Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846:2012)

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EESTI STANDARDI EESSÕNA	NATIONAL FOREWORD
See Eesti standard EVS-EN ISO 12846:2012 sisaldab Euroopa standardi EN ISO 12846:2012 ingliskeelset teksti.	This Estonian standard EVS-EN ISO 12846:2012 consists of the English text of the European standard EN ISO 12846:2012.
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Tagasisidet standardi sisu kohta on võimalik edastada, kasutades EVS-i veebilehel asuvat tagasiside vormi või saates e-kirja meiliaadressile standardiosakond@evs.ee.

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English Version

Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846:2012)

Qualité de l'eau - Dosage du mercure - Méthode par spectrométrie d'absorption atomique (SAA) avec et sans enrichissement (ISO 12846:2012)

Wasserbeschaffenheit - Bestimmung von Quecksilber - Verfahren mittels Atomabsorptionsspektrometrie (AAS) mit und ohne Anreicherung (ISO 12846:2012)

This European Standard was approved by CEN on 14 April 2012.

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

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Foreword

This document (EN ISO 12846:2012) has been prepared by Technical Committee ISO/TC 147 “Water quality” in collaboration with 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of an identical text or by endorsement, at the latest by October 2012, and conflicting national standards shall be withdrawn at the latest by October 2012.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 1483:2007, EN 12338:1998.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Endorsement notice

The text of ISO 12846:2012 has been approved by CEN as a EN ISO 12846:2012 without any modification.

Contents

Introduction

In natural water sources, mercury compounds generally occur in very low 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 sediments and sludges.

In order to fully decompose all of the mercury compounds in the presence of particles in the sample, an additional digestion procedure is necessary. This additional digestion can be omitted only if significant amounts of previous comparison data clearly demonstrate this.

For reliable measurements in the low-concentration range, the highest purity reagents, clean vessels, mercury-free air in the laboratory and a very stable measurement system are essential.

This International Standard is a state-of-the-art revision of existing standards for the determination of mercury by AAS with and without a pre-enrichment step combining the advantages of the existing methods with new developments and technique. The following methods are considered:

A) Methods without enrichment:

— ISO 5666:1999, *Water quality — Determination of mercury*;

— EN 1483:2007, *Water quality — Determination of mercury — Method using atomic absorption spectrometry*.

B) Methods with enrichment:

— ISO 16590:2000, *Water quality — Determination of mercury — Methods involving enrichment by amalgamation*;

— EN 12338:1998, *Water quality — Determination of mercury — Enrichment methods by amalgamation*.

Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment

WARNING – Potassium bromate, used in significant quantities for sample preservation in this International Standard, is carcinogenic and suitable safety precautions shall be taken. Precautions should be taken to detoxify any residual bromate by reduction to bromide before disposal.

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 in accordance with this International Standard be carried out by suitably qualified staff. Mercury and mercury compounds are very toxic. Extreme caution should be exercised when handling samples and solutions which contain or may contain mercury.

1 Scope

This International Standard specifies two methods for the determination of mercury in drinking, surface, ground, rain and waste water after appropriate pre-digestion. For the first method (described in Clause 6), an enrichment step by amalgamation of the Hg on, for example, a gold/platinum adsorber is used. For the method given in Clause 7, the enrichment step is omitted.

The choice of method depends on the equipment available, the matrix and the concentration range of interest. Both methods are suitable for the determination of mercury in water. The method with enrichment (see Clause 6) commonly has a practical working range from 0,01 µg/l to 1 µg/l. The mean limit of quantification (LOQ) reported by the participants of the validation trial (see Annex A) was 0,008 µg/l. This information on the LOQ gives the user of this International Standard an orientation and does not replace the estimation of performance data based on laboratory-specific data. It has to be considered that it is possible to achieve lower LOQs with specific instrumentation (e.g. single mercury analysers).

The method without enrichment (in Clause 7) commonly has a practical working range starting at 0,05 µg/l. The LOQ reported by the participants of the validation trial (see Annex A) was 0,024 µg/l. It is up to the user, based on the specific application, to decide whether higher concentrations are determined by omitting the enrichment step and/or by diluting the sample(s). The sensitivity of both methods is dependent on the selected operating conditions.

Another possibility for the determination of extremely low Hg concentrations down to 0,002 µg/l without pre-concentration is the application of atomic fluorescence spectrometry (see ISO 17852). Specific atomic-absorption mercury analysers allow determinations down to 0,010 µg/l without pre-concentration.

In general, the determination of trace concentrations of Hg by AAS (or AFS) is dependent on clean operating conditions in the laboratory and on the use of high-purity chemicals with negligible low-Hg blanks.

NOTE This International Standard may be applied to industrial and municipal waste water after an additional digestion step performed under appropriate conditions and after suitable method validation (see 7.4). A potential sample stability issue (mercury loss) for anaerobic reducing industrial effluents has to be considered thoroughly.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second order calibration functions*

3 Principle

Mono- or divalent mercury and organo-mercury compounds as well are converted to divalent mercury by oxidation with $KBrO_3$-KBr and then reduced to the elemental form by tin(II) chloride in an acid medium.

Elemental mercury is then stripped from the solution with the aid of a stream of inert gas or mercury-free air.

Alternatively, samples may be preserved with dichromate/HNO_3 and digested under appropriate conditions (e.g. using potassium permanganate/potassium peroxodisulfate). This technique is not part of this International Standard and has therefore to be validated appropriately by the user.

If the enrichment step is applied, the mercury (in the form of atomic vapour) is transported in a stream of inert gas with negligible mercury content to a quartz tube with a suitable heating and adsorbent (e.g. gold-platinum gauze) on which the mercury is adsorbed.

Other adsorbents based on the principle of amalgamation are allowed if the user demonstrates fitness for purpose.

The mercury is then released by rapid heating of the adsorbent (desorption at 600 °C as a minimum) and further transported in a stream of carrier gas to the absorption cell where the absorbance is measured at 253,7 nm in the radiation beam of an atomic absorption spectrometer. Concentrations are calculated using a calibration curve or using the standard addition method.

If the enrichment step is omitted, the mercury is transported directly into a cuvette. Absorbances are also measured at a wavelength of 253,7 nm.

4 General interferences

With mercury, there is a risk that exchange reactions, that is adsorption and desorption, will occur on the walls of the sampling and reaction vessels. The instructions in 6.2.5.2 should therefore be followed exactly.

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 [FEP = perfluoro(ethene-propene)], should be used. Silicone tubing, for example, is unsuitable.

Easily reducible elements, such as gold, silver and platinum, amalgamate with elemental mercury and may therefore cause suppression. Additionally, iodide is a significant interferent causing severe suppression of the mercury signal.

Volatile organic substances can absorb in the UV range and although automatic background correction is used to compensate for this, it still results in a degraded signal-to-noise ratio.

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 has to be prevented, e.g. by heating the cuvette with, for example, an infrared lamp.

NOTE