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Water quality — Determination of mercury — Method using atomic fluorescence spectrometry

Qualité de l'eau — Dosage du mercure — Méthode par spectrométrie de fluorescence atomique

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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 17852 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This International Standard is the equivalent of European Standard EN 13506. The preservation procedure with potassium dichromate solution, described in EN 13506, was replaced by a combined on site preservation and digestion procedure with the potassium bromide - potassium bromate reagent (see 5.4)

Introduction

In natural water sources, mercury compounds generally occur in very small 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 sediment and sludge.

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 pre-treatment.

The user should be aware that particular problems could require the specification of additional marginal conditions.

Water quality — Determination of mercury — Method using atomic fluorescence spectrometry

WARNING — 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 according to this International Standard are carried out by suitably qualified staff.

1 Scope

This International Standard specifies a method for the determination of mercury in drinking, surface, ground and rain water using atomic fluorescence spectrometry.

NOTE This International Standard may be applied to industrial and municipal waste water after an additional digestion step under appropriate conditions.

The potential linear dynamic range is approximately 1 ng/l to 100 μg/l. In practice, the working range is often from 10 ng/l to 10 μg/l.

Samples containing mercury at concentrations higher than the working range can be analysed following appropriate dilution of the sample.

The method detection limit (x_{DL}) will be dependent on the selected operating conditions and calibration range. With high purity reagents, a x_{DL} of less than 1 ng/l is obtainable.

The relative standard deviation is typically less than 5 % for concentrations greater than twenty times the method detection limit.

The sensitivity of this method is dependent on the selected operating conditions.

2 Normative references

The following referenced documents are indispensable for the application of this document. 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 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

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

3 Principle

Atomic fluorescence is an emission process in which atoms are excited by the absorption of a beam of electromagnetic radiation. The excited species then relax to the ground state, giving up their excess energy as photons. Intensity of the photons is measured.

An aliquot of sample is digested using chemically generated bromine and bromine chloride (BrCl)[1],[2]. This is known to break down all of the commonly occurring organomercury species to mercury(II). Immediately prior to analysis, the excess bromine is removed by ascorbic acid (see A.2).

Elemental mercury vapour is generated from the digested sample by reduction with tin(II) chloride, and is purged from solution by an argon gas carrier stream. Moisture is continually removed from the gas stream and the mercury vapour is detected by atomic fluorescence spectrometry (AFS). The procedure is usually automated by means of an autosampler and control software.

4 Interferences

With mercury there is a risk that exchange reactions, that is adsorption and desorption, will occur on the walls of sampling and reaction vessels.

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[1)] tubes, may be used. Silicone tubing, for example, is unsuitable.

Suppression effects resulting from quenching of the atomic fluorescence signal may be encountered. Dissolved gaseous species are usually removed during the digestion stage.

The presence of water vapour or aerosol in the fluorescence cell may cause suppression due to quenching. Water vapour should be removed from the carrier gas stream using a hygroscopic membrane before entering the detector[3].

Anions which complex strongly with mercury can cause suppression. These include sulfide, iodide and bromide. The potassium bromide - potassium bromate reagent (5.4) causes no suppression if it is applied as required.

The noble metals, such as gold, silver and platinum, amalgamate with mercury vapour and, therefore, may cause suppression.

Volatile organics do not cause interference with the AFS method[4].

5 Reagents and standards

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

5.1 Water, with a purity fulfilling the requirements for grade 1 water according to ISO 3696 for all sample preparations and dilutions.

5.2 Potassium bromate solution, $c(KBrO_3) = 0{,}0333$ mol/l.

Dissolve 1,39 g of potassium bromate in 250 ml of water (5.1). 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 a week.

1) FEP = perfluoro(ethene-propene).

5.3 Potassium bromide solution, c(KBr) = 0,2 mol/l.

Dissolve 5,95 g of potassium bromide in 250 ml of water (5.1). 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 a month.

5.4 Potassium bromide - potassium bromate reagent.

Mix equal volumes of potassium bromate (5.2) and potassium bromide solution (5.3). A total volume of 200 ml will allow digestion for 100 samples.

Prepare on the day of use.

