INTERNATIONAL STANDARD

ISO 12846

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Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment

Qualité de l'eau — Dosage du mercure — Méthode par spectrométrie d'absorption atomique (SAA) avec et sans enrichissement

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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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12846 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This first edition of ISO 12846 cancels and replaces the editions (ISO 5666:1999, ISO 16590:2000), which have been technically revised.

Introduction

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

In order to fully decompose all of the mercury compounds in the presence of particles in the sample, an additional digestion procedure is necessary. This additional digestion can be omitted only if significant amounts of previous comparison data clearly demonstrate this.

For reliable measurements in the low-concentration range, the highest purity reagents, clean vessels, mercury-free air in the laboratory and a very stable measurement system are essential.

This International Standard is a state-of-the-art revision of existing standards for the determination of mercury by AAS with and without a pre-enrichment step combining the advantages of the existing methods with new developments and technique. The following methods are considered:

A) Methods without enrichment:

- ISO 5666:1999, *Water quality — Determination of mercury*;
- EN 1483:2007, *Water quality — Determination of mercury — Method using atomic absorption spectrometry*.

B) Methods with enrichment:

- ISO 16590:2000, *Water quality — Determination of mercury — Methods involving enrichment by amalgamation*;
- EN 12338:1998, *Water quality — Determination of mercury — Enrichment methods by amalgamation*.

Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment

WARNING – Potassium bromate, used in significant quantities for sample preservation in this International Standard, is carcinogenic and suitable safety precautions shall be taken. Precautions should be taken to detoxify any residual bromate by reduction to bromide before disposal.

Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably qualified staff. Mercury and mercury compounds are very toxic. Extreme caution should be exercised when handling samples and solutions which contain or may contain mercury.

1 Scope

This International Standard specifies two methods for the determination of mercury in drinking, surface, ground, rain and waste water after appropriate pre-digestion. For the first method (described in Clause 6), an enrichment step by amalgamation of the Hg on, for example, a gold/platinum adsorber is used. For the method given in Clause 7, the enrichment step is omitted.

The choice of method depends on the equipment available, the matrix and the concentration range of interest. Both methods are suitable for the determination of mercury in water. The method with enrichment (see Clause 6) commonly has a practical working range from 0,01 µg/l to 1 µg/l. The mean limit of quantification (LOQ) reported by the participants of the validation trial (see Annex A) was 0,008 µg/l. This information on the LOQ gives the user of this International Standard an orientation and does not replace the estimation of performance data based on laboratory-specific data. It has to be considered that it is possible to achieve lower LOQs with specific instrumentation (e.g. single mercury analysers).

The method without enrichment (in Clause 7) commonly has a practical working range starting at 0,05 µg/l. The LOQ reported by the participants of the validation trial (see Annex A) was 0,024 µg/l. It is up to the user, based on the specific application, to decide whether higher concentrations are determined by omitting the enrichment step and/or by diluting the sample(s). The sensitivity of both methods is dependent on the selected operating conditions.

Another possibility for the determination of extremely low Hg concentrations down to 0,002 µg/l without pre-concentration is the application of atomic fluorescence spectrometry (see ISO 17852). Specific atomic-absorption mercury analysers allow determinations down to 0,010 µg/l without pre-concentration.

In general, the determination of trace concentrations of Hg by AAS (or AFS) is dependent on clean operating conditions in the laboratory and on the use of high-purity chemicals with negligible low-Hg blanks.

NOTE This International Standard may be applied to industrial and municipal waste water after an additional digestion step performed under appropriate conditions and after suitable method validation (see 7.4). A potential sample stability issue (mercury loss) for anaerobic reducing industrial effluents has to be considered thoroughly.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second order calibration functions*

3 Principle

Mono- or divalent mercury and organo-mercury compounds as well are converted to divalent mercury by oxidation with $KBrO_3$-KBr and then 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.

