5 \text{ mol/l}$, $\rho(\text{HNO}_3) \approx 1,40 \text{ g/ml}$.

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

When different batches of acids are used throughout the procedure, the blank shall be controlled for each batch.

4.3 Nitric acid, diluted solution (1+4), $c(\text{HNO}_3) \approx 4 \text{ mol/l}$.

Add slowly 250 ml of nitric acid (4.2) to 500 ml of water in a 1000 ml volumetric flask, mix and fill to the mark with water.

4.4 Aqua regia, diluted solution (1+9).

Add 21 ml hydrochloric acid (4.1) and 7 ml nitric acid (4.2) to 500 ml of water in a 1000 ml volumetric flask, mix and fill to the mark with water.

4.5 Tin(II) chloride solution, $\rho(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}) = 100 \text{ g/l}$, $c(\text{Sn}) = 0,443 \text{ mol/l}$.

Dissolve 10 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 ml of hydrochloric acid (4.1), 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 min, if necessary. Prepare this solution on the day of use.

NOTE Other concentrations of tin(II) chloride may be necessary using other systems.

4.6 Mercury, stock solution corresponding to $\rho(\text{Hg}) = 1000 \text{ mg/l}$.

4.6.1 General

Two sources of stock solutions can be used:

- commercially available stock solutions (4.6.2);
- stock solutions prepared in the laboratory from elemental mercury (4.6.3).

4.6.2 Commercially available stock solutions

Certified commercial stock solutions should preferably be used.

Commercial as well as home-made stock solutions should be checked on a regular basis.

NOTE Commercially available stock solutions have the advantage that they limit the need to handle toxic mercury. However, special care needs to be taken that these solutions are supplied with a certified composition from a reputable source.

4.6.3 Stock solutions prepared in the laboratory from elemental mercury

In a beaker covered with a watch glass, dissolve $100 \text{ mg} \pm 0,4 \text{ mg}$ of mercury metal [minimum purity $w(\text{Hg}) = 99,99 \%$] with 17 ml nitric acid (4.2). Dilute with water, boil gently to expel nitrous oxides, cool and transfer quantitatively into a 100 ml volumetric flask and fill to the mark with water. This solution is stable for at least six months.

4.7 Mercury, standard solution corresponding to $\rho(\text{Hg}) = 20 \text{ mg/l}$.

Pipette 2 ml of the stock mercury solution (4.6) into a 100 ml volumetric flask, add 10 ml nitric acid (4.3), mix and fill to the mark with water.

4.8 Mercury, standard solution corresponding to $\rho(\text{Hg}) = 0,2 \text{ mg/l}$.

Pipette 1 ml of the standard mercury solution (4.7) into a 100 ml volumetric flask, add 10 ml of nitric acid (4.3), mix and fill to the mark with water. Prepare this solution on the day of use.

Low-level mercury standard solutions should be stored in suitable silica flasks or use PFA or FEP bottles as mercury vapour diffuses through low density polyethene bottles.

4.9 Argon or nitrogen.

Argon or nitrogen with a purity of 99,99% should be used as carrier gases. For atomic fluorescence spectrometric techniques, argon is strongly recommended because the sensitivity is higher than with nitrogen.

5 Apparatus

5.1 Usual laboratory glassware.

All glassware or PFA, FEP bottles shall be carefully cleaned for determinations involving trace elements, e.g. by immersion in aqueous nitric acid solution of 5 % volume fraction for a minimum of 6 h, followed by rinsing with water before use. The nitric acid shall be replaced each week. Grade B volumetric glassware is adequate for this analysis (see ISO 648 and ISO 1042).

5.2 Atomic absorption spectrometer (AAS), equipped with a mercury hollow cathode or an electrodeless discharge lamp (which gives a greater light intensity) operated at a current recommended by the lamp and instrument manufacturer, and an automatic background correction device.

5.3 Atomic fluorescence spectrometer (AFS), equipped with a specific mercury lamp, a fixed 254 nm filter and a photomultiplier tube for the detection of fluorescence radiation.

Operate at a current recommended by the lamp and instrument manufacturer (see also EN 13506).

5.4 Cold-vapour generator, batch system or an automated flow injection analysis system (FIAS), adaptable either to the atomic absorption spectrometer (5.2) or to the atomic fluorescence spectrometer (5.3), according to the detection technique used for the determination of mercury.