NOTE Pre-mixed ampoules for potassium bromate-bromide stock solution are commercially available (see C.1). This reagent has been found to contain negligible mercury concentrations.

The pre-mixed reagent may be stable for several days up to one week. This shall be checked.

5.5 L-ascorbic acid solution, $\rho(C_6H_8O_6)$ = 100 g/l.

Dissolve 10 g of L-ascorbic acid in water (5.1) in a 100 ml volumetric flask and make up to volume.

The solution is stable for about a week.

5.6 Nitric acid, $\rho(HNO_3)$ = 1,4 g/ml.

See C.2.

5.7 Hydrochloric acid, (HCl), w(HCl) = 120 g/kg.

Dilute 167 ml of high purity hydrochloric acid w(HCl) = 360 g/kg [ρ(HCl) = 1,19 g/ml] to 500 ml with water (5.1).

5.8 Tin(II)chloride solution, $\rho(SnCl_2 \cdot 2\,H_2O)$ = 20 g/l.

Add 10,0 g of tin(II)chloride dihydrate to 150 ml of hydrochloric acid (5.7). Heat to dissolve. Dilute to 500 ml with water (5.1). To remove any traces of mercury, bubble the solution with argon, nitrogen or air, e.g. at a flow rate of 2 l per minute for 15 min.

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

5.9 Reagent blank.

For each 100 ml, prepare a solution containing 15 ml of hydrochloric acid (5.7) and 2 ml of potassium bromide - potassium bromate reagent (5.4) per 100 ml. Add 100 µl of ascorbic acid solution (5.5) for each 10 ml prepared [5]. It is essential that the same reagents used for sample and standard preparation are used for preparation of the reagent blank. Treat the reagent blank like a sample.

NOTE On the continuous flow system, the reagent blank solution is run as background for automatic blank subtraction. This solution may contain trace levels of detectable amounts of mercury.

5.10 Mercury standard solutions

5.10.1 Mercury stock solution A, ρ(Hg) = 1 000 mg/l.

Use a commercially available quantitative standard solution.

This solution is stable for at least six months.

Alternatively use a stock solution prepared from ultra high purity grade chemicals (99,99/99,999 % mass fraction pure). Dissolve 0,135 4 g of mercury(II)chloride $HgCl_2$ in 20 ml water (5.1). Add 5 ml of nitric acid (5.6) and dilute to 100 ml.

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

5.10.2 Mercury stock solution B, $\rho(Hg) = 10$ mg/l.

Dilute 1 ml of stock solution A (5.10.1) with water (5.1) to approximately 20 ml. Add 2 ml of potassium bromide - potassium bromate reagent (5.4) and dilute to 100 ml in a borosilicate volumetric flask with water.

Prepare weekly.

5.10.3 Mercury stock solution C, $\rho(Hg) = 100$ µg/l.

Dilute 1 ml of stock solution B (5.10.2) to 100 ml with reagent blank (5.9) in a borosilicate flask.

Prepare the solution on the day of use.

5.10.4 Mercury stock solution D, $\rho(Hg) = 1$ µg/l.

Dilute 1 ml of stock solution C (5.10.3) to 100 ml with reagent blank (5.9) in a borosilicate flask.

Prepare the solution freshly before each series of measurements.

5.10.5 Calibration standards.

Prepare a minimum of five mercury calibration standards spanning the concentration range of interest by serial dilution of the stock solution D (5.10.4). Each calibration standard shall contain 15 ml of hydrochloric acid (5.7) and 2 ml of potassium bromide - potassium bromate reagent (5.4) 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 from 10 ng/l to 100 ng/l, for example, proceed as follows.

  Prepare 5 calibration standards of concentrations 10 ng/l, 30 ng/l, 50 ng/l, 70 ng/l and 100 ng/l by taking 1 ml, 3 ml, 5 ml, 7 ml and 10 ml respectively of mercury stock solution D (5.10.4) and diluting accurately to 100 ml with reagent blank (5.9).

— For the concentration range from 2 ng/l to 20 ng/l, for example, proceed as follows.

