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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.

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# 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<sub>2</sub>, or sodium tetrahydroborate, NaBH<sub>4</sub>, 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.

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

Reducing agent	NaBH <sub>4</sub>	NaBH <sub>4</sub>	SnCl <sub>2</sub>
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 <sup>-</sup>	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.

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### 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**,  $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$ .

**4.4.3 Sulfuric acid**,  $\rho(\text{H}_2\text{SO}_4) = 1,84 \text{ g/ml}$ .

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

**4.4.5 Potassium permanganate solution.**

Dissolve 50 g of potassium permanganate,  $\text{KMnO}_4$ , in 1 000 ml of water.

**4.4.6 Stabilizer solution.**

Dissolve 5 g of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , 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,  $\text{K}_2\text{S}_2\text{O}_8$ , in 1 000 ml of water.

**4.4.8 Hydroxylamine chloride solution.**

Dissolve 10 g of hydroxylamine chloride,  $\text{H}_2\text{NOH}\cdot\text{HCl}$ , in 100 ml of water.

**4.4.9 Tin(II) chloride solution.**

Dissolve 5 g of tin(II) chloride dihydrate,  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ , 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,  $\rho(\text{Hg}) = 100 \text{ mg/l}$ .**

Dissolve 108,0 mg of mercury(II) oxide,  $\text{HgO}$ , 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,  $\rho(\text{Hg}) = 1 \text{ mg/l}$ .**

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  $\mu\text{g}$  of mercury. The solution is stable for about 1 week.

**4.4.12 Mercury standard solution I,  $\rho(\text{Hg}) = 100 \mu\text{g/l}$ .**

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,  $\rho(\text{Hg}) = 10 \mu\text{g/l}$ .**

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,  $\rho(\text{Hg}) = 1 \mu\text{g/l}$ .**

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  $\mu\text{g/l}$  to 0,1  $\mu\text{g/l}$ , 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,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , 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.

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### 4.5 Apparatus

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

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**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.

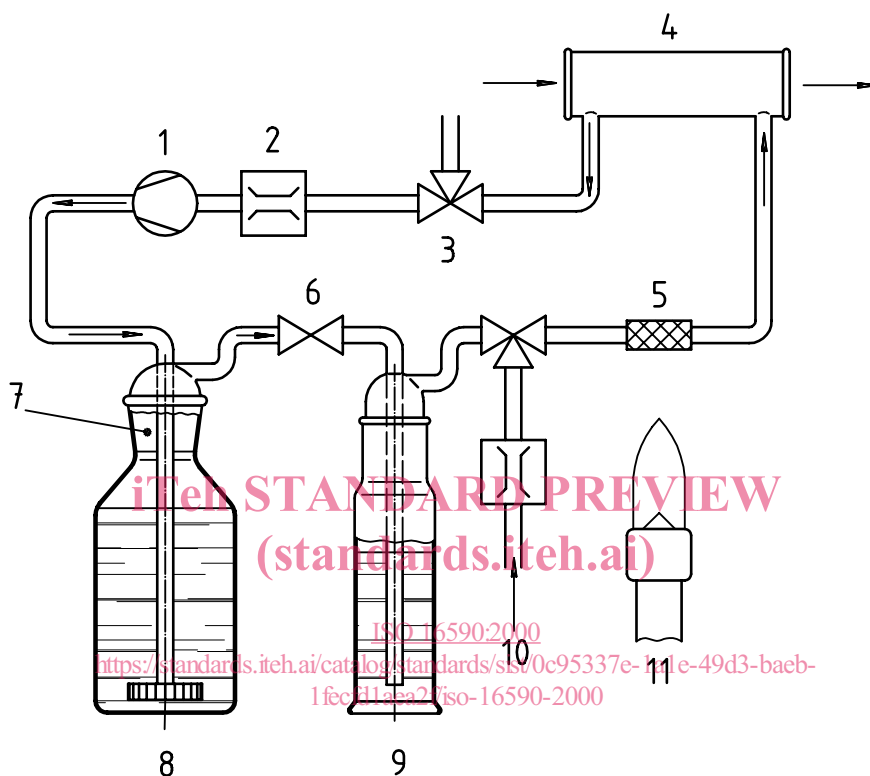
**4.5.3 Mercury attachment with amalgam accessory**, consisting of

- 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<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>
- 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).