Alternatively, samples may be preserved with dichromate/HNO_3 and digested under appropriate conditions (e.g. using potassium permanganate/potassium peroxodisulfate). This technique is not part of this International Standard and has therefore to be validated appropriately by the user.

If the enrichment step is applied, the mercury (in the form of atomic vapour) is transported in a stream of inert gas with negligible mercury content to a quartz tube with a suitable heating and adsorbent (e.g. gold-platinum gauze) on which the mercury is adsorbed.

Other adsorbents based on the principle of amalgamation are allowed if the user demonstrates fitness for purpose.

The mercury is then released by rapid heating of the adsorbent (desorption at 600 °C as a minimum) and further transported in a stream of carrier gas to the absorption cell where the absorbance is measured at 253,7 nm in the radiation beam of an atomic absorption spectrometer. Concentrations are calculated using a calibration curve or using the standard addition method.

If the enrichment step is omitted, the mercury is transported directly into a cuvette. Absorbances are also measured at a wavelength of 253,7 nm.

4 General interferences

With mercury, there is a risk that exchange reactions, that is adsorption and desorption, will occur on the walls of the sampling and reaction vessels. The instructions in 6.2.5.2 should therefore be followed exactly.

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. FEP tubes [FEP = perfluoro(ethene-propene)], should be used. Silicone tubing, for example, is unsuitable.

Easily reducible elements, such as gold, silver and platinum, amalgamate with elemental mercury and may therefore cause suppression. Additionally, iodide is a significant interferent causing severe suppression of the mercury signal.

Volatile organic substances can absorb in the UV range and although automatic background correction is used to compensate for this, it still results in a degraded signal-to-noise ratio.

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

NOTE Tin(II) chloride causes extensive contamination of the apparatus with tin. Considerable interferences occur if tin has to be determined afterwards on the same system.

Table 1 provides acceptable maximum concentrations of some matrix elements in the measurement solution known not to cause interference. Above the given concentrations, the elements listed may cause significant interferences by reducing the original signal for more than 10 %. Interference effects were tested with a 100 ng/l standard.

Table 1 — Acceptable concentrations of some matrix elements in a measurement solution

Values in mg/l

Reducing agent	$SnCl_2$ (6.1.8)
Medium	0,5 mol/l HCl
Element	
Cu(II)	500
Ni(II)	500
Ag(I)	1
I(-I)	0,1
As(V)	0,5
Bi(III)	0,5
Sb(III)	0,5
Se(IV)	0,05

5 Sample collection and pre-treatment for drinking, surface, ground and rain-water samples

Carry out the sampling as specified in ISO 5667-1 and ISO 5667-3 using only the sampling vessels specified in 6.2.5.2.

Make sure that the sampling vessel contains no mercury and causes no loss of mercury by adsorption or diffusion.

With the following approach, a combined preservation and digestion step is carried out on the arrival of samples in the laboratory.

Stabilize the samples by adding 1,0 ml of hydrochloric acid (6.1.7) per 100 ml of the sample, preferably during the sampling in the field. To avoid handling the acid during field sampling and to minimize the risk of contamination, it is recommended that the hydrochloric acid (6.1.7) be placed in a bottle in the laboratory prior to sampling. In this case, the bottle shall be filled without first being rinsed with the sample. On arrival of the samples at the laboratory, add 2 ml of the potassium bromide/potassium bromate reagent (6.1.4) per 100 ml of the sample. Samples shall be preserved within 48 h of collection. The maximum allowable time for adding the bromide/bromate reagent is 6 d after collection. Allow the samples to stand for at least 30 min. If the yellow colouration due to free bromine does not persist after 30 min, add a further 1 ml of the potassium bromide/potassium bromate reagent (6.1.4) and allow the samples to stand for another 30 min.

NOTE In order to calculate the dilution factor of the sample caused by adding the reagent, the volume of the sample can, for example, be determined by weighing both the full sample bottle and the empty and dry sample bottle.

WARNING — The bromate/bromide reagent should be added in the laboratory due to potential health and safety hazards to sampling operatives.