  Prepare a working stock solution of 100 ng/l by taking 10 ml of mercury stock solution D (5.10.4) and diluting it accurately to 100 ml with reagent blank (5.9). Prepare on the day of use. From this solution, prepare a series of calibration standards of concentrations 2 ng/l, 5 ng/l, 10 ng/l, 15 ng/l and 20 ng/l by diluting 2 ml, 5 ml, 10 ml, 15 ml and 20 ml accurately to 100 ml in borosilicate volumetric flasks with reagent blank (5.9).

5.11 Nitric acid cleaning mixture.

Dilute nitric acid (5.6) with equal volume of water (5.1).

5.12 Potassium bromide - potassium bromate cleaning mixture.

For each 100 ml, prepare a solution containing 15 ml of hydrochloric acid (5.7) and 2 ml of potassium bromide - potassium bromate reagent (5.4).

Prepare as required and keep sealed.

6 Apparatus and instrumentation

6.1 Atomic fluorescence system

A schematic block diagram of an example of an automated mercury analysis system is shown in Annex B. This consists of an autosampler (where operated in an automatic regime), a continuous flow vapour generator, a gas liquid separator, a moisture removal system, an atomic fluorescence spectrometer, a control computer and an interface card.

6.2 Gas supply

Use argon with high purity grade 99,99 % for maximum sensitivity. The gas supply should be with a two stage regulator. The use of a gas purifier consisting of activated carbon is recommended. Nitrogen gas may also be used but will have a reduced sensitivity.

6.3 Moisture removal

Moisture removal is provided using a hygroscopic membrane; details are provided in C.3. Argon or nitrogen gas (6.2) can be used as the drier gas.

6.4 Labware

6.4.1 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. At a minimum, this shall consist of a clean air station. All re-usable labware in contact with the sample shall be cleaned prior to use. Labware shall be soaked in nitric acid cleaning mixture (5.11) for at least 48 h and rinsed three times with water. [Following this, refill labware with the potassium bromide - potassium bromate cleaning mixture (5.12) and leave for 24 h. Add the excess of L-ascorbic acid solution (5.5) to remove free bromine, empty and rinse three times with water.] Disposable (single-use) plastics labware does not require special cleaning, provided that negligible mercury contamination in that material is demonstrated. Clean labware shall be stored in double-bagged plastics in a clean area until ready for use.

6.4.2 Storage/sample processing bottles

Narrow neck bottles, e.g. polytetrafluoroethene (PTFE), perfluoro(ethene-propene) (FEP), borosilicate glass or quartz.

6.4.3 Instrument reagent reservoir

Glass reagent bottles equipped with valved cap and PTFE tubing for transfer of contents via peristaltic pump.

6.4.4 Autosampler vials

Use polystyrene vials or materials specified in 6.4.2.

6.5 Sample processing equipment

6.5.1 Air displacement pipette

Micropipette system capable of delivering volumes from 10 µl to 1 000 µl with an assortment of metal-free, disposable pipette tips.

6.5.2 Balances

Analytical balance, capable of accurately weighing to ± 0,1 mg; and **top-pan balance**, accurate to ± 0,1 g.

7 Sample collection and pre-treatment

Carry out the sampling in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3, using sampling vessels (as specified in 6.4.2). The preservation technique described in ISO 5667-3 is not to be applied when using the technique described in this International Standard. ISO 5667-3 suggests to preserve the samples with HNO_3 and $K_2Cr_2O_7$ whereas this International Standard is based on a combined preservation and digestion step using a potassium bromide - potassium bromate reagent.

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 site.

Stabilize the samples preferably on site by adding 15 ml of hydrochloric acid (5.7) and 2 ml potassium bromide - potassium bromate reagent (5.4) per 100 ml of the sample. Allow the samples to stand for at least 30 min. If the yellow coloration due to free bromine does not persist after 30 min, add a further 1 ml of potassium bromide - potassium bromate reagent (5.4).

NOTE This combined preservation and digestion step has not been validated in the interlaboratory trial (see EN 13506[7]). But experience has shown that the precision data are at least as good as described in Annex D.

Note that volume correction is necessary (see 9.2).

Prepare a reagent blank (5.9) containing the same amounts of reagents and analyse along with the corresponding sample.

If the samples are to be stored, analyse within seven days after collection.

