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Water quality — Determination of mercury

Qualité de l'eau — Dosage du mercure

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International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

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.

International Standard ISO 5666 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This first edition cancels and replaces the first editions of ISO 5666-1:1983 and ISO 5666-2:1983, which have been technically revised.

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

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Introduction

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

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

For measurements in the low concentration range, highest purity reagents, clean reaction vessels, mercury-free air in the laboratory and a very stable measurement system are essential. It should be investigated whether, and to what extent, particular problems will require the specification of additional marginal conditions.

It is absolutely essential that tests conducted according to this International Standard are carried out by suitably qualified staff.

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Water quality — Determination of mercury

1 Scope

This International Standard specifies two methods for the determination of mercury in water, for example in ground, surface and waste waters.

In the method described in clause 4, tin(II) chloride is used as reducing agent. In the method given in clause 5, sodium tetrahydroborate is used as reducing agent. The choice of the method depends on the equipment available and the matrix (see clause 3). Both methods are suitable for the determination of mercury in the concentration range from 0,1 µg/l to 10 µg/l. Higher concentrations can be determined if the water sample is diluted.

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, i.e. adsorption and desorption, will occur on the walls of the reaction vessel (see 4.4).

Mercury vapour can diffuse through various plastics; this phenomenon needs to be taken into consideration in the choice of tubing material. Glass or special plastics tubing, e.g. perfluoro(ethylene-propylene) (FEP) tubes, may be used. Silicone tubing is unsuitable.

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

All solutions have to 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 interferences which occur due to the presence of other elements in the matrix are dependent on the choice of reducing agent. Element concentrations in excess of those listed in Table 1 can cause results which are too low.

Fewer interferences from heavy metals arise if tin(II) chloride is used as reducing agent rather than sodium tetrahydroborate. When using flow systems, interference effects due to heavy metals can be less than indicated in Table 1.

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

Reducing agent (element)	NaBH ₄ directly	NaBH ₄ directly	SnCl ₂ directly
Medium	0,5 mol/l HCl	5 mol/l HCl + 0,2 g/l Fe(III)	0,5 mol/l HCl
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

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

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

4 Determination of mercury after tin(II) chloride reduction without enrichment

4.1 Principle

Mono- or divalent mercury is reduced to the elemental form by tin(II) chloride in an acid medium. Elemental mercury is then stripped from the solution with the aid of a stream of inert gas or mercury-free air and, in the form of an atomic gas, transported into a 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.

4.2 Interferences

NOTE See also clause 3.

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

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

4.3 Reagents

4.3.1 General requirements

As a minimum, use "analytical grade" reagents or those with particularly low mercury content. Water shall be double-distilled or of similar purity. The mercury content of the water and reagents shall be negligible compared to the lowest analyte concentration.

4.3.2 Nitric acid, $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$.

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

4.3.4 Hydrochloric acid, $\rho(\text{HCl}) = 1,16 \text{ g/ml}$

4.3.5 Potassium permanganate solution

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

4.3.6 Stabilizer solution

Dissolve 5 g of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, in 500 ml of nitric acid (see 4.3.2) and dilute to 1000 ml with water.

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

4.3.7 Potassium peroxodisulfate solution

Dissolve 40 g of potassium peroxodisulfate, $\text{K}_2\text{S}_2\text{O}_8$, in 1 000 ml of water.

4.3.8 Hydroxylammonium chloride solution

Dissolve 10 g of hydroxylammonium chloride, NH_2OCl , in 100 ml of water.

4.3.9 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 (4.3.4); dilute to 100 ml with water. With flow systems, use a solution of lower concentration, e.g. 0,5 g in 100 ml. Prepare this solution fresh daily from the more concentrated solution by diluting with water.

If a high result for the blank (4.6) is obtained, pass nitrogen through the solution for 30 min in order to remove traces of mercury.

4.3.10 Mercury stock solution I, $\rho(\text{Hg}) = 100 \text{ mg/l}$

Dissolve 108,0 mg of mercury(II) oxide, HgO , in 10 ml of the stabilizer solution (4.3.6); dilute to 1 000 ml with water.

1 ml of this solution corresponds to 0,1 mg of mercury.

It is possible for stock solution I to be prepared from a commercially available mercury standard. This solution is stable for at least 1 year.

4.3.11 Mercury stock solution II, $\rho(\text{Hg}) = 1 \text{ mg/l}$

Add 10 ml of stabilizer solution (4.3.6) to 10 ml of stock solution I (4.3.10) and dilute to 1000 ml with water. 1 ml of this solution corresponds to 1 μg of mercury.

The solution is stable for about 1 week.

4.3.12 Mercury standard solution (1), $\rho(\text{Hg}) = 100 \mu\text{g/l}$

Add 10 ml of stabilizer solution (4.3.6) to 100 ml of stock solution II (4.3.11) and dilute to 1 000 ml with water. 1 ml of this solution corresponds to 100 ng of mercury.

Prepare this solution on the day of use.