Note that volume correction is necessary.

Prepare a reagent blank (6.1.9) containing the same amounts of reagents and analyse along with the corresponding sample. If additional potassium bromide/potassium bromate reagent (6.1.4) is added to the samples, the same amounts shall be added to the standards used for the calibration.

If preserved samples are to be stored, analyse them within 2 weeks after collection. The maximum storage time is 4 weeks after collection. An indication of insufficient stability of the sample is the decolourisation caused by the progressing consumption of free bromine.

For all aqueous samples, prepare a field blank and analyse as required. Use the same type of container and the same quantity of all reagents as were used in the sample collection. Treat the field blank like a sample.

If waste waters are to be analysed, see 7.4 with regard to the pre-treatment of samples.

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

6.1 Reagents and standards

Reagents and water can contain mercury as an impurity. For high sensitivity, use ultra-pure reagents or those with a particularly low mercury content compared to the lowest analyte concentration.

6.1.1 Water, with a purity fulfilling the requirements for grade 1, as specified in ISO 3696 for all sample preparations and dilutions.

6.1.2 Potassium bromate solution, $c(\text{KBrO}_3) = 0{,}033\ 3$ mol/l.

Dissolve 1,39 g of potassium bromate in 250 ml of water (6.1.1). Potassium bromate can be purified, if necessary, by heating in a muffle furnace overnight at 250 °C ± 20 °C.

The solution is stable for about 1 month.

6.1.3 Potassium bromide solution, $c(\text{KBr}) = 0{,}2$ mol/l.

Dissolve 5,95 g of potassium bromide in 250 ml of water (6.1.1). Potassium bromide can be purified, if necessary, by heating in a muffle furnace overnight at 300 °C ± 20 °C.

The solution is stable for about 1 month.

6.1.4 Potassium bromide/potassium bromate reagent.

Mix equal volumes of potassium bromate (6.1.2) and potassium bromide solution (6.1.3). A total volume of 200 ml will allow digestion for 100 samples.

NOTE Pre-mixed ampoules for potassium bromate/bromide stock solution are commercially available. This reagent has been found to contain negligible mercury concentrations.

The reagent can remain stable for several days and up to several weeks. This point shall be checked. The solution should be colourless.

6.1.5 Hydroxylammonium chloride solution, $\rho(\text{NH}_4\text{ClOH}) = 120$ g/l.

Dissolve 6,0 g of hydroxylammonium chloride in water (6.1.1) in a 50 ml volumetric flask and make up to volume.

This solution may be purified by the addition of 1,0 ml of SnCl_2 solution (6.1.8) and purging overnight at 500 ml/min with Hg-free N_2. Flow injection systems may require less SnCl_2 for purification of the solution.

The solution is stable for about 1 month.

NOTE An ascorbic acid solution (L-ascorbic acid, 100 g/l) is also permissible. It is up to the user of this International Standard to demonstrate the fitness for purpose of this reduction procedure.

6.1.6 Nitric acid, $\rho(\text{HNO}_3) = 1{,}4$ g/ml.

NOTE Nitric acid is available both as $\rho(\mathrm{HNO_3}) = 1{,}40$ g/ml [$w(\mathrm{HNO_3}) = 650$ g/kg] and $\rho(\mathrm{HNO_3}) = 1{,}42$ g/ml [$w(\mathrm{HNO_3}) = 690$ g/kg]. Both are suitable for use in this method provided the mercury content is negligible.

6.1.7 **Hydrochloric acid**, (HCl), $w(\mathrm{HCl}) = 360$ g/kg [$\rho(\mathrm{HCl}) = 1{,}19$ g/ml].

Depending on the working range of the method, the hydrochloric acid used to stabilize the sample and standards can be further purified using the following procedure.

Add 1 ml of the tin(II) chloride solution (6.1.8) to 1 l of the acid. Bubble the solution with argon, nitrogen or air, e.g. at a flow rate of 2 l/min for 15 min. The initial $\mathrm{SnCl_2}$ concentration in the HCl is 0,002 %.

