

Water quality — Determination of mercury — Enrichment methods by amalgamation

The European Standard EN 12338:1998 has the status of a
British Standard

ICS 13.060.01

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National foreword

This British Standard is the English language version of EN 12338:1998.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical analysis, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

It is essential that users evaluate this standard in their own laboratories and demonstrate its fitness for purpose.

The provisions of this standard allow alternative procedures (for example, those described in the annexes) to be carried out in place of those specified in the standard. Alternative procedures should be used only where it can be demonstrated that performance data generated using these procedures is equivalent to, or better than, the performance data given obtained using the procedures described in this standard. Appropriate calculations, using procedures given in BS 5497-1, should be used.

When comparing the performance data obtained using the alternative procedures with those obtained using procedures given in this standard, appropriate calculations, using procedures given in BS 2846-4, should be used.

NOTE The tests described in this British Standard should only be carried out by suitably qualified persons with an appropriate level of chemical expertise. Standard chemical procedures should be followed throughout.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

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This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 14, an inside back cover and a back cover.

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English version

Water quality — Determination of mercury — Enrichment methods by amalgamation

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Méthodes après d'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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CEN

European Committee for Standardization
Comité Européen de Normalisation
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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, SnCl₂, or sodium tetrahydroborate, NaBH₄, 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 = perfluoroethenepropene 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 °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.

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

Reducing agent	NaBH ₄	NaBH ₄	SnCl ₂
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	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 µg/l to 1 µg/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.

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

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

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

4.4.5 Potassium permanganate solution. Dissolve 50 g of potassium permanganate, 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, H_4ClNO , 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, HgO , in 10 ml of the stabilizer (see 4.4.6), dilute to 1 000 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 1 000 ml with water. 1 ml of this solution corresponds to 1 µg of mercury. The solution is stable for about 1 week.