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Water quality — Determination of mercury — Methods involving enrichment by amalgamation

Qualité de l'eau — Dosage du mercure — Méthodes après enrichissement par amalgame

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 16590 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A, B and C of this International Standard are for information only.

This International Standard is equivalent to EN 12338.

Water quality — Determination of mercury — Methods involving enrichment by amalgamation

WARNING — Mercury and mercury compounds are very toxic. Extreme caution is recommended when handling samples and solutions which contain or may contain mercury.

1 Scope

This International Standard specifies two methods for the determination of mercury, one using tin(II) chloride and the other sodium tetrahydroborate as reducing agent. The methods are suitable for the determination of mercury in water, for example in ground, surface or waste water, in the concentration range 0,01 µg/l to 1 µg/l. Higher concentrations may be determined if the water sample is diluted.

The total mercury content of the water is determined after digestion of the sample. If only soluble mercury compounds are to be determined, the sample is filtered through a 0,45 µm membrane filter prior to digestion.

Mono- or divalent mercury is reduced to the elemental form by a reducing agent such as tin(II) chloride, $SnCl_2$, or sodium tetrahydroborate, $NaBH_4$, in an acid medium. Elemental mercury is then stripped from the solution with the aid of a stream of inert gas with negligible mercury content and transported over a noble-metal surface with a large area, such as gold/platinum gauze, on which the mercury is adsorbed. The mercury is released by rapid heating of the adsorbent and further transported in a stream of carrier gas to a suitable cuvette. Absorbances are measured at a wavelength of 253,7 nm in the radiation beam of an atomic absorption spectrometer. Concentrations are calculated using a calibration curve.

In order to fully decompose all of the mercury compounds, a digestion procedure is required. Digestion can be omitted only if it is certain that the mercury concentration may be measured without this pretreatment.

Careful consideration should be given to whether, and to what extent, particular problems will require the specification of additional conditions.

It is absolutely essential that analyses conducted in accordance with this International Standard are carried out by suitably qualified staff.

In natural water sources, mercury compounds generally occur only in very small concentrations of less than 0,1 µg/l. Higher concentrations may be found, for example, in waste water. Both inorganic and organic compounds of mercury can be present. Mercury may accumulate in sediment and sludge.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*.

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

3 General interferences

With mercury, there is a risk that exchange reactions, that is adsorption and desorption, will occur on the walls of the reaction vessel. It is therefore essential that 4.6 is followed exactly.

Mercury vapour can diffuse through various plastics. Therefore, special consideration shall be given to the choice of tubing material. Glass or special plastics tubing, e.g. FEP tubes, may be used (FEP = perfluoroethene-hexafluoropropene copolymer). Silicone tubing, for example, is unsuitable.

Volatile organic substances can absorb in the UV range and be mistaken for mercury. They are in most cases destroyed by adding potassium permanganate until the solution is permanently coloured red and removed by purging for 10 min with an inert gas, prior to reduction of the mercury compounds. Often, such interference by non-specific absorption can also be eliminated by using a background compensation system.

All solutions shall be brought to the same temperature (< 25 °C) before reduction and stripping of the mercury vapour. Water condensation on the cuvette windows can be prevented by heating the cuvette with, for example, an infrared lamp.

The interference which occurs due to the presence of other elements in the matrix depends on the choice of reducing agent. Element concentrations in excess of those listed in Table 1 may cause too low results.

Less interference arises from heavy metals if 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.

Tin(II) chloride causes such extensive contamination of the apparatus with tin that considerable interference occurs if sodium tetrahydroborate is used afterwards. Separate systems are therefore used for reductions with tin(II) chloride and with sodium tetrahydroborate.

Table 1 — Acceptable concentrations of some matrix elements in the test solution

Reducing agent	$NaBH_4$	$NaBH_4$	$SnCl_2$
Medium	0,5 mol/l HCl	5 mol/l HCl + 0,2 g/l Fe(III)	0,5 mol/l HCl
Element	**Acceptable concentration (mg/l)**		
Cu(II)	10	10	500
Ni(II)	1	500	500
Ag(I)	0,1	10	1
I^-	100	10	0,1
As(V)	0,5	0,5	0,5
Bi(III)	0,05	0,5	0,5
Sb(III)	0,5	0,5	0,5
Se(IV)	0,005	0,05	0,05

4 Determination of mercury after tin(II) chloride reduction and enrichment by amalgamation

4.1 Working range

The method is applicable to the determination of the mercury content in concentrations from 0,01 µg/l to 1 µg/l. Higher concentrations may also be determined if the water sample is diluted.

NOTE Measurements in this concentration range require the use of highest-purity reagents and clean flasks, mercury-free laboratory air and a very stable measurement system.