6.1.8 **Tin(II) chloride solution**, $\rho(\mathrm{SnCl_2{\cdot}2H_2O}) = 20$ g/l.

Add 10,0 g of tin(II) chloride dihydrate to 50 ml of hydrochloric acid (6.1.7). Heat to dissolve. Dilute to 500 ml with water (6.1.1). To remove any traces of mercury, bubble the solution with argon or nitrogen, e.g. at a flow rate of 2 l/min for 15 min.

NOTE The hydrochloric acid used to prepare this solution can be of analytical grade since any mercury present will be removed on bubbling.

6.1.9 **Reagent blank**.

For each 100 ml, prepare a solution containing 1,0 ml of hydrochloric acid (6.1.7) and 2 ml of the potassium bromide/potassium bromate reagent (6.1.4). It is essential that the same reagents used for sample and standard preparation be used to prepare the reagent blank. Treat the reagent blank like a sample.

On the continuous-flow system, the reagent blank solution is run as a background for automatic blank subtraction. This solution should be checked for mercury and, if found to exceed twice the reported quantification limit (LOQ), should be rejected and prepared again using reagents with acceptably low mercury concentrations.

6.1.10 **Mercury standard solutions**.

All standards shall contain the same concentration of the potassium bromide/potassium bromate reagent (6.1.4) as the samples. Increased levels of bromide suppress the mercury signal.

6.1.10.1 **Mercury stock solution A**, $\rho(\mathrm{Hg}) = 1\,000$ mg/l.

Use a commercially available quantitative standard solution.

This solution is stable for at least 6 months.

Alternatively, use a stock solution prepared from ultra-purehemicals (99,99 %/99,999 % mass fraction pure). Dissolve 0,135 4 g of mercury(II) chloride $\mathrm{HgCl_2}$ in 20 ml water (6.1.1). Add 5 ml of nitric acid (6.1.6) and dilute to 100 ml with water (6.1.1).

WARNING — Do not dry the inorganic salt, it is highly toxic and volatile.

6.1.10.2 **Mercury stock solution B**, $\rho(\mathrm{Hg}) = 10$ mg/l.

Dilute 1 ml of stock solution A (6.1.10.1) to 100 ml with reagent blank (6.1.9) in a volumetric borosilicate flask.

Prepare weekly.

6.1.10.3 **Mercury stock solution C**, $\rho(\mathrm{Hg}) = 100$ µg/l.

Dilute 1 ml of stock solution B (6.1.10.2) to 100 ml with reagent blank (6.1.9) in a volumetric borosilicate flask.

Prepare the solution on the day of use.

6.1.10.4 **Mercury stock solution D**, $\rho(\mathrm{Hg}) = 1$ µg/l.

Dilute 1 ml of stock solution C (6.1.10.3) to 100 ml with reagent blank (6.1.9) in a volumetric borosilicate flask.

Prepare the solution freshly before each series of measurements.

6.1.10.5 **Calibration standards**.

Prepare a minimum of five mercury calibration standards spanning the concentration range of interest by serial dilution of stock solution D (6.1.10.4). Each calibration standard shall contain 1,0 ml of hydrochloric acid (6.1.7) and 2 ml of the potassium bromide/potassium bromate reagent (6.1.4) per 100 ml in borosilicate volumetric flasks. Plastic flasks should not be used if they are permeable to mercury(0) vapour. Prepare on the day of use.

The matrix of the reagent blank solution shall be identical to that of the standard solutions.

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

Prepare five calibration standards of concentrations 0,010 µg/l, 0,030 µg/l, 0,050 µg/l, 0,070 µg/l and 0,100 µg/l by taking 1 ml, 3 ml, 5 ml, 7 ml and 10 ml, respectively, of mercury stock solution D (6.1.10.4) and diluting it accurately to 100 ml with reagent blank (6.1.9).

