



SLOVENSKI STANDARD  
SIST EN 12338:2000

01-januar-2000

Water quality - Determination of mercury - Enrichment methods by amalgamation

Water quality - Determination of mercury - Enrichment methods by amalgamation

Wasserbeschaffenheit - Bestimmung von Quecksilber - Verfahren nach Anreicherung durch Amalgamierung

Qualité de l'eau - Dosage du mercure - Méthodes après enrichissement par amalgame

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**ICS:**

13.060.50 Ú!^ã \ æ ç ð [ å ^ Á æ { ã } ^ Examination of water for chemical substances

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EUROPEAN STANDARD

EN 12338

NORME EUROPÉENNE

EUROPÄISCHE NORM

July 1998

ICS 13.060.01

Descriptors: water tests, surface water, ground water, sewage, chemical analysis, determination of content, mercury, reduction methods, sodium tetraborate, tin chloride

English version

## Water quality - Determination of mercury - Enrichment methods by amalgamation

Qualité de l'eau - Dosage du mercure - Méthodes après  
enrichissement par amalgame

Wasserbeschaffenheit - Bestimmung von Quecksilber -  
Verfahren nach Anreicherung durch Amalgamierung

This European Standard was approved by CEN on 21 June 1998.

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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 Central Secretariat has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

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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of an identical text or by endorsement, at the latest by January 1999, and conflicting national standards shall be withdrawn at the latest by January 1999.

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.

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

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## Introduction

It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

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

In natural water sources, mercury compounds generally occur only in very small concentrations of less than 0,1 µg/l. Higher concentrations may be found, for example, in waste water.

Both inorganic and organic compounds of mercury can be present. Mercury may accumulate in sediment and sludge.

## WARNING:

Mercury and mercury compounds are very toxic. Extreme caution is recommended when handling samples and solutions which contain or may contain mercury.

## 1 Scope

This European Standard specifies the determination of mercury in two parts which use either tin(II)chloride or sodium tetrahydroborate as reducing agent. The methods described in clauses 4 and 5 are suitable for the determination of mercury in water, for example in ground, surface and waste waters, in the concentration range from 0,01 µg/l to 1 µg/l. Higher concentrations may be determined if the water sample is diluted.

The total mercury content of water is determined after digestion of the sample. If only soluble mercury compounds are to be determined, a filtration step using a 0,45 µm membrane filter is applied prior to digestion.

Mono- or divalent mercury is reduced to the elemental form by a reducing agent such as tin(II) chloride, SnCl<sub>2</sub>, or sodium tetrahydroborate, NaBH<sub>4</sub>, in an acid medium. Elemental mercury is then stripped from the solution with the aid of a stream of inert gas and transported over a noble metal surface with a large area, such as gold/platinum gauze, on which the mercury is adsorbed. The mercury is released by rapid heating of the adsorbant and further transported in a stream of carrier gas to a suitable cuvette. Absorbances are measured at a wavelength of 253,7 nm in the radiation beam of an atomic absorption spectrometer. Concentrations are calculated using a calibration curve.

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

## 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.

- |                      |   |
|----------------------|---|
| EN 25667-1 : 1993    | Water quality – Sampling – Part 1: Guidance on the design of sampling programmes (ISO 5667-1 : 1980)        |
| EN 25667-2 : 1993    | Water quality — Sampling – Part 2 : Guidance on sampling techniques (ISO 5667-2 : 1991)                     |
| EN ISO 5667-3 : 1995 | Water quality – Sampling – Part 3: Guidance on the preservation and handling of samples (ISO 5667-3 : 1994) |

### 3 General Interferences

With mercury there is a risk that exchange reactions, that is adsorption and desorption, will occur on the walls of the reaction vessel. The description in 4.6 should therefore be followed exactly.

Mercury vapour can diffuse through various plastics, therefore, special consideration should be given to the choice of tubing material. Glass or special plastics tubing, e. g. FEP tubes may be used (FEP = perfluoroethene-propene polymer). Silicone tubing, for example, is unsuitable.

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

All solutions should be brought to the same temperature ( $< 25\text{ }^{\circ}\text{C}$ ) before reduction and stripping of the mercury vapour. Water condensation on the cuvette windows can be prevented by heating the cuvette with, for example, an infrared lamp.

The interferences which occur due to the presence of other elements in the matrix depend on the choice of reducing agent. Element concentrations in excess of those listed in table 1 may cause too low results.

Fewer interferences from heavy metals arise if tin(II) chloride is used rather than sodium tetrahydroborate. Using flow systems, interference effects due to heavy metals may be less than indicated in table 1.