4.2 Principle

Mercury is reduced to the elemental form by tin(II) chloride and transported in a stream of inert gas with negligible mercury content over a noble-metal surface with a large area, such as gold/platinum gauze, on which the mercury is adsorbed.

The mercury is released by rapid heating of the adsorbent and further transported in a stream of carrier gas to the absorption cell where the absorbance is measured at 253,7 nm.

4.3 Interferences

See also clause 3.

Iodide in concentrations of $> 0{,}1$ mg/l causes interference with the determination due to the formation of mercury complexes. In this case, use another method such as reduction with sodium tetrahydroborate (see clause 5).

Because of the reduction potential of the tin(II) chloride solution, various inorganic mercury compounds, such as mercury sulfide, and organic mercury compounds cannot be fully reduced without digestion.

4.4 Reagents

At least "analytical grade" reagents or those with the lowest possible mercury content shall be used. The mercury content of the water and reagents shall be negligible compared to the lowest analyte concentration.

4.4.1 Water, double-distilled or of similar purity, for preparing solutions.

4.4.2 Nitric acid, $\rho(HNO_3) = 1{,}40$ g/ml.

4.4.3 Sulfuric acid, $\rho(H_2SO_4) = 1{,}84$ g/ml.

4.4.4 Hydrochloric acid, $\rho(HCl) = 1{,}19$ g/ml.

4.4.5 Potassium permanganate solution.

Dissolve 50 g of potassium permanganate, $KMnO_4$, in 1 000 ml of water.

4.4.6 Stabilizer solution.

Dissolve 5 g of potassium dichromate, $K_2Cr_2O_7$, in 500 ml of nitric acid (4.4.2) and dilute to 1 000 ml with water.

WARNING — Potassium dichromate is toxic. Caution should be exercised when handling the solid material and its solutions.

4.4.7 Potassium peroxodisulfate solution.

Dissolve 40 g of potassium peroxodisulfate, $K_2S_2O_8$, in 1 000 ml of water.

4.4.8 Hydroxylamine chloride solution.

Dissolve 10 g of hydroxylamine chloride, $H_2NOH \cdot HCl$, in 100 ml of water.

4.4.9 Tin(II) chloride solution.

Dissolve 5 g of tin(II) chloride dihydrate, $SnCl_2 \cdot 2H_2O$, in 30 ml of hydrochloric acid (4.4.4) and dilute to 100 ml with water. A solution of lower concentration, e.g. 0,5 g in 100 ml, may be used with flow systems. Prepare this latter solution freshly daily from the more concentrated solution by diluting with water.

If a high result for the blank is obtained, pass nitrogen through the solution for 30 min in order to remove traces of mercury.

4.4.10 Mercury stock solution I, $\rho(\mathrm{Hg}) = 100$ mg/l.

Dissolve 108,0 mg of mercury(II) oxide, HgO, in 10 ml of the stabilizer solution (4.4.6) and dilute to 1 000 ml with water. 1 ml of this solution corresponds to 0,1 mg of mercury.

Stock solution I may be prepared from a commercially available mercury standard. The solution is stable for about 1 month.

4.4.11 Mercury stock solution II, $\rho(\mathrm{Hg}) = 1$ mg/l.

Add 10 ml of stabilizer solution (4.4.6) to 10 ml of stock solution I (4.4.10) and dilute to 1 000 ml with water. 1 ml of this solution corresponds to 1 µg of mercury. The solution is stable for about 1 week.

4.4.12 Mercury standard solution I, $\rho(\mathrm{Hg}) = 100$ µg/l.

Add 10 ml of stabilizer solution (4.4.6) to 100 ml of stock solution II (4.4.11) and dilute to 1 000 ml with water. 1 ml of this solution corresponds to 100 ng of mercury.

Prepare the solution on the day of use.

4.4.13 Mercury standard solution II, $\rho(\mathrm{Hg}) = 10$ µg/l.

Dilute 1 ml of stabilizer solution (4.4.6) and 10 ml of standard solution I (4.4.12) to 100 ml with water. 1 ml of this solution corresponds to 10 ng of mercury. The solution is stable for only a short time and shall be freshly prepared before use.

4.4.14 Mercury standard solution III, $\rho(\mathrm{Hg}) = 1$ µg/l.

Dilute 1 ml of stabilizer solution (4.4.6) and 10 ml of standard solution II (4.4.13) to 100 ml with water. 1 ml of this solution corresponds to 1 ng of mercury. Prepare the solution freshly before each series of measurements.

4.4.15 Mercury calibration solutions.

Prepare calibration solutions appropriate to the volume and expected mercury concentrations of the test solutions.