For the concentration range of 0,005 µg/l to 0,050 µg/l, for example, proceed as follows.

From mercury stock solution D (6.1.10.4), prepare a series of calibration standards of concentrations 0,005 µg/l, 0,010 µg/l, 0,020 µg/l, 0,040 µg/l and 0,050 µg/l by diluting accurately 0,5 ml, 1 ml, 2 ml, 4 ml and 5 ml to 100 ml in borosilicate volumetric flasks with reagent blank (6.1.9).

6.1.11 **Nitric acid cleaning mixture**.

Dilute nitric acid (6.1.6) with an equal volume of water (6.1.1).

6.1.12 **Potassium bromide/potassium bromate cleaning mixture**.

For each 100 ml, prepare a solution containing 1,0 ml of hydrochloric acid (6.1.7) and 2 ml of potassium bromide/potassium bromate reagent (6.1.4) to be added in water (6.1.1). Prepare as required and keep sealed.

6.2 Apparatus and instrumentation

Before use, rinse all glassware thoroughly with diluted nitric acid (6.1.6), then several times with water (6.1.1).

6.2.1 **Atomic absorption spectrometer**.

The atomic absorption spectrometer (AAS) shall be equipped with

- a suitable cold-vapour generation system, based on an automated flow injection or continuous flow (6.2.3) or a manual or semi-automatic batch system, and
- a quartz, or
- glass tube atomizer, and
- a background correction.

Automated stand-alone mercury flow systems are also suitable. They allow for a lower concentration range. For all systems, it is up to the user to demonstrate the fitness for purpose.

6.2.2 **Radiation source**, for the determination of mercury.

Source which emits intense radiation at the mercury resonance line $\lambda = 253{,}7$ nm, such as:

- hollow cathode lamp;

- boosted hollow cathode lamp;
- electrodeless discharge lamp;
- mercury low-pressure lamp;
- continuum radiation source (e.g. xenon short-arc lamp) in combination with a high resolution AA-spectrometer.

6.2.3 Continuous-flow vapour generator.

Use a suitable mercury accessory, mainly consisting of:

6.2.3.1 Peristaltic pump, e.g. for four channels, with tubing to pump sample, waste, reduction solution and carrier solution separately.

6.2.3.2 Valves, for selecting gas flows.

6.2.3.3 Integrated-mass flow controller, enabling the carrier gas flow to be controlled and monitored through the system software.

6.2.3.4 Reaction coil or reaction cell, where the reagent streams are being mixed and mercury(I/II) is reduced to the Hg(0) state.

6.2.3.5 Gas/liquid separator, for separating the gas from the liquid.

6.2.3.6 Data station control, which provides full autosampling operation with a suitable computer and a control system.

6.2.3.7 Autosampler.

The continuous-flow principle eliminates the need to clean the reaction coil or reaction cell (6.2.3.4) after each sample.

6.2.4 Quartz tube with suitable heating and an adsorbent which enables the enrichment with amalgamation (e.g. gold-platinum gauze).

Other adsorbents which enable amalgamation are allowed if the user demonstrates the fitness for purpose.

The desorption of Hg should be performed at 600 °C (minimum temperature).

6.2.5 Labware.

6.2.5.1 General.

For the determination of mercury at very low concentrations, contamination and loss are of critical consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area, designated for trace-element sample handling shall be used. Special attention has to be given to the air quality. Is has to be ensured that the laboratory air has a negligibly low Hg blank compared with the analyte concentration in the samples. All re-usable labware in contact with the sample shall be cleaned prior to use. Labware shall be soaked in nitric-acid cleaning mixture (6.1.11) for at least 48 h and rinsed three times with water (6.1.1). Following this, refill the labware with the potassium bromide/potassium bromate cleaning mixture (6.1.12) and leave for 24 h. Add any excess hydroxylammonium chloride solution (6.1.5) to remove free bromine, empty and rinse three times with water (6.1.1). Disposable (single-use) plastics labware does not require special cleaning, provided that negligible mercury contamination in the material has been demonstrated. Cleaned labware shall be protected against re-contamination and shall be stored in a clean area until ready for use.

