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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.

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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.