For the concentration range from 0,01 µg/l to 0,1 µg/l, for example, proceed as follows:

- Pipette into each of six 100 ml volumetric flasks 1,0 ml, 2,0 ml, 4,0 ml, 6,0 ml, 8,0 ml and 10 ml respectively of mercury standard solution III (4.4.14).
- Add 1 ml of stabilizer solution (4.4.6) to each.
- Fill each flask to the mark with water and mix thoroughly.

These calibration solutions contain 0,01 µg/l, 0,02 µg/l, 0,04 µg/l, 0,06 µg/l, 0,08 µg/l and 0,1 µg/l mercury respectively. Prepare them freshly before each series of measurements.

For the concentration range from 0,1 µg/l to 1 µg/l, proceed in the same manner using mercury standard solution II (4.4.13). In this case, the reference solutions contain 0,1 µg/l, 0,2 µg/l, 0,4 µg/l, 0,6 µg/l, 0,8 µg/l and 1 µg/l of mercury respectively. If relatively large volumes of the test solution are used, increase the volumes of the reference solutions and the amount of standard solution added accordingly. Prepare the solutions freshly before each series of measurements.

If the calibration measurements are to be done in duplicate, prepare another set of solutions.

4.4.16 Reagent blank solution.

Prepare a volume of blank solution corresponding to that of the test solution by diluting 10 ml of stabilizer solution (4.4.6) to 1 000 ml with water. Use the same digestion procedure as for the sample (see 4.7). The reagent blank shall be included in each batch of analyses.

4.4.17 Gas-washing solution.

Dissolve 2,5 g of tin(II) chloride dihydrate, $SnCl_2 \cdot 2H_2O$, with 7,5 ml of sulfuric acid (4.4.3) in a small amount of water and dilute to 50 ml with water.

4.4.18 Washing solution for glassware.

Dilute 150 ml of nitric acid (4.4.2) to 1 000 ml with water.

4.5 Apparatus

Before use, wash all glassware thoroughly with dilute nitric acid (4.4.18) and then rinse thoroughly several times with water.

4.5.1 Atomic absorption spectrometer (AAS), with an appropriate monitoring system. A background correction system is recommended.

4.5.2 Radiation source, for the determination of mercury, e.g. a hollow-cathode or electrodeless discharge lamp.

4.5.3 Mercury attachment with amalgam accessory, consisting of

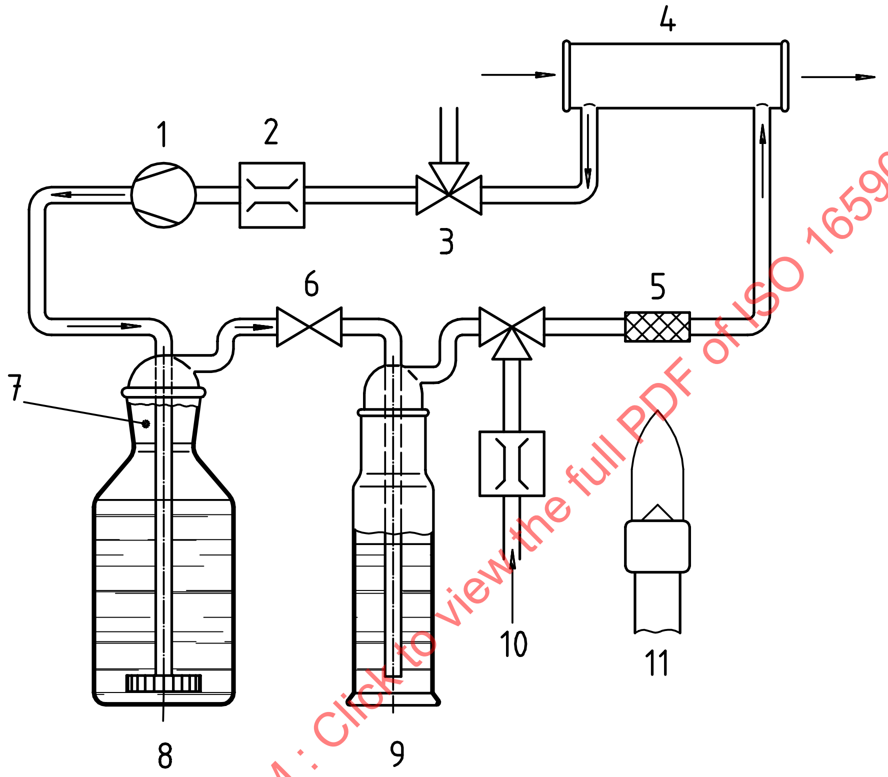
- an absorption cell consisting of a glass or quartz tube, inner diameter about 2 cm, at least 15 cm long (depending on the AAS instrument) and with quartz windows;
- an air-circulating pump (e.g. membrane pump, peristaltic pump), capacity 1 l/min to 2 l/min, with plastics tubing (closed system);
- a cylinder, with a pressure-reducing valve, of inert gas (e.g. nitrogen or argon) with a negligible mercury content;
- a flow meter with plastics tubing (see clause 3);
- a reaction vessel consisting of, for example, a 100 ml, 250 ml or 1 000 ml flat-bottomed flask as shown in Figure 1, with a ground-glass stopper and wash bottle insert with glass frit, porosity 1;
- a heating source for the absorption cell, with sufficient heating capacity to prevent condensation of water (the temperature of the absorption cell shall remain the same throughout the analysis);
- a quartz tube with a heating element and noble-metal adsorbent (such as gold/platinum gauze);