A flow-controlled nitrogen or argon stream (4.9) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing solution (4.5) in combination with automatic start of the read signal of the spectrometer is required. Systems with a 10 cm or longer silica cell path length with silica windows adapted for atomic absorption spectrometry (5.2) are commercially available. In this case, the silica cell is electrically heated to a temperature of 50 °C to 100 °C to avoid condensation of water. For the atomic fluorescence spectrometer (5.3), condensation in the silica cell is avoided by inclusion of a high efficiency permeation drying tube in the detection system.

If an automated system is used, where the reaction occurs continuously (FIAS), the concentration of tin(II) chloride solution, reaction time and the gas-liquid separator configuration shall be optimized due to the slow reaction kinetics of the reducing system.

WARNING — It is essential that the manufacturer's safety recommendations be strictly observed.

6 Quality control

Users of this International Standard are advised to operate their laboratories to accepted quality control procedures. Certified reference materials (CRM) should be used to establish the amounts of mercury in in-house reference materials. The latter can be used for routine quality control of the procedures given in this International Standard. Results shall be established with control charts, within the laboratory. No result shall be accepted which falls outside an agreed limit. Quality control procedures based on widely accepted statistical techniques shall be used to establish such limits, to ensure that these are stable and that no long-term drift is occurring. CRMs should be used regularly to maintain the integrity of the in-house reference materials and, thereby, the quality control system.

7 Procedure

7.1 Test solution

Transfer 10 ml of aqua regia soil extracts prepared according to ISO 11466 into a 100 ml volumetric flask and fill to the mark with water.

7.2 Blank test solution

Carry out a blank test at the same time as the extraction with aqua regia, using cleaned silica sand instead of the soil sample, and following the sampling procedure given in ISO 11466. Use the same quantities of all the reagents for the determination, but omit the test portion. Transfer 10 ml of the blank test 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 blank calibration solution and from the 0,2 mg/l mercury standard solution (4.8) at least five calibration solutions covering the range of concentrations to be determined.

Depending on the sensitivity of the instrument used, different calibration concentration levels may be necessary. For example, the following procedure can be used:

Pipette 0 ml, 1 ml, 2 ml, 3 ml, 5 ml and 8 ml of mercury standard solution (4.8) into a series of 100 ml volumetric flasks. Fill to the mark with diluted aqua regia solution (4.4) and mix well. These solutions correspond to mercury concentrations of 0 µg/l, 2 µg/l, 4 µg/l, 6 µg/l, 10 µg/l and 16 µg/l, respectively. For manual sample systems, a 10 ml standard aliquot corresponds to 0 ng, 20 ng, 40 ng, 60 ng, 100 ng and 160 ng of mercury respectively. Prepare the solutions on the day of use.

NOTE If instabilities of highly diluted standard solutions are observed, stabilization is necessary. This can be done by addition of, e. g., 1 ml of 5 g/l $K_2Cr_2O_7$ solution to each of the standard solution flasks.

7.4 Calibration

7.4.1 Cold-vapour atomic absorption spectrometer (CV – AAS)

Set up the atomic absorption spectrometer (5.2) and the cold-vapour generator (5.4) according to the manufacturer's instructions, select a wavelength of 253,7 nm and adjust the silica cell, the gas flow rate and the reaction time and flow rate of tin(II) chloride solution (4.5) to obtain acceptable sensitivity and peak shape. Transfer 10 ml of blank calibration solution (7.3) into the cold-vapour generator bottle, connect the bottle to the system and start the time-controlled programme. The signal from the blank calibration solution should be negligible compared with that from the lowest standard calibration solution. Adjust the response of the instrument to zero signal. Repeat the measurement with each standard calibration solution (7.3) at least twice, and record the signal. If the two values fall within an accepted range, calculate the calibration function. Follow the manufacturer's instructions to obtain fit-for-purpose performance of the system.

