

Determination of mercury in aqua regia and nitric acid digests with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry

1 Scope

This horizontal standard specifies a method for the determination of mercury in nitric acid digest or aqua regia extract of soil, sludge and waste, obtained in accordance with ISO 11466 with cold-vapour atomic absorption spectrometric method. Alternatively a cold vapour atomic fluorescence spectrometric method may be used. The matrix of the solution analyzed is dominated by the acids used in the digestion step. Tin(II)-chloride as a reduction substance is specified in this standard because sodium borohydride reduces many elements commonly found in soil, sludge and waste extract solutions, to the elemental state, which cause matrix problems under particular circumstances. The concentration range 0,1 – 10 µg/l in the digested solution, corresponding to 0,005 – 0,5 µg/g of mercury when a 2,0 g sample has been digested, can be determined directly. Higher concentrations can be determined if the digested solution is diluted.

2 Normative references

Horizontal standard for digestion of soil, sludge and waste with nitric acid.

Horizontal standard for digestion of soil, sludge and waste with aqua regia.

ISO 3696, Water for analytical laboratory use – Specification and test methods.

ISO 16772, Soil quality, Determination of mercury in aqua regia soil extracts with cold-vapour atomic absorption spectrometry or cold-vapour atomic fluorescence spectrometry.

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

3 Principle

Mono- and divalent mercury is reduced to the elemental form by tin(II)-chloride solution in acid medium. Elemental mercury is stripped off from the solution in a closed system, by means of a stream of nitrogen or mercury-free air. 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.

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, usually about 254 nm. The intensity of the fluorescence radiation is a function of mercury concentration, and are linear over 10^6 to 10^7 orders of concentration.

4 Interferences

As the samples are digested before determination of mercury, there is no problem with organic substances that can absorb in the UV range. Neither are there any problems with mercury compounds which cannot be fully reduced with tin(II) chloride alone. The interference due to the presence of other elements in the matrix are dependent on their concentrations. Element concentrations in excess of those listed in Table 1 may cause negative bias. Iodide in concentrations $> 0,1$ mg/l causes interferences in the determination due to the formation of mercury complexes. In this case another reduction agent (e.g. sodium tetrahydroborate) may be used.

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

Less interferences arises from heavy metals when tin(II) chloride is used rather than sodium tetrahydroborate. When flow systems are used, interference effects due to heavy metals may be less than indicated in Table 1.

Table 1 – Acceptable concentrations of some matrix elements in a measurement solution, in milligrams per litre.

Element	Atomic absorbance	Atomic fluorescence
Cu(II)	500	
Ni(II)	500	
Ag(I)	1	
I ⁻	0,1	
As(V)	0,5	
Bi(III)	0,5	
Sb(III)	0,5	
Se(IV)	0,05	

5 Reagents and gases

All reagents shall be of recognised analytical grade with particularly low mercury content. 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 concentration to be determined in the sample solutions.

Purity of argon or nitrogen should be $\geq 99,99\%$.

Note: For atomic fluorescence measurements argon should always be used, as nitrogen results in a significant signal reduction due to quenching of excited mercury atoms.

5.1 Hydrochloric acid, 37 %; $\rho \sim 1,18$ g/ml

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

5.2 Nitric acid, 65 %; $\rho \sim 1,40$ g/ml

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

5.2.1 Nitric acid, diluted solution

Pour 250 ml of water into a 500 ml volumetric flask. Add 50 ml of nitric acid (5.2) with caution, mix and fill to the mark with water. The acid concentration is corresponding to the digested sample when it has been diluted to a 100 ml solution.

5.2.2 Nitric acid, rinsing solution for glassware, ~ 2 mol/l

Add 150 ml of nitric acid (5.2) to about 500 ml of water, and dilute with water to 1000 ml.

5.3 Aqua regia, diluted solution

Add 105 ml hydrochloric acid (5.1) and 35 ml nitric acid (5.2) to 250 ml of water in a 500 ml volumetric flask, mix and fill to the mark with water. The acid concentration is corresponding to the digested sample when it has been diluted to a 100 ml solution.

5.4 Tin(II)-chloride solution, 10 % (m/v)

Dissolve 10 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 ml of hydrochloric acid (5.1), 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 minutes, 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 the day of use from the more concentrated solution by diluting with water.

5.5 Mercury stock solution, 1000 mg/l

Use a commercially available quantitative stock solution with a mercury concentration of (1000 ± 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.

5.6 Mercury, standard solution I, 100 mg/l

Pipette 10 ml of the stock mercury solution (5.5) into a 100 ml volumetric flask, add 10 ml nitric acid (5.2.1), or 10 ml aqua regia (5.4), mix and fill to the mark with water.

5.7 Mercury, standard solution II, 1 mg/l

Pipette 1 ml of the standard mercury solution I (5.6) into a 100 ml volumetric flask, add 10 ml nitric acid (5.2.1), or 10 ml aqua regia (5.4), mix and fill to the mark with water.