— a 100 ml gas-washing flask with a flashback prevention valve;

— a three-way stopcock.

An example of a closed system is shown in Figure 1.

NOTE Caution should be used with regard to the choice of plastics material for pumps and tubing (see clause 3). A continuous-flow or flow-injection system is permissible. It is recommended that the user follow the instructions given by the manufacturer.



Key

1 Air-circulating pump, capacity 1 l/min to 2 l/min
2 Flow meter
3 Three-way stopcock
4 Absorption cell: internal diameter 2 cm; length 15 cm
5 Au-Pt gauze
6 Flashback prevention valve
7 Ground-glass stopper
8 Reaction flask, 100 ml, 250 ml or 1 000 ml
9 $SnCl_2$ in H_2SO_4
10 Inert gas
11 Heating device

Figure 1 — Attachment apparatus for the determination of mercury after tin(II) chloride reduction and enrichment by amalgamation (closed system)

4.6 Sampling and sample pretreatment

In sampling and sample pretreatment, the requirements in ISO 5667-1, ISO 5667-2 and ISO 5667-3 shall be taken into account.

Suitable materials for sampling vessels shall be used: these are borosilicate glass, quartz, polysulfone (PSF) and perfluoroethene-hexafluoropropene copolymer (FEP).

Make sure that the sampling vessel contains no mercury and causes no losses of mercury by adsorption.

In order to limit the losses by, for example, adsorption on the vessel walls, add 10 ml of stabilizer solution (4.4.6) and make up to 1 000 ml with the sample.

The sample shall have a pH of approximately 1 and shall show a yellow-orange colour indicating an excess of dichromate.

If these conditions are not met, add additional stabilizer, and include the appropriate volume correction factor in the calculations.

4.7 Digestion method using permanganate and peroxodisulfate

The wet-chemical digestion procedure as described hereafter should preferably be carried out. Alternatively, one of the digestion methods given in annexes A to C may be used. In the latter case, however, the efficiency of the method compared to the wet-digestion method shall be checked.

Transfer 100 ml of the stabilized water sample (see 4.6) or an appropriate volume (maximum 1 000 ml) of sample to a flask made from one of the materials mentioned in 4.6.

Carefully add 15 ml of potassium permanganate solution (4.4.5), 1 ml of nitric acid (4.4.2) and 1 ml of sulfuric acid (4.4.3).

Shake the mixture well after each addition.

Allow the solution to stand for 15 min, then add 10 ml of potassium peroxodisulfate solution (4.4.7).

Place the loosely stoppered flask on a heating block or water bath at 95 °C for 2 h.

During the digestion, ensure that there is an excess of potassium permanganate. If this is not the case, increase the amount of potassium permanganate added or start with a smaller volume of sample.

Allow the solution to cool to room temperature.

If different sample volumes, and accordingly different reagent volumes, have been used, dilute the digests to a specific volume.

Analyse the digests as soon as possible.

Prepare a reagent blank solution in the same manner (4.4.16), using the corresponding volume of water (4.4.1) with stabilizer solution (4.4.6) instead of the water sample.

The permanganate can cause blank problems. In this case, reduce the permanganate concentration, provided the content of organic matter is low, or use a different digestion method (see annexes A to C).

4.8 Procedure

4.8.1 Preparation for determination

Before beginning the measurement procedure, set the instrument parameters in accordance with the manufacturer's instructions and align the absorption cell.

If the digest was prepared in accordance with the instructions in 4.7, immediately before measurement add to the entire digestion solution 5 ml (or more, if required) of hydroxylamine chloride solution (4.4.8). The 5 ml of hydroxylamine chloride solution are generally sufficient for reducing excess oxidizing agents and for dissolving the precipitated manganese dioxide. If the solution has not cleared after 30 min, make another addition of hydroxylamine chloride.

If an aliquot of the sample is taken for analysis, the sample solution shall first be made up to a specific volume, e.g. 200 ml.

Transfer the test solution (digest or aliquot) to the reaction vessel and connect to the analytical apparatus.

To 100 ml of test solution (or less), add 2 ml of tin(II) chloride solution (4.4.9).