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

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Table 1: Acceptable concentrations of some matrix Elements in a measurement solution in mg/l

Reducing agent	NaBH <sub>4</sub>	NaBH <sub>4</sub>	SnCl <sub>2</sub>
Medium	0,5 mol/l HCl	5 mol/l HCl + 0,2 g/l Fe(III)	0,5 mol/l HCl
Element			
Cu(II)	10	10	500
Ni(II)	1	500	500
Ag(I)	0,1	10	1
I <sup>-</sup>	100	10	0,1
As(V)	0,5	0,5	0,5
Bi(III)	0,05	0,5	0,5
Sb(III)	0,5	0,5	0,5
Se(IV)	0,005	0,05	0,05

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

### 4.1 Working range

The method is applicable to the determination of the mercury content in concentrations from 0,01  $\mu\text{g/l}$  to 1  $\mu\text{g/l}$ . Higher concentrations may also be determined if the water sample is diluted.

NOTE: Measurements in this concentration range require the use of highest purity reagents and clean flasks, mercury-free laboratory air and a very stable measurement system.

## 4.2 Principle

Mercury is reduced to the elemental form by tin(II) chloride and transported in a stream of inert carrier gas over a noble metal surface with a large area, such as gold/platinum gauze, on which the mercury is adsorbed.

The mercury is released by rapid heating of the adsorbent and further transported in a stream of carrier gas to the absorption cell where the absorbance is measured at 253,7 nm.

## 4.3 Interferences

See also clause 3.

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

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

## 4.4 Reagents

### 4.4.1 General requirements

At least "analytical grade" reagents or those with lowest possible mercury content shall be used. Water shall be double distilled or of similar purity. The mercury content of the water and reagents shall be negligible compared to the lowest analyte concentration.

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

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

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

### 4.4.5 Potassium permanganate solution:

Dissolve 50 g of potassium permanganate,  $\text{KMnO}_4$ , in 1 000 ml of water.

### 4.4.6 Stabilizer solution:

Dissolve 5 g of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , in 500 ml of nitric acid (see 4.4.2) and dilute to 1 000 ml with water.

## WARNING:

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

### 4.4.7 Potassium peroxodisulfate solution

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



#### 4.4.8 Hydroxylammonium chloride solution:

Dissolve 10 g of hydroxylammonium chloride,  $\text{H}_2\text{CINO}$ , in 100 ml of water.

#### 4.4.9 Tin(II)chloride solution:

Dissolve 5 g of tin(II)chloride dihydrate,  $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ , in 30 ml of hydrochloric acid (see 4.4.4), dilute to 100 ml with water. A solution of smaller concentration, e. g. 0,5 g in 100 ml, may be used with flow systems. Prepare this solution freshly daily from the more concentrated solution by diluting with water. If a high result for the blank is obtained, pass nitrogen through the solution for 30 min in order to remove traces of mercury.

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

Dissolve 108,0 mg of mercury (II) oxide,  $\text{HgO}$ , in 10 ml of the stabilizer (see 4.4.6), dilute to 1000 ml with water. 1 ml of the solution corresponds to 0,1 mg of mercury. Stock solution I may be prepared from a commercially available mercury standard. The solution is stable for about 1 month.

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

Add 10 ml of stabilizer (see 4.4.6) to 10 ml of stock solution I (see 4.4.10) and dilute to 1000 ml with water. 1 ml of this solution corresponds to 1  $\mu\text{g}$  of mercury. The solution is stable for about 1 week.

#### 4.4.12 Mercury standard solution I, $\rho(\text{Hg}) = 100 \mu\text{g/l}$

Add 10 ml of stabilizer (see 4.4.6) to 100 ml of mercury stock solution II (see 4.4.11) and dilute to 1000 ml with water. 1 ml of this solution corresponds to 100 ng of mercury. Prepare the solution on the day of use.

#### 4.4.13 Mercury standard solution II, $\rho(\text{Hg}) = 10 \mu\text{g/l}$

Dilute 1 ml of stabilizer solution (see 4.4.6) and 10 ml of standard solution I (see 4.4.12) to 100 ml with water. 1 ml of this solution corresponds to 10 ng of mercury. The solution is stable only a short time and shall be freshly prepared before use.

#### 4.4.14 Mercury standard solution III, $\rho(\text{Hg}) = 1 \mu\text{g/l}$

Dilute 1 ml of stabilizer solution (see 4.4.6) and 10 ml of standard solution II (see 4.4.13) to 100 ml with water. 1 ml of this solution corresponds to 1 ng of mercury. The solution shall be freshly prepared before each series of measurements.

#### 4.4.15 Mercury calibration solutions

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

For the concentration range from 0,01  $\mu\text{g/l}$  to 0,1  $\mu\text{g/l}$ , for example, proceed as follows:

- Pipette into each of six 100 ml volumetric flasks 1,0 ml, 2,0 ml, 4,0 ml, 6,0 ml, 8,0 ml or 10 ml respectively of mercury standard solution III (see 4.4.14).
- Add 1 ml stabilizer solution (see 4.4.6) to each.
- Fill each flask to the mark with water and mix thoroughly.

