

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, with cold-vapour atomic absorption spectrometry method or cold-vapour atomic fluorescence spectrometry.

2 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 preferred in this standard because sodium borohydride reduces many elements common in soil extract solutions to the elemental state, which cause matrix problems under particular circumstances.

3 Reagents and gases

All reagents shall be of recognised 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 concentration to be determined in the sample solutions.

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

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

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

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

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

3.2.1 Nitric acid, diluted solution

Pour 500 ml of water into a 1000 ml volumetric flask. Add 250 ml of nitric acid (3.2) with caution, mix and fill to the mark with water.

3.3 Aqua regia, diluted solution

Add 21 ml hydrochloric acid (3.1) and 7 ml nitric acid (3.2) to 500 ml of water in a 1000 ml volumetric flask, mix and fill to the mark with water.

3.4 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 (3.1), 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.

3.5 Mercury, stock solution corresponding to 1000 mg/l of mercury

Two sources of stock solutions can be used:

- commercially available stock solutions.
- stock solutions prepared in the laboratory from pure elements or stoichiometrically defined and dried salts or oxides.

Dissolve $100 \text{ mg} \pm 0,4 \text{ mg}$ of mercury metal (minimum purity 99,99 %) in a 100 ml volumetric flask with 17 ml nitric acid (3.2) and fill to the mark with water.

NOTE Commercially available stock solutions have the advantage that they remove 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 and are checked on a regular basis.

3.6 Mercury, standard solution corresponding to 20 mg/l of mercury

Pipette 2 ml of the stock mercury solution (3.5) into a 100 ml volumetric flask, add 10 ml nitric acid (3.2.1), mix and fill to the mark with water.

3.7 Mercury, standard solution corresponding to 0,2 mg/l of mercury

Pipette 1 ml of the standard mercury solution (3.6) into a 100 ml volumetric flask, add 10 ml nitric acid (3.2.1), mix and fill to the mark with water.

4 Apparatus

4.1 Usual laboratory apparatus

All glassware shall be carefully cleaned for low trace element determinations, e.g. by immersion in 5 % (V/V) aqueous nitric acid solution for a minimum of six hours, followed by rinsing with water before use. The nitric acid shall be replaced each week. Grade A volumetric glassware shall be used throughout.

4.2 Atomic absorption spectrometer (AAS)

Equipped with an element hollow cathode 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 automatic background correction device and a computerised read out.

4.3 Atomic fluorescence spectrometer (AFS)

It is equipped with a specific Hg lamp, a fixed 254 filter, a photomultiplier tube for the detection of fluorescence radiation and a computerised read out. Operate at a current recommended by the lamp and instrument manufacturer.

4.4 Cold-vapour generator, batch system or an automated flow injection analysis system (FIAS)

Which should be adaptable to the atomic absorption spectrometer (4.2) or to the atomic fluorescence spectrometer (4.3), according to the detection technique used for the determination of mercury. A flow-controlled nitrogen (3) or argon stream (3) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing solution (3.4) 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 (4.2) are commercially available. In this case, the quartz cell is electrically heated to a temperature of 100 °C to avoid condensation of water. For the atomic fluorescence spectrometer (4.3), 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.

5 Procedure

5.1 Test solution

Transfer 10 ml nitric acid or aqua regia soil extracts according to ISO 15587-2 or ISO 11466, respectively, into a 100 ml volumetric flask and fill to the mark with water.

5.2 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.

5.3 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 (3.7) at least five calibration solutions covering the range of concentrations to be determined.

Pipette 1 ml, 2 ml, 3 ml, 5 ml and 8 ml of mercury standard solution (3.7) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (3.2.1) or diluted aqua regia solution (3.3) and mix well. These solutions correspond to mercury concentrations of 2 µg/l, 4 µg/l, 6 µg/l, 10 µg/l and 16 µg/l, respectively. Using 10 ml of each solution for the cold-vapour generator these solutions correspond to 20 ng, 40 ng, 60 ng, 100 ng and 150 ng of mercury, respectively.

5.4 Calibration

5.4.1 Cold vapour atomic absorption spectrometer (CV-AAS)

Set up the atomic absorption spectrometer (4.2) and the cold-vapour generator (4.4) 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 (3.4) to get acceptable sensitivity. Transfer 10 ml of blank calibration solution (5.3) 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. Adjust the response of the instrument to zero signal. Repeat the measurement with each standard calibration solution (5.3) at least twice and record the signal and, if the two values fall within an accepted range, average the values.

5.4.2 Cold vapour atomic fluorescence spectrometer (CV-AFS)

Set up the atomic fluorescence spectrometer (4.3) and the cold-vapour generator (4.4) according to the manufacturer's instructions. Adjust the quartz cell, 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. Set the instrument to zero. Read the signal for each standard solution at least twice. If the two values fall within an accepted range, average the values.

5.5 Plotting the calibration graph

Plot a graph having the mercury concentrations of the calibration solutions (5.3), from which the blank calibration solution reading has been subtracted, as abscissa, and the corresponding signal values as ordinate.

5.6 Test portion measurement

Transfer 10 ml of blank test solution (5.2) 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 (5.1) at least twice, record the signal and, if the two values fall within an accepted range, average the values.

If the mercury concentration of the test solution exceeds the range of calibration, the test solution shall be diluted with diluted nitric acid solution (3.2.1) or diluted aqua regia solution (3.3) 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.

5.7 Calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the signal of the test solution (5.1) and of the blank test solution (5.2). Calculate the mercury content (w) of the sample, expressed as mg/kg per dried matter using the equation:

$$w(\text{Hg}) = (p_1 - p_0) \cdot f \cdot V \cdot C / m \cdot 1000$$

where

w is the mass fraction of mercury in the sample, in mg/kg dry matter;

p_1 is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the test portion (5.1);

p_0 is the mercury concentration, in $\mu\text{g/l}$, corresponding to the signal of the same blank (5.2);

f $f = 10$ is the dilution factor of the test solution (5.1) used in this standard;

V is the volume, in l, of the test portion taken for the analysis (0,1 l);

m is the mass of the sample in kg, treated according to ISO 11466 or...;

C is the correction factor for the dry soil sample, $C = 100/\text{wdm}$;

wdm is the dry matter content of the soil expressed as a percentage according to ISO 11465.

5.8 Expression of results

Values shall be rounded to 0,01 mg/kg, but only significant figures should be expressed.

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

6 Precision

For aqua regia the informations given in ISO 16772 can be used, for nitric acid an interlaboratory comparison should be carried through for the current sample types.

7 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.