If the reducing agent has to be added manually, connect the reaction vessel to the apparatus immediately after the addition of the tin(II) chloride solution.

For larger volumes of test solution (up to 1 000 ml), increase the volume of reducing agent up to a maximum of 5 ml.

In a closed system with an air-circulating pump, pass inert gas at a rate of 1 l/min to 2 l/min through the reaction vessel and noble-metal adsorbent. When adsorption is complete, turn off the pump and open the three-way stopcock.

In an open system, strip the water sample in an inert-gas stream with a negligible mercury content.

Release the adsorbed mercury by rapid heating of the adsorbent to at least 600 °C.

Transport the mercury vapour in an inert-gas stream, flowing at e.g. 75 ml/min, which shall not pass through the test solution, into the absorption cell and measure the peak height or, preferably, the peak area.

Measure the absorbances of the calibration solutions (4.4.15) and the reagent blank (4.4.16) in the same manner as the water sample.

4.8.2 Analysis using the method of standard calibration

For the analysis, prepare a calibration curve as follows:

Prepare the mercury calibration solutions as described in 4.4.15.

Measure the absorbances of the calibration and blank solutions as described in 4.8.

From the series of results obtained, determine the equation corresponding to the linear calibration line.

4.8.3 Analysis using the standard additions method of calibration

If the method of standard calibration does not yield sufficiently accurate results, e.g. because of matrix effects, the standard additions method shall be used, provided no additive errors occur and that the absorbances of the spiked water samples lie in the linear working range, i.e. the results are in the linear region of the calibration curve. The concentration of added mercury shall correspond to the expected mercury content of the sample. As an example, for a sample volume of 50 ml and an expected mercury concentration of 0,1 µg/l, proceed as follows:

Into each of four 100 ml reaction flasks, place 50 ml of the test solution (see 4.8.1).

To three of the flasks, add 0,5 ml, 1,0 ml or 1,5 ml respectively of mercury standard solution II (4.4.13). The spikes correspond to 0,1 µg/l, 0,2 µg/l and 0,3 µg/l of mercury respectively.

Measure the mercury concentration of the contents of all four flasks in accordance with the instructions in 4.8.

With the reagent blank solution (4.4.16), follow the same procedure as used for the test solution.

4.9 Calculation

4.9.1 Calculation using the calibration curve

Calculate the concentration of mercury using the following equation:

$$\rho = \frac{(A - A_0) \times V_m}{b \times V_p}$$

where

ρ is the concentration of mercury in the sample, in micrograms per litre;

A is the absorbance or integrated absorbance of the water sample;

A_0 is the absorbance or the integrated absorbance of the reagent blank solution;

b is the slope of the calibration curve (a measure of the sensitivity), in litres per microgram;

V_p is the volume of sample used to prepare the test solution, in millilitres;

V_m is the volume of the test solution, in millilitres.

4.9.2 Calculation using the standard additions method

Prepare a calibration line using the measured absorbances of the water sample and of the series of calibration solutions including the sample (made by spiking the sample with standard solutions containing increasing quantities of mercury).

Determine the mercury concentration of the test solution by extrapolating the calibration line to zero absorbance. Determine the mercury concentration of the reagent blank solution in a similar manner and subtract it from the value obtained for the test solution.

The mercury concentration may also be calculated using a linear-regression approach.

Any additional dilution steps will have to be allowed for in the calculation.

4.10 Expression of results

Report the results rounded to the nearest 0,01 µg/l.

EXAMPLE

Mercury (Hg) 0,04 µg/l;

Mercury (Hg) 0,20 µg/l.

4.11 Test report

The test report shall contain the following details:

a) a reference to this International Standard;

b) identification of the water sample analysed;

c) the result stated as specified in 4.10;

d) the sample pretreatment and digestion method used;

e) details of any deviations from the method specified and of any circumstances that may have affected the result;

f) the date of the analysis.

5 Determination of mercury after sodium tetrahydroborate reduction and enrichment by amalgamation

5.1 Working range

The method is applicable to the determination of the mercury content in concentrations from 0,01 µg/l to 1 µg/l. Higher concentrations can also be determined by appropriate dilution of the sample.

NOTE Measurements in this concentration range require the use of highest-purity reagents and clean flasks, mercury-free laboratory air and a very stable measurement system.

5.2 Principle

Mercury is reduced to the elemental form by sodium tetrahydroborate and transported in a stream of inert gas, together with the hydrogen released, over a noble metal surface with a large area, such as gold/platinum gauze, on which the mercury is adsorbed. The mercury is released by rapid heating of the adsorbent and further transported in a stream of carrier gas to the absorption cell where the absorbance is measured at 253,7 nm.

5.3 Interferences

See also clause 3.