Sample containers made of polytetrafluoroethene (PTFE), perfluoro(ethene-propene) (FEP), borosilicate glass or quartz are recommended for storage, collection and processing of samples (6.4.2).

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

8 Instrumental set up

Configure the instrumentation as described in the instrument manufacturer's manual. An example for the configuration is given in Annex B.

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

Fill the reagent reservoir(s) with reagent blank (5.9) and tin(II) chloride solution (5.8).

Turn on the pump and ensure that all lines are pumping properly and at a constant ratio of flow rates. The ratio of flow rates of tin(II) chloride (5.8) lines to blank/sample lines is important and shall be consistent.

Turn on the argon to provide the required gas flows. Flow rates shall be set according to the instrument manufacturer´s recommendation.

Select the required amplification range for the atomic fluorescence detector according to the manufacturer's recommendation. Ensure that the selected detector range is appropriate to the mercury concentration being determined.

For samples whose mercury concentrations are off scale for a given range setting, either re-analyse at a lower sensitivity or dilute a fresh undigested sample into the calibration range. If a digested sample is diluted, use the diluent as reagent blank solution (5.9).

9 Procedure

9.1 General

Establish instrument software run procedures for quantitative analysis.

Immediately before measurements add 100 µl of L-ascorbic acid solution (5.5) per 10 ml of the sample, standard or reagent blank solution prepared according to 5.9. This removes excess bromine which is indicated by the disappearance of yellow colour from the sample. For samples and blanks with additional potassium bromide - potassium bromate reagent (5.4), additional L-ascorbic acid solution (5.5) may also be necessary to remove excess bromine.

NOTE Hydroxylamine hydrochloride is permissible instead of ascorbic acid. However, this may generate dissolved nitrogen gas which can cause quenching.

With the reagent blank and tin(II) chloride flowing to the gas/liquid separator, ensure that the system is equilibrated by monitoring for a stable fluorescence detector background. If sufficient time is not allowed, the detector baseline can change during an analysis cycle.

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

Load the autosampler tray with standards, samples and blanks and start the autosampler programme. Analysis of the field 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. A minimum of two replicate data measurements shall be taken for each sample and be averaged for the data calculations. Ensure that reagents and blank provide a stable baseline. Proceed with data analysis and calculations.

9.2 Calculation

The mass dilution factor of each sample shall be applied. If additional dilutions were made to any samples, the appropriate factor shall be applied to the calculated sample concentrations. Correct all results by subtraction of the field blank if relevant. Concentrations of samples where additional reagents were added to complete digestion or to preserve the sample shall be corrected with the corresponding blank subtraction.

Calculate using linear calibration curve, plotting the fluorescence response (Y-axis) against the concentration of mercury (X-axis). The calibration curve should not be forced through the origin. Calculate the concentration of mercury using the following formula:

$$\rho = \frac{(A - A_s) \cdot V_M}{b \cdot V_p}$$

where

ρ is the concentration of mercury in the sample in nanograms per litre, ng/l;

A is the fluorescence response of the water sample;

A_s is the fluorescence response of the reagent blank solution;

b is the slope of the calibration curve and a measure of the sensitivity in litre per nanogram, l/ng;

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

V_p is the volume of sample used to prepare the measurement solution, in millilitres, ml.

Non-linear calibration curves are also permissible.

9.3 Expression of results

The instrument is calibrated over a suitable operating range using a series of standard solutions prepared according to 5.10.5. Samples are analysed under similar conditions and values for these samples are calculated from the calibration graph. 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) 14 ng/l

10 Test report

The test report shall specify the following:

a) a reference to this International Standard (ISO 17852:2006);

b) complete identification of the sample;

c) expression of results as indicated in 9.3;

d) any details not specified by this International Standard or which are optional as well as any factor which may have affected the results.

11 Precision

An interlaboratory trial was organized in the United Kingdom by the Environment Agency (National Laboratory Service, Llanelli Laboratory) in November 1999. Twenty laboratories from Denmark (L = 1), France (L = 1), Germany (L = 8), Norway (L = 2), Sweden (L = 2), the Netherlands (L = 3) and the United Kingdom (L = 3) took part in this trial. The statistical data of results, evaluated according to ISO 5725-2, are presented in Annex D.

