



SLOVENSKI STANDARD  
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Water quality - Determination of mercury by atomic fluorescence spectrometry

Wasserbeschaffenheit - Bestimmung von Quecksilber mittels Atomfluoreszenzspektrometrie

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

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

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ICS 13.060.50

English version

## Water quality - Determination of mercury by atomic fluorescence spectrometry

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

Wasserbeschaffenheit - Bestimmung von Quecksilber mittels Atomfluoreszenzspektrometrie

This European Standard was approved by CEN on 4 October 2001.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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## Foreword

This European Standard has been prepared by Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by May 2002, and conflicting national standards shall be withdrawn at the latest by May 2002.

Annexes designated "informative" are only given for information. In this standard, annexes A, B and C are informative.

**WARNING — Persons using this 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.**

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

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## Introduction

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

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.

## 1 Scope

This European Standard specifies a method for the determination of mercury in drinking, surface, ground and rain water.

NOTE It is permissible, that this standard is also 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 (MDL) will be dependent on the selected operating conditions and calibration range. With high purity reagents a MDL 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

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 25667-1, *Water quality - Sampling - Part 1: Guidance on the design of sampling programmes (ISO 5667-1:1980)*.

EN 25667-2, *Water quality - Sampling - Part 2: Guidance on sampling techniques (ISO 5667-2:1991)*.

EN ISO 5667-3, *Water quality - Sampling - Part 3: Guidance on the preservation and handling of samples (ISO 5667-3:1994)*.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)*.

### 3 Principle

An aliquot of sample is digested using chemically generated bromine [1] [2]. This is known to breakdown 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 auto sampler 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 tubes, may be used (FEP = perfluoro(ethylene-propylene)). Silicone tubing, for example, is unsuitable.

Suppression effects resulting from quenching of the atomic fluorescence signal can 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 (5.5) 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

### 5.1 General

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.

### 5.2 Water

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

### 5.3 Potassium bromate solution, $c(\text{KBrO}_3) = 0,0333 \text{ mol/l}$

Dissolve 1,39 g of potassium bromate in 250 ml of water (5.2). Potassium bromate can be purified, if necessary, by heating in a muffle furnace overnight at  $250 \text{ }^\circ\text{C} \pm 20 \text{ }^\circ\text{C}$ . Prepare weekly.

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

Dissolve 5,95 g of potassium bromide in 250 ml of water (5.2). Potassium bromide can be purified, if necessary, by heating in a muffle furnace overnight at  $300 \text{ }^\circ\text{C} \pm 20 \text{ }^\circ\text{C}$ . Prepare monthly.

### 5.5 Potassium bromide - potassium bromate reagent

Mix equal volumes of potassium bromate (5.3) and potassium bromide solution (5.4). A total volume of 200 ml will allow digestion for 100 samples. Prepare daily.

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.

### 5.6 L -ascorbic acid solution, $\rho(\text{C}_6\text{H}_8\text{O}_6) = 100 \text{ g/l}$

Dissolve 10 g of L-ascorbic acid in water (5.2) in a 100 ml volumetric flask and make up to volume. Prepare weekly.

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

See C.2.

### 5.8 Potassium dichromate solution, $\rho(\text{K}_2\text{Cr}_2\text{O}_7) = 0,05 \text{ g/l}$

Dissolve 50 mg of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 50 ml nitric acid (5.7) and dilute to 1 000 ml with water (5.2).

### 5.9 Hydrochloric acid (HCl), $w(\text{HCl}) = 120 \text{ g/kg}$

Dilute 167 ml of high purity hydrochloric acid  $w(\text{HCl}) = 360 \text{ g/kg}$  ( $\rho(\text{HCl}) = 1,19 \text{ g/ml}$ ) to 500 ml with water (5.2).

### 5.10 Tin(II)chloride solution, $\rho(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}) = 20 \text{ g/l}$

Add 10,0 g of tin(II)chloride dihydrate to 150 ml of hydrochloric acid (5.9). Heat to dissolve. Dilute to 500 ml with water (5.2). To remove any traces of mercury, bubble the solution with argon, nitrogen or air e.g. at a flow rate of 2 l/min for 15 min.

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

### 5.11 Reagent blank

For each 100 ml, prepare a solution containing 15 ml of hydrochloric acid (5.9) and 2 ml of potassium bromide - potassium bromate reagent (5.5). Add 100  $\mu\text{l}$  of ascorbic acid solution (5.6) 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 can contain trace levels of detectable amounts of mercury.

### 5.12 Mercury standard solutions

#### 5.12.1 Mercury stock solution A, $\rho(\text{Hg}) = 1\,000 \text{ mg/l}$

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 0,1354 g of mercury(II)chloride  $\text{HgCl}_2$  in 20 ml water (5.2). Add 5 ml of nitric acid (5.7) and dilute to 100 ml.

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

#### 5.12.2 Mercury stock solution B, $\rho(\text{Hg}) = 10 \text{ mg/l}$

Dilute 1 ml of stock solution A (5.12.1) with water (5.2) to approximately 20 ml. Add 2 ml of potassium bromide - potassium bromate reagent (5.5) and 15 ml of hydrochloric acid (5.9) and dilute to 100 ml in a borosilicate volumetric flask with water. Prepare weekly.



**5.12.3 Mercury stock solution C,  $\rho$  (Hg) = 100  $\mu\text{g/l}$** 

Dilute 1 ml of stock solution B (5.12.2) to 100 ml with reagent blank (5.11) in a borosilicate flask.

Prepare the solution on the day of use.

**5.12.4 Mercury stock solution D,  $\rho$  (Hg) = 1  $\mu\text{g/l}$** 

Dilute 1 ml of stock solution C (5.12.3) to 100 ml with reagent blank (5.11) in a borosilicate flask.

Prepare the solution freshly before each series of measurements.

**5.12.5 Calibration standards**

Prepare a minimum of five mercury calibration standards spanning the concentration range of interest by serial dilution of the stock solution D (5.12.4). Each calibration standard shall contain 15 ml of hydrochloric acid (5.9) and 2 ml of potassium bromide - potassium bromate reagent (5.5) per 100 ml in borosilicate volumetric flasks. Plastic flasks should not be used if they are permeable to mercury(0) vapour. Prepare daily.

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 (5.12.4) and diluting accurately to 100 ml with reagent blank (5.11).

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 (5.12.4) and diluting it accurately to 100 ml with reagent blank (5.11). Prepare daily. 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 (5.11).

**5.13 Nitric acid cleaning mixture**

Dilute nitric acid (5.7) with equal volume of water (5.2).

**5.14 Potassium bromide - potassium bromate cleaning mixture**

For each 100 ml, prepare a solution containing 15 ml of hydrochloric acid (5.9) and 2 ml of potassium bromide - potassium bromate reagent (5.5). 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.