Nickel in concentrations of > 1 mg/l and silver in concentrations of $> 0,1$ mg/l in the test solution interfere with the determination of mercury. In the presence of 1:1 hydrochloric acid [500 ml of concentrated hydrochloric acid (4.4.4) diluted to 1 000 ml with water] and an iron(III) solution, nickel at up to 500 mg/l and silver at up to 10 mg/l cause no interference.

The noble-metal adsorbent shall be cooled to < 100 °C in order to avoid interference which may otherwise be caused by elements such as As, Sb and Se which form volatile hydrides with sodium tetrahydroborate.

5.4 Reagents

In addition to those reagents described in 4.4 [except tin(II) chloride solution], the following are required:

5.4.1 Gas-washing solution I: sodium hydroxide solution.

Dissolve 10 g of NaOH in 100 ml of water.

5.4.2 Gas-washing solution II: water as described in 4.4.1.

5.4.3 **Drying agent:** magnesium perchlorate, $Mg(ClO_4)_2$, coarse-grain.

5.4.4 Sodium tetrahydroborate solution.

Dissolve 3 g of sodium tetrahydroborate, $NaBH_4$, and 1 g of sodium hydroxide, NaOH, in a small amount of water. Dilute to 100 ml with water and pass through a paper filter.

The solution is stable for only a few days.

In flow systems, a lower concentration is permissible, e.g. 0,02 g of sodium tetrahydroborate and 0,03 g of sodium hydroxide in 100 ml of water.

Prepare this solution on the day of use.

5.4.5 Iron(III) buffer solution.

Dissolve 14 g of iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, in water and dilute to 100 ml with water.

In flow systems, a lower concentration is permissible.

Prepare fresh solutions daily.

5.5 Apparatus

Before use, wash all glassware thoroughly with dilute nitric acid (4.4.18) and then rinse thoroughly several times with water.

NOTE This method produces a large volume of H_2. An extraction device is recommended.

5.5.1 Atomic absorption spectrometer, with an appropriate monitoring system. A background correction system is recommended.

5.5.2 Radiation source, for the determination of mercury, e.g. a hollow-cathode or electrodeless discharge lamp.

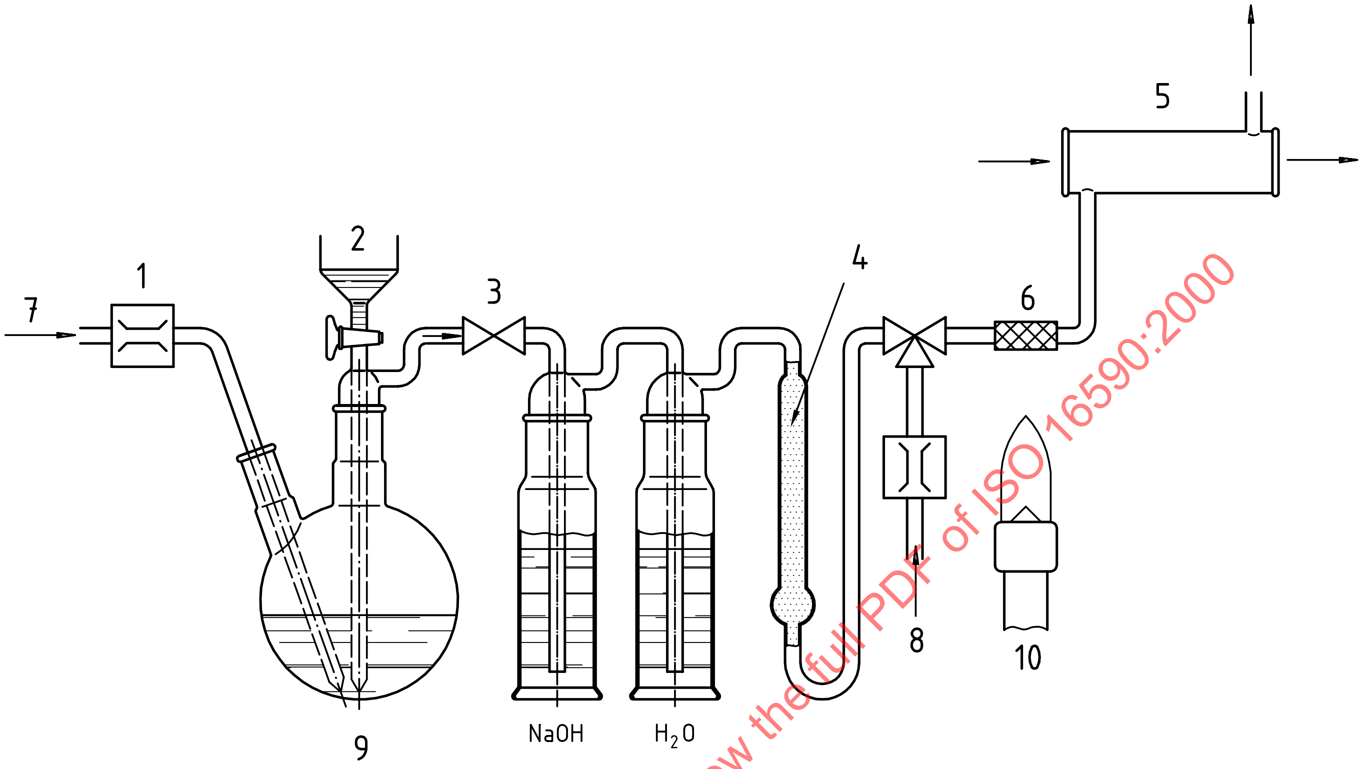
5.5.3 Mercury attachment with amalgamation accessory, consisting of