Annex A
(informative)

Additional information

A.1 The method requires proper attention to detail to attain the low levels of measurement. Other stabilization strategies have been proven, particularly the addition of high purity nitric acid.

A.2 Excess bromine can also be removed using a hydroxylamine hydrochloride reagent [$\rho(NH_2OH \cdot HCl) = 120$ g/l]. This is particularly useful where nitric acid alone is used as a preservative.

For other preservation procedures as outlined in the method, the quantity of hydroxylamine hydrochloride can be significantly increased which can result in the presence of dissolved nitrogen in the samples. This gas can quench the atomic fluorescence signals produced and provide incorrect values. The nitrogen gas can be removed from the solution in some cases using ultra sonic bath for about 10 min. This shall be checked thoroughly.

A.3 The method and any variation from it should be rigorously checked for performance using statistical data and Analytical Quality Control Sample materials, including certified reference materials.

A.4 Whilst any inert gas may be used to purge the mercury from the gas/liquid separator, the optimum signal, response will be provided using argon. Air or nitrogen are often used but will quench the fluorescence signal by differing amounts.

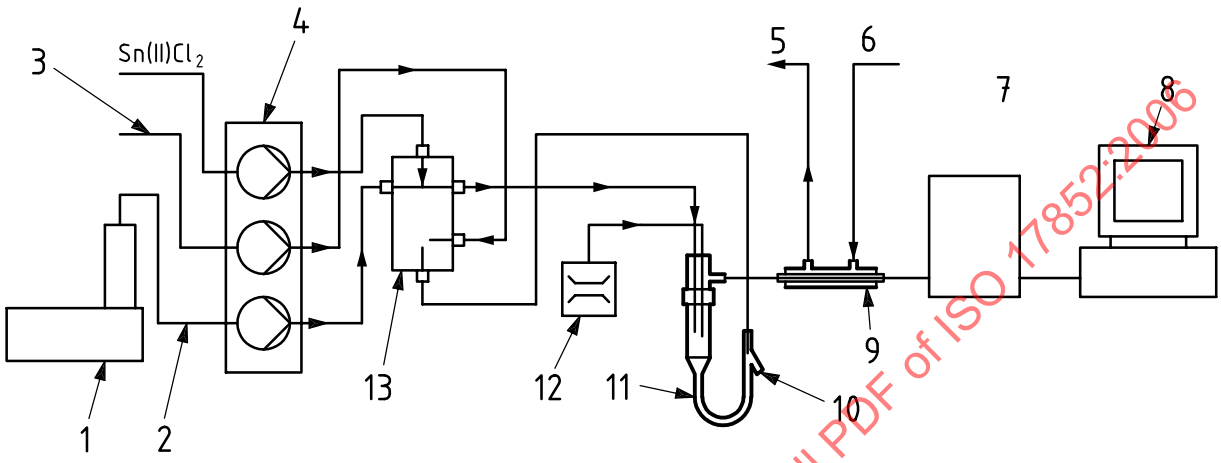
A.5 Water vapour may also be removed using a desiccant tube. Care must be taken using this approach to avoid trapping mercury in the tube due to excess moisture retention.

A.6 The method is applicable as presented for low level mercury determinations. The linear dynamic range can be extended to 10 mg/l when a discrete sample injection approach is used.

A.7 Polypropene and polyethene containers are not recommended since they are permeable to ambient mercury vapour. Should samples be submitted in such containers, they will have to be used within 3 d or discarded.

Annex B
(informative)

Schematic block diagram



Key

1 autosampler
2 sample
3 blank
4 peristaltic pump
5 dryer gas out
6 dryer gas in
7 fluorescence detector
8 computer
9 hygroscopic dryer tube
10 waste
11 gas/liquid separator
12 argon carrier gas rotameter
13 switching valve; sample position; selects sample standards or blank

NOTE This continuous flow vapour generator consists of a constant speed peristaltic pump to deliver tin(II) chloride (5.8), reagent blank (5.9) and sample. A switching valve alternates between the reagent blank and sample or standard solutions. The vapour generator switches between reagent and sample solution on a prescribed sequence so that the measured signal is directly related to the background levels of mercury in the sample.

Figure B.1 — Schematic block diagram