5.8 Mercury, standard solution III, 100 µg/l

Pipette 10 ml of the standard mercury solution II (5.7) into a 100 ml volumetric flask, add 10 ml nitric acid (5.2.1), or 10 ml aqua regia (5.4), mix and fill to the mark with water.

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 (5.2.2) for a minimum of six hours, 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 tube atomizer. As radiation source use a hollow cathode lamp or, preferably, an electrodeless discharge lamp (which give a greater and more stable light intensity) operated at a current recommended by the lamp and instrument manufacturer. An AAS system with background correction device is recommended.

6.3 Atomic absorption spectrometer (AAS)

It is equipped with a specific Hg lamp, a fixed 254 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 argon gas supply should be with a two stage regulator. The use of a gas purifier consisting of activated carbon is recommended. Nitrogen gas will have reduced sensitivity.

Automated mercury flow systems (flow injection systems or continuous flow systems) are very common both for cold vapour atomic absorption spectrometry and 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 (FIAS)

The system should be adaptable to the atomic absorption spectrometer (6.2) or to the atomic fluorescence spectrometer (6.3), according to the detection technique used for the determination of mercury. A flow-controlled nitrogen (5) or argon stream (5) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing solution (5.4) 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 is electrically heated to a temperature of 60 - 100 °C to avoid condensation of water. For the atomic fluorescence spectrometer (6.3), condensation in the cell is avoided by the inclusion of a drying tube in the detection system.

NOTE If an automated system is used, where the reaction occurred continuously (FIA-System), the concentration of stannous chloride solution, reaction time and the gas-liquid separator configuration must be optimised due to the slow reaction kinetics of the reducing system.

Warning - It is essential that the manufacturer's safety recommendations are strictly observed.

7 Procedure

7.1 Test solution

The nitric acid or aqua regia digested samples are transferred to 100 ml volumetric flasks and filled to the mark with water. The digested samples are prepared according to the Horizontal standards for digestion of soil, sludge and waste with nitric acid or aqua regia, respectively.

7.2 Blank test solution

Carry out a blank test at the same time as the extraction with nitric acid or aqua regia using cleaned quartz sand instead of the soil sample and following the sample procedure, using the same quantities of all reagents for the determination, but omitting 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 100 µg/l mercury standard solution III (5.8) at least five calibration solutions covering the range of concentrations to be determined.

Pipette 1 ml, 2 ml, 5 ml, 10 ml and 20 ml of mercury standard solution (5.8) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (5.2.1) or diluted aqua regia solution (5.3) 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

7.4.1 Cold vapour atomic absorption spectrometer (CV-AAS)

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 (5.4) to get maximum transmissim intensity. Transfer 10 ml of blank calibration solution (7.3) into the cold-vapour generation bottle, connect the bottle to the system and start the time-controlled programme. The signal of the blank calibration solution should be negligible compared to with the lowest standard solution.

7.4.2 Cold vapour atomic fluorescence spectrometer (CV-AFS)

Set up the atomic fluorescence spectrometer (6.3) and the cold-vapour generator (6.4) according to the manufacturer's instructions. Adjust the quartz cell (if the instrument is equipped with one), the gas flow and the flow rate of stannous chloride. Wait until the system is in equilibrium. Aspirate a blank and start the measurement procedure. The signal should be negligible.

7.5 Plotting the calibration graph

Plot a graph having 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.

7.6 Test portion measurement

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), and record the signal.

If the mercury concentration of the test solution exceeds the range of calibration, the test solution shall be diluted with diluted nitric acid solution (5.2.1), or diluted aqua regia solution (5.3) 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.

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) of the sample, expressed as $\mu\text{g/g}$ per dried matter using the equation:

$$w = (C - C_b) \times f \times V / (m \times 1000)$$

where

- w is the mass fraction of mercury in the sample, in $\mu\text{g/g}$ dry matter,
- C is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the test portion (7.1),
- C_b is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the same blank (7.2),
- f is the dilution factor if the test solution (7.1) is diluted before the determination step,
- V is the volume, in l, of the digested solution after dilution to the mark (usually 100 ml),
- m is the mass of the sample in g,

7.8 Expression of results

Values shall be rounded to 0,01 $\mu\text{g/g}$, but only significant figures should be expressed.

Example: $w(\text{Hg}) = 0,45 \mu\text{g/g}$
 $w(\text{Hg}) = 12,5 \mu\text{g/g}$

8 Precision

For atomic fluorescence spectrometric determination of mercury in aqua regia digestions the information given in ISO 16772 may be used, for nitric acid an interlaboratory comparison should be carried through for the current sample types.

9 Test report

The test report shall contain the following information:

- a) a reference to this horizontal standard;
- b) a reference to the method used (nitric acid or aqua regia);
- c) complete identification of the sample;
- d) the results of the determination;
- e) any details not specified in this standard or which are optional, as well as any factor which may have affected the results.