- an absorption cell consisting of a glass or quartz tube, inner diameter about 2 cm, at least 15 cm long (depending on the AAS instrument) and with quartz windows;
- a cylinder, with a pressure-reducing valve, of inert gas (e.g. nitrogen or argon) with a negligible mercury content;
- a flow meter with plastics tubing (see clause 3);
- a reaction vessel consisting of, for example, a 100 ml or 250 ml double-necked round-bottomed flask as shown in Figure 2, with a ground-glass stopper, a wash bottle insert and a tube for gas introduction;
- 100 ml gas-washing flasks and a flashback prevention valve (see Figure 2);
- a tube for drying agent;
- a heating source for the absorption cell, with sufficient heating capacity to prevent condensation of water (the temperature of the absorption cell shall remain the same throughout the analysis);
- a quartz tube with a heating element and noble-metal adsorbent (such as gold/platinum gauze).

An example of the apparatus is given in Figure 2.

NOTE 1 Caution should be used with regard to the choice of plastics material for pumps and tubing (see clause 3).

NOTE 2 A continuous-flow system is permissible.



Key

1 Flow meter
2 $NaBH_4$ solution
3 Flashback prevention valve
4 Drying agent
5 Absorption cell: internal diameter 2 cm; length 15 cm
6 Au-Pt gauze
7 Inert gas inlet 1
8 Inert gas inlet 2
9 Reaction flask, 100 ml or 250 ml
10 Heating device

Figure 2 — Attachment apparatus for the determination of mercury after sodium tetrahydroborate reduction and enrichment by amalgamation (open system)

5.6 Sampling and sample pretreatment

See 4.6.

5.7 Digestion method

See 4.7

5.8 Procedure

5.8.1 Preparation for determination

Before beginning the measurement procedure, set the instrument parameters in accordance with the manufacturer's instructions and align the absorption cell.

If the digest was prepared in accordance with the instructions in 4.7, immediately before measurement add to the entire digestion solution 5 ml (or more, if required) of hydroxylamine chloride solution (4.4.8). The 5 ml of hydroxylamine chloride is generally sufficient for reducing excess oxidizing agents and for dissolving the precipitated manganese dioxide. If the solution has not cleared after 30 min make another addition of hydroxylamine chloride.

If an aliquot of the sample is taken for analysis, the sample solution shall first be made up to a specific volume, e.g. 200 ml.

First place 0,5 ml of hydrochloric acid (4.4.4) per 10 ml of test solution in the reaction flask.

Transfer the test solution (digest or aliquot) to the reaction flask and connect to the analytical apparatus.

To 10 ml of test solution, add 2,5 ml of sodium tetrahydroborate solution (5.4.4). For 50 ml of test solution, add 7,5 ml of sodium tetrahydroborate solution.

In a stream of the inert gas (inlet 1 in Figure 2), strip the mercury and pass it over the noble-metal adsorbent.

If the nickel or silver content of the sample is high, place 25 ml of hydrochloric acid (4.4.4) and 0,5 ml of iron(III) buffer solution (5.4.5) into the reaction flask before adding 25 ml of test solution.

If smaller aliquots are used, make these up to 25 ml with water.

Release the adsorbed mercury by rapid heating of the adsorbent to at least 600 °C.

Transport the mercury vapour in a stream of the inert gas (inlet 2 in Figure 2), flowing at e.g. 75 ml/min, which shall not pass through the test solution, into the absorption cell and measure the peak height or, preferably, the peak area.

Measure the absorbances of the calibration solutions (4.4.15) and the reagent blank (4.4.16) in the same manner as the water sample.

5.8.2 Analysis using the method of standard calibration

See 4.8.2.

5.8.3 Analysis using the standard additions method of calibration

See 4.8.3.

5.9 Calculation

See 4.9.

5.10 Expression of results

See 4.10.