7.4.2 Cold-vapour atomic fluorescence spectrometer (CV – AFS)

Set up the atomic fluorescence spectrometer (5.3) and the cold-vapour generator (5.4) according to the manufacturer's instructions. Adjust the silica cell, the gas flow rate and the flow rate of tin(II) chloride solution. Wait until the system is in equilibrium. Aspirate a blank and start the measurement procedure. The signal should be negligible. Set the instrument to zero. Read the signal for each standard solution at least twice. If the two values fall within an accepted range, calculate the calibration function. Follow the manufacturer's instructions to obtain fit for purpose performance of the system.

7.5 Test portion measurement

For a manual system, transfer 10 ml of blank test 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 solution (7.1) at least twice, record the signal and, if the two values fall within an accepted range, average the values.

For an automated system, measure the blank test solution (7.2) and test portion solutions (7.1) using the same conditions as under 7.4.1 and 7.4.2, based on the manufacturer's instructions for the system used.

If the mercury concentration of the test solution exceeds the range of calibration, the test solution shall be diluted with diluted aqua regia solution (4.4) accordingly.

For each type of soil, it is mandatory to determine the mercury concentration of the corresponding extract solution at least once by means of the standard addition method. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied. If the analytical results are different, matrix interferences are likely and the standard addition method shall be used for each corresponding soil extract solution.

7.6 Plotting the calibration graph

Plot a graph giving the mercury concentrations of the calibration solutions (7.3), from which the blank calibration solution reading has been subtracted, as abscissa, and the corresponding signal values as ordinate.

When using the atomic fluorescence spectrometer, the calibration curve shall be linear.

7.7 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, $w(\text{Hg})$, of the sample, expressed as milligrams per kilogram dry matter using Equation (1):

$$w(\text{Hg}) = \frac{(\rho_1 - \rho_0)}{m} \cdot f \cdot \frac{V}{1000} \cdot C \quad (1)$$

where

$w(\text{Hg})$ is the mass fraction of mercury in the sample, in milligrams per kilogram dry matter;

ρ_1 is the mercury concentration, in micrograms per litre, corresponding to the signal of the test solution (7.1);

ρ_0 is the mercury concentration, in micrograms per litre, corresponding to the signal of the blank test solution (7.2);

f $f = 10$ is the dilution factor of the test solution (7.1). The dilution depends on the working range of the apparatus;

- V is the volume, in litres, of the final volume taken for the analysis (0,1 l according to ISO 11466);
- m is the mass of the test sample, in kilograms, pretreated according to ISO 11464;
- C is the correction factor for the dry soil sample, $C = 100/w_{dm}$; where w_{dm} is the dry matter content of the soil, expressed as a percentage (mass fraction) according to ISO 11465.

7.8 Expression of results

Report the results with up to three significant figures, depending upon the mass fraction found and the method validation data.

EXAMPLE $w(\text{Hg}) = 0,45 \text{ mg/kg}$
 $w(\text{Hg}) = 12,5 \text{ mg/kg}$

If a laboratory reports more than three significant figures, the reason should be given in the report.

8 Precision

An interlaboratory comparison was organized in May 2000. Two polluted topsoils were selected having low and high contents of trace elements respectively. The data obtained are given in Table 1. Repeatability and reproducibility were calculated according to the principles of ISO 5725-2.

Table 1 — Precision data for the determination of mercury using cold vapour atomic absorption spectrometry

Sample	N_{lab}	$N_{lab,rej}$	N_{res}	N_{rej}	$w(\text{Hg})$ mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %	R mg/kg	r mg/kg
Soil 1	11	0	33	0	0,43	0,1	22,06	0,02	5,4	0,27	0,07
Soil 2	11	0	32	1	12,49	1,1	8,84	0,32	2,56	3,12	0,91

N_{lab}	Number of accepted laboratories
$N_{lab,rej}$	Number of rejected laboratories
N_{res}	Number of accepted results
N_{rej}	Number of rejected results
s_R	Reproducibility standard deviation
CV_R	Variation coefficient of reproducibility
s_r	Repeatability standard deviation
CV_r	Variation coefficient of repeatability
R	Reproducibility limit
r	Repeatability limit
$w(\text{Hg})$	mean mass fraction of mercury from 11 laboratories with 3 replicates

9 Test report

The test report shall contain the following information:

- a) a reference to this International Standard (ISO 16772:2004);
- b) a complete identification of the sample;
- c) a reference to the method used;
- d) the results of the determination;
- e) any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

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