6.2.5.2 Storage/sample processing bottles.

Sample containers made of, for example, fluorinated ethylene propylene (FEP), borosilicate glass or quartz are recommended for storage, collection and processing of samples. It is critical that the bottles have gas-tight sealing caps to avoid diffusion of Hg vapour through the threads.

6.3 Instrumental set-up

Configure the instrumentation as described in the instrument manufacturer's manual.

Check tubing on the day of use and replace if necessary. All tube distances between the autosampler, vapour generator and glass-tube atomizer shall be kept to a minimum length.

Fill the reagent reservoir(s) with reagent blank (6.1.9) and tin(II) chloride solution (6.1.8).

Turn on the pump and ensure that solutions are pumped through tubings properly and at a constant flow-rate ratio. The flow-rate ratio of tin(II) chloride solution (6.1.8) to blank/sample is important and should be consistent.

Turn on the inert gas to provide the required gas flows. Flow rates shall be set in accordance with the instrument manufacturer's recommendation.

6.4 Procedure

Establish instrument software run procedures for quantitative analysis. Establish the run procedures for the continuous-flow vapour generator (6.2.3) and the enrichment system (6.2.4) in accordance with the instrument manufacturer's recommendations.

Immediately prior to carrying out the measurement, add 100 µl of hydroxylammonium chloride solution (6.1.5) per 10 ml of the sample, standard or reagent blank solution (6.1.9). This removes excess bromine which is indicated by the yellow colour vanishing from the sample. For samples and blanks with additional potassium bromide/potassium bromate reagent (6.1.4), additional hydroxylammonium chloride solution (6.1.5) might also be necessary to remove excess bromine.

With the reagent blank (6.1.9) and tin(II) chloride (6.1.8) flowing to the gas/liquid separator, ensure that the system is equilibrated by monitoring for a stable absorption background. If insufficient time is allowed, the detector baseline can change during an analysis cycle.

Analyse standards, samples and blanks sequentially using the required procedure or run the analysis automatically in the following manner.

> Load the autosampler tray with standards, samples and blanks and start the autosampler programme. Analysis of a reagent blank within a sample run will establish whether contamination has occurred. Should a significant level of contamination be established, the analytical results may be brought into question.
>
> For samples with mercury concentrations outside the range, dilute new test portions so that their concentrations fit to the calibration range. Alternatively, re-analyse the samples in accordance with Clause 7 (without enrichment). If a digested sample is diluted, use the reagent blank solution (6.1.9) as diluent.

6.4.1 Analysis using the method of standard calibration

Prepare a calibration curve as follows.

Prepare the mercury calibration solutions according to 6.1.10.5.

Measure the absorbances of the calibration and reagent blank solutions.

Establish the equation for the linear calibration line from the series of results obtained (see ISO 8466-1). Usually, this step is carried out with the aid of the integrated instrument software of the AAS system.

Check the validity of the calibration function on a regular basis.

Non-linear calibration functions in accordance with ISO 8466-2 are also allowed, but, in general, the calibration function shall be linear.

6.4.2 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 within the linear working range, that is: 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 concentration of the sample.

6.5 Calculation

6.5.1 Calculation using the calibration curve

Take account of the dilution factor during sampling and sample pre-treatment in the calculation and any further dilution steps, if appropriate. Calculate the concentration of mercury using Equation (1). The mass concentration is usually determined with the aid of the instrument software.

$$\rho = \frac{(A - A_\mathrm{S}) \cdot V_\mathrm{M}}{b \cdot V_\mathrm{P}} \tag{1}$$

where

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

A is the absorbance or integrated absorbance of the measurement solution;

A_S is the absorbance or integrated absorbance of the blank solution;

b is the slope of the calibration curve and a measure of the sensitivity, in litres per microgram, l/µg;

V_P is the volume of sample used to prepare the measurement solution, in millilitres, ml;

V_M is the volume of measurement solution, in millilitres, ml.