4.3.13 Mercury standard solution (2), $\rho(\text{Hg}) = 50 \mu\text{g/l}$

Add 10 ml of stabilizer solution (4.3.6) to 50 ml of stock solution II (4.3.11) and dilute to 1000 ml with water. 1 ml of this solution corresponds to 50 ng of mercury.

Prepare this solution on the day of use.

4.3.14 Mercury calibration solutions

Prepare calibration solutions appropriate for the volume and expected mercury concentrations of the measurement sample solutions:

For the concentration range from 0,5 $\mu\text{g/l}$ to 5 $\mu\text{g/l}$, for example, proceed as follows.

- Pipette into a series of six 100 ml volumetric flasks 1 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml respectively of mercury standard solution (2) (4.3.13).
- Add 1 ml of stabilizer solution (4.3.6) to each 100 ml volumetric flask.
- Fill to the mark with water and mix thoroughly.

These calibration solutions contain 0,5 $\mu\text{g/l}$, 1 $\mu\text{g/l}$, 2 $\mu\text{g/l}$, 3 $\mu\text{g/l}$, 4 $\mu\text{g/l}$ and 5 $\mu\text{g/l}$ mercury respectively. They shall be prepared freshly before each series of measurements. If calibration measurements shall be done in duplicate prepare another set of solutions.

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4.3.15 Reagent blank solution

Prepare a volume of blank solution corresponding to that of the measurement solution by adding 10 ml of stabilizer solution (4.3.6) per 1000 ml of water. Use the same digestion procedure as for the sample (4.6). Include the reagent blank in each batch of analyses.

4.3.16 Rinsing solution for glassware

Add to about 500 ml of water 150 ml of nitric acid (4.3.2) and dilute with water to 1 000 ml.

4.4 Apparatus

4.4.1 General requirement

Before use, all glassware shall be washed thoroughly with dilute nitric acid (4.3.16) and then rinsed thoroughly several times with water (4.3.1).

4.4.2 Atomic absorption spectrometer with a monitoring system. An instrument with background correction system is recommended.

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

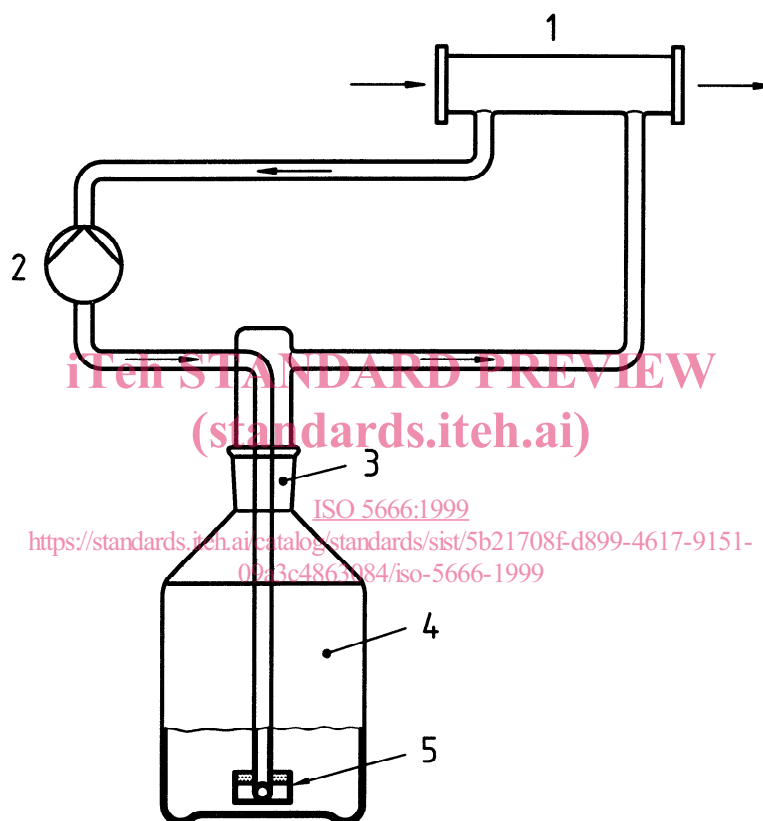
4.4.4 Mercury accessory (see Figure 1), consisting of:

- absorption cell comprised of a borosilicate glass or quartz cuvette, of inside diameter about 2 cm, length at least 15 cm (dependent on the AAS instrument) with quartz end-windows;

- air-circulating pump (e.g. membrane pump, peristaltic pump), capacity 1 l/min to 2 l/min, with plastics tubing (closed system) or inert gas cylinder with pressure-reducing valve (open system);
- flow meter with plastics (see clause 3) tubing (open system). An open system is advantageous for high concentrations of mercury;
- reaction vessel consisting of, for example, a 100 ml, 250 ml or 1 000 ml flat-bottomed flask as shown in the diagram, with ground glass stopper, wash-bottle insert with glass frit of porosity 1;
- heating source for the measuring cell, sufficient to prevent condensation of water.

The temperature of the measuring cell shall be the same throughout the analysis.