5.11 Test report

See 4.11

6 Precision data

An interlaboratory test programme based on the methods given in this International Standard was carried out in 1995.

Types of sample:

Samples No. 1 and 2	Potable water
Sample No. 3	Surface water
Sample No. 4	Waste water

The mercury compound used for spiking was 2-[(ethylmercuro)thio]-benzoic acid, sodium salt.

The mercury content of the water samples was determined using the methods given in this International Standard and, in addition, by independent laboratory methods.

An aqueous stock solution was prepared from the mercury salt. Appropriate portions of the stock solution were added, with stirring, to defined volumes of the water samples. Stirring was continued for 4 h to ensure complete mixing.

The artificial samples thus prepared were bottled in 1 litre vessels with screw caps for mailing.

All the vessels used were made of borosilicate glass.

Table 2 — Summary of results from all the digestion modes

Sample No.	L	N	NAP %	**Nominal value** µg/l	$\bar{x}$ µg/l	σ_R µg/l	VC$_R$ %	σ_r µg/l	VC$_r$ %	WFR %
1	21	72	5	0,060	0,070 5	0,027 4	38,8	0,012 1	17,2	117,5
2	21	72	5	0,088	0,085 4	0,024 7	28,9	0,012 8	15,0	97,0
3	21	72	5	0,283	0,260	0,049 1	18,9	0,023 0	8,8	91,9
4	21	71	0	0,800	0,756	0,216 2	28,6	0,063 4	8,4	94,5

where

L is the total number of participating laboratories;

N is the number of analytical values per level;

NAP is the percentage of outlying analytical values from the replicates performed by all laboratories;

$\bar{x}$ is the overall mean;

σ_R is the standard deviation of the reproducibility;

VC$_R$ is the coefficient of variation of the reproducibility (relative to σ_R);

σ_r is the standard deviation of the repeatability;

VC$_r$ is the coefficient of variation of the repeatability (relative to σ_r);

WFR is the recovery rate.

Table 3 — Results obtained using the digestion method specified in 4.7 ($KMnO_4/K_2S_2O_8$)

Sample No.	L	N	NAP %	**Nominal value** µg/l	$\bar{x}$ µg/l	σ_R µg/l	VC$_R$ %	σ_r µg/l	VC$_r$ %	WFR %
1	6	24	0	0,060	0,075	0,022 2	29,5	0,011 2	14,9	125,0
2	6	23	0	0,088	0,099	0,034 1	34,4	0,017 6	17,7	112,5
3	6	22	0	0,283	0,305	0,095 3	31,2	0,036 8	12,1	107,8
4	6	22	0	0,800	0,695	0,215 2	31,0	0,073 6	10,6	86,9

For definitions of symbols, see Table 2.

Table 4 — Results obtained using the digestion method specified in annex A (ultrasonic method)

Sample No.	L	N	NAP %	**Nominal value** µg/l	$\bar{x}$ µg/l	σ_R µg/l	VC$_R$ %	σ_r µg/l	VC$_r$ %	WFR %
1	3	10	0	0,060	0,089	0,035 1	39,4	—	—	148,3
2	3	10	0	0,088	0,114	0,043 0	37,7	—	—	129,5
3	3	10	0	0,283	0,294	0,033 9	11,5	—	—	103,9
4	3	10	0	0,800	0,730	0,172 1	23,6	—	—	91,3

For definitions of symbols, see Table 2.

Table 5 — Results obtained using the digestion method specified in annex B (autoclave method)

Sample No.	L	N	NAP %	**Nominal value** µg/l	$\bar{x}$ µg/l	σ_R µg/l	VC$_R$ %	σ_r µg/l	VC$_r$ %	WFR %
1	4	11	0	0,060	0,081 1	0,050 3	73,0	—	—	135,2
2	4	11	0	0,088	0,076	0,020 6	27,1	—	—	86,4
3	4	12	0	0,283	0,211	0,051 5	24,4	—	—	74,6
4	4	11	0	0,800	0,777	0,335 2	43,1	—	—	97,1

For definitions of symbols, see Table 2.

Table 6 — Results obtained using the digestion method specified in annex C (microwave method)

Sample No.	L	N	NAP %	**Nominal value** µg/l	$\bar{x}$ µg/l	σ_R µg/l	VC$_R$ %	σ_r µg/l	VC$_r$ %	WFR %
1	8	27	0	0,060	0,065 5	0,029 5	45,0	0,014 2	21,7	109,2
2	8	28	0	0,088	0,081 0	0,015 2	18,8	0,010 2	12,6	92,0
3	8	28	0	0,283	0,266	0,021 8	8,2	0,010 8	4,1	94,0
4	7	24	0	0,800	0,809	0,179 6	22,2	0,063 8	7,9	101,1

For definitions of symbols, see Table 2.