The calibration solutions contain 0,01 µg/l, 0,02 µg/l, 0,04 µg/l, 0,06 µg/l, 0,08 µg/l, and 0,1 µg/l mercury respectively. These shall be prepared freshly before each series of measurements.

For the concentration range from 0,1 µg/l to 1 µg/l proceed in the same manner using mercury standard solution II (see 4.4.13). In this case the reference solutions contain 0,1 µg/l, 0,2 µg/l, 0,4 µg/l, 0,6 µg/l, 0,8 µg/l and 1 µg/l of mercury respectively. If larger volumes of the measurement solution are used the volumes of the reference solutions and the amount of standard solution added shall be increased accordingly.

The solutions shall be freshly prepared before each series of measurements.

If the calibration measurements shall be done in duplicate prepare another set of solutions.

#### 4.4.16 Reagent blank solution

Prepare a volume of blank solution corresponding to that of the measurement solution by adding 10 ml of stabilizer solution (see 4.4.6) per 1000 ml of water. Use the same digestion procedure as for the sample (see 4.7). The reagent blank shall be included in each batch of analyses.

#### 4.4.17 Gas washing solution:

Dissolve 2,5 g of tin(II) chloride dihydrate,  $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$  with 7,5 ml of sulfuric acid (see 4.4.3) in a small amount of water and dilute to 50 ml with water.

#### 4.4.18 Washing solution for glass ware

Dilute 150 ml of nitric acid (see 4.4.2) to 1000 ml with water.

### 4.5 Apparatus

#### 4.5.1 General requirements

Before use, all glassware shall be washed thoroughly with diluted nitric acid (see 4.4.18) and then rinsed thoroughly several times with water.

**4.5.2 Atomic absorption spectrometer (AAS)** with an appropriate monitoring system. A background correction system is recommended.

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

#### 4.5.4 Mercury attachment with amalgam accessory, consisting of

- absorption cells consisting of a glass or quartz tube, inner diameter about 2 cm, at least 15 cm long (dependent on the AAS instrument) with quartz windows.
- air circulating pump (e. g. membrane pump, peristaltic pump), capacity 1 l/min to 2 l/min, with plastics tubing (closed system).
- inert gas cylinder with pressure reducing valve.
- flow meter with plastics (see clause 3) tubing.
- reaction vessel consisting of, for example, 100 ml, 250 ml or 1000 ml flat-bottomed flask as shown in the figure, with ground glass stopper, wash bottle insert with glass frit, porosity 1.

- heating source for the measuring cell, with sufficient heating capacity to prevent condensation of water. The temperature of the measuring cell shall be the same throughout the analysis.
- quartz tube with heating element and noble metal adsorbent (such as gold-platinum gauze) .
- 100 ml gas washing flask including flashback prevention valve.
- three-way stopcock.

An example for a closed system is shown in figure 1.

NOTE : Caution should be used with regard to the choice of plastics material for pumps and tubing (see clause 3).

A continuous flow or flow injection system is permissible. It is recommended to follow the instructions given by the manufacturer.

#### 4.6 Sampling and sample pretreatment

In sampling and pretreatment, the requirements in EN 25667 Parts 1, 2 and 3 shall be taken into account.

Suitable materials for sampling vessels shall be used; these are borosilicate glass, quartz, polysulfone (PSF) and tetrafluoroethene propene polymer (FEP).

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

In order to limit the losses by, for example, adsorption on the vessel walls add 10 ml of stabilizer solution (see 4.4.6) and make up to 1000 ml with the sample.

The sample shall have a pH of approximately 1 and shall show a yellow-orange colour indicating an excess of dichromate.

If these conditions are not met, add additional stabilizer, and include the appropriate volume correction factor in the calculations.

#### 4.7 Digestion method using permanganate peroxodisulfate

The wet chemical digestion procedure as described hereafter shall be carried out. Alternatively a digestion method as given in the annexes A to C may be used. In all such cases the efficiency of that method compared to the wet digestion method shall be tested.

Transfer 100 ml of the stabilized water sample (see 4.6) or an appropriate volume (maximum 1000 ml) of sample to a flask made from one of the materials mentioned in 4.6.

Carefully add 15 ml of potassium permanganate solution (see 4.4.5), 1 ml of nitric acid (see 4.4.2) and 1 ml of sulfuric acid (see 4.4.3).

Shake the mixture well after each addition.

Allow the solution to stand for 15 min, then add 10 ml of potassium peroxodisulfate solution (see 4.4.7).

Place the loosely stoppered flask on a heating block or water bath at 95 °C for 2 h.

During the digestion ensure that there is an excess of potassium permanganate. If this is not the case, increase the amount of potassium permanganate added or start with a smaller volume of sample.

Allow the solution to cool to room temperature.

If different sample volumes, and accordingly different reagent volumes have been used, dilute the digests to a specific volume.