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



Key

- 1 Absorption cell, i.d. 2 cm; length 15 cm
- 2 Air circulating pump, of capacity 1 l/min to 2 l/min
- 3 Ground glass stopper 29/32
- 4 Reaction flask, capacity 100 ml, 250 ml or 1 000 ml
- 5 Glass frit

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

NOTE 2 A continuous flow or flow injection system is possible as an alternative. The instructions given by the manufacturer should be followed.

Figure 1 — Accessory for the determination of mercury with tin(II) chloride (closed system)

4.4.5 100 ml, 200 ml, and 1000 ml volumetric flasks.

4.4.6 1 ml, 5 ml and 10 ml pipettes.

NOTE Rather than pipettes, it is advantageous to use a dispensing apparatus, since the risk of introducing trace contaminants is significantly reduced.

4.5 Sampling and sample pretreatment

Carry out sampling in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3.

Use sampling vessels constructed of borosilicate glass, quartz, polysulfone (PSU) or fluoridized ethylene-propylene polymerizate (FEP).

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

In order to limit losses due to, for example, adsorption on the vessel walls, add 10 ml of stabilizer solution (4.3.6) and make up to 1 000 ml with the sample.

Verify that the sample has a pH of approximately 1 and shows a yellow-orange colour, indicating an excess of dichromate.

If necessary, add additional stabilizer solution, and include the appropriate volume correction factor in the calculations.

4.6 Digestion method using potassium permanganate/potassium peroxodisulfate

Carry out the wet chemical digestion procedure as follows. Alternatively, use one of the digestion methods indicated in annex A, B, or C but verify that the efficiency of that method compared to the wet digestion method is equivalent.

- Transfer 100 ml of the stabilized (see 4.5) water sample or an appropriate volume (maximum 1 000 ml) of sample to a flask made of one of the materials listed in 4.5.
- Carefully add 15 ml of potassium permanganate solution (4.3.5), 1 ml of nitric acid (4.3.2) and 1 ml of sulfuric acid (4.3.3).
- Shake the mixture well after each addition.
- Allow the solution to stand for 15 min, then add 10 ml of potassium peroxodisulfate solution (4.3.7).
- Place the loosely stoppered flask on a heating block or water bath and digest at 95 °C for 2 h.
- During the digestion, ensure that there is an excess of potassium permanganate. If necessary, 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.
- Analyze the digests as soon as possible.
- Prepare a reagent blank solution in the same manner, using the corresponding volume of water (4.3.1) with stabilizer solution (4.3.6) added instead of the water sample.

NOTE Permanganate can cause blank problems. In this case the permanganate concentration should be reduced, provided the content of organic matter is low, or another digestion method should be used (see annex A, B, or C).

4.7 Procedure

4.7.1 General requirements

Before beginning the measurement procedure, set the instrument (4.4.2) parameters according to the manufacturer's instructions and align the absorption cell.

If the digest was prepared according to the instructions in 4.6, immediately before measurement add to the entire digestion solution 5 ml (or more, if required) of hydroxylammonium chloride solution (4.3.8). The 5 ml of hydroxylammonium 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 hydroxylammonium chloride.

If an aliquot of the sample has been taken for analysis, make up the sample solution to a specific volume, e.g. 200 ml.

Transfer the measurement solution (digested solution or diluted aliquot) to the reaction vessel and connect to the analytical apparatus.

Add 2 ml of tin(II) chloride solution (4.3.9) for every 100 ml of measurement solution.

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

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

In a closed system with an air circulating pump, pass air at the rate of 1 l/min to 2 l/min through the reaction vessel and absorption cell, until a stable absorbance is reached.

In an open system, purge the measuring solution with a stream of mercury-free compressed air or inert gas and measure the peak height or, preferably, the peak area.

Adjust the flowrate according to the manufacturer's instructions and retain it throughout the measurement.

Measure the absorbances of the calibration (4.3.14) and reagent blank solutions (4.3.15) in the same manner as the water sample.

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4.7.2 Analysis using the method of standard calibration

Prepare a calibration curve as follows.

- Prepare the mercury calibration solutions as described in 4.3.14.
- Measure the absorbances of the calibration and reagent blank solutions as described in 4.7.1.
- Establish the equation for the linear calibration line from the series of results obtained.

4.7.3 Analysis using the standard addition method of calibration

The use of the standard addition method can compensate for errors due to matrix effects, provided that no additive errors occur and that the absorbances of the spiked measurement solutions lie in the linear working range, i.e. the results are in the linear region of the calibration curve. Ensure that the concentration of added mercury corresponds to the volume and the expected mercury content of the sample. As an example, for a sample volume of 50 ml and an expected mercury concentration of 1 µg/l proceed as follows:

- Into each of four 100 ml reaction flasks, place 50 ml of the measurement solution (4.7.1).
- To three of the flasks add 0,5 ml, 1,0 ml or 1,5 ml respectively of standard mercury solution (1) (4.3.12). The spikes correspond to 1 µg/l, 2 µg/l and 3 µg/l of mercury.
- Measure the mercury concentration of the contents of all four flasks according to the instructions in 4.7.1.
- With a blank solution (4.3.15), follow the same procedure as used for the water sample.