6.5.2 Calculation with the standard addition method

Prepare reference solutions by spiking the sample with the standard solutions and increasing mercury concentrations stepwise.

Prepare a calibration curve using the measured absorbances of the spiked measurement solutions (6.4.1).

Obtain the concentration of a sample solution by extrapolating the calibration curve to absorbance $A = 0$. Similarly, determine the mercury concentration of the blank solution and subtract the value from the result obtained for the sample. Alternatively, carry out the evaluation by linear regression.

Compensate for any additional dilution steps in the calculation.

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

7.1 Reagents and standards

See 6.1

7.2 Apparatus and instrumentation

Before use, rinse all glassware thoroughly with diluted nitric acid (6.1.6), then several times with water (6.1.1).

All apparatus and instrumentation shall be as described in 6.2, but without the enrichment system mentioned in 6.2.4.

7.3 Sample collection and pre-treatment for drinking, surface, ground and rain-water samples

See Clause 5.

7.4 Sample collection and pre-treatment for waste-water samples

Carry out the sampling as specified in ISO 5667-1 and ISO 5667-3, but only use the sampling vessels specified in 6.2.5.2.

Make sure that the sampling vessel contains no mercury and causes no loss of mercury by adsorption or diffusion.

With the following approach, a combined preservation and digestion step for waste-water samples is carried out on the arrival of samples in the laboratory.

Stabilize the samples by adding 1,0 ml of hydrochloric acid (6.1.7) per 100 ml of sample, preferably during the sampling in the field. To avoid the handling of the acid on site and to minimize the risk of contamination, it is recommended that the hydrochloric acid (6.1.7) be placed in a bottle in the laboratory prior to sampling. In this case, the bottle shall be filled without first being rinsed with the sample. Samples shall be preserved within 48 h of collection. On their arrival in the laboratory, add 2 ml of the potassium bromide/potassium bromate reagent (6.1.4) per 100 ml of the sample. Allow the samples to stand for at least 24 h. If the yellow coloration due to free bromine does not persist during this period, add a further 1 ml of the potassium bromide/potassium bromate reagent (6.1.4) and allow to stand for another 24 h.

NOTE In order to calculate the dilution factor of the sample caused by adding the reagent, the volume of the sample can, for example, be determined by weighing both the full sample bottle and the empty, dry sample bottle.

WARNING — The bromate/bromide reagent should be added in the laboratory due to potential health and safety hazards to sampling operatives.

Note that volume correction is necessary.

Prepare a reagent blank (6.1.9) containing the same amounts of reagents and analyse along with the corresponding sample. If additional potassium bromide/potassium bromate reagent (6.1.4) is added to the samples, the same amounts are to be added to the standards used for the calibration.

If the preserved samples are to be stored, analyse them within 2 weeks after collection.

For all aqueous samples, prepare a field blank and analyse as required. Use the same type of container and the same quantity of all reagents as are used in sample collection. Treat the field blank like a sample.

7.5 Instrumental set-up

See 6.3

7.6 Procedure

Establish instrument software run procedures for quantitative analysis. Establish the run procedures for the continuous-flow vapour generator (6.2.3) in accordance with the instrument manufacturer's recommendations.

The user of this approach should take the necessary precautions to avoid mercury carry-over problems when analysing waste-water samples with high mercury contents. If other sample matrices with very low mercury contents are to be analysed as well, consider running them on another system or at least in another sample batch. It is up to the user to demonstrate that carry-over problems are properly taken into account.

Further steps of the procedure are described in 6.4.

7.7 Calculation

See 6.5.

8 Expression of results

Results are expressed in appropriate units applying the dilution factors used for each sample. Report the results with two significant figures.

EXAMPLE

Mercury (Hg)	0,17 µg/l.
Mercury (Hg)	0,078 µg/l.

9 Test report

This test report shall contain at least the following information:

a) the test method used, together with a reference to this International Standard (ISO 12846);

b) the complete identification of the sample;

c) the test results obtained, expressed in accordance with Clause 8;

d) any details not specified in this International Standard, or regarded as optional, as well as details of any incident liable to have affected the results.

Annex A
(informative)

Performance data

An interlaboratory validation trial was organized by the IWW Water Centre in Germany in March/April 2010. Twenty-six laboratories from Austria ($n = 1$), France ($n = 1$), Germany ($n = 11$), Hungary ($n = 3$), Israel ($n = 2$), Italy ($n = 1$), Mexico ($n = 1$), the Netherlands ($n = 1$), Norway ($n = 3$), the Russian Federation ($n = 1$) and Slovakia ($n = 1$) took part in this trial. Four different water samples were analysed:

Sample A: Drinking water

(Public Water Supply of Muelheim, Germany)

Sample B: Membrane-filtered surface water (no additional digestion necessary); (0,45 µm pore size filters)

(River Ruhr, near Muelheim, Germany)

Sample C: Municipal waste water with low COD (about 20 mg/l O_2)

(effluent of a waste-water treatment plant in Duisburg, Germany)

Sample D: Waste water with high COD (about 500 mg/l O_2)

(industrial waste water from a food manufacturer)

Traceable mercury reference values (X) were provided by the German National Metrological Institute (PTB). The measurements were carried out by double isotope dilution mass spectrometry (IDMS). The statistical data of results, evaluated according to ISO 5725-2, are presented in Tables A.1 to A.3.

Table A.1 — Performance data for the method described in Clause 7 (without enrichment), standard calibration procedure

Sample	Matrix	l	n	o %	X µg/l	$\bar{\bar{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
A	drinking water	19	57	0,0	0,091 3	0,094 6	103,7	0,013 6	14,4	0,006 0	6,3
B	filtered surface water	17	51	15,0	0,853	0,841	98,6	0,040 5	4,8	0,014 0	1,7
C	waste water, low COD	18	54	10,0	3,593	3,596	100,1	0,222 1	6,2	0,073 3	2,0
D	waste water, high COD	20	60	0,0	8,54	8,69	101,8	0,939	10,8	0,195	2,2

l	number of laboratories after outlier rejection
n	number of individual results after outlier rejection
o	percentage of outliers
X	assigned value
$\bar{\bar{x}}$	overall mean of results
η	recovery rate
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

Table A.2 — Performance data for the method described in Clause 7 (without enrichment), standard addition method of calibration

Sample	Matrix	l	n	o %	X µg/l	$\bar{\bar{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
A	drinking water	10	26	0,0	0,091 3	0,092 2	101,0	0,009 7	10,6	0,003 8	4,1
B	filtered surface water	10	28	0,0	0,853	0,846	99,1	0,030 5	3,6	0,007 1	0,8
C	waste water, low COD	9	25	10,7	3,593	3,789	105,5	0,228 3	6,0	0,069 0	1,8
D	waste water, high COD	9	25	10,7	8,54	8,92	104,4	0,475	5,3	0,205	2,3

For an explanation of the symbols, see Table A.1.

Table A.3 — Performance data for the method described in Clause 6 (with enrichment), standard calibration procedure

Sample	Matrix	l	n	o %	X µg/l	$\bar{\bar{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
A	drinking water	6	18	0,0	0,091 3	0,089 5	98,0	0,005 1	5,7	0,003 3	3,7
B	filtered surface water	6	18	0,0	0,853	0,856	100,3	0,032 5	3,8	0,009 2	1,1
C	waste water, low COD	6	18	0,0	3,593	3,645	101,4	0,122 5	3,4	0,050 3	1,4
D	waste water, high COD	6	18	0,0	8,54	8,55	100,1	0,402	4,7	0,064	0,7
For an explanation of the symbols, see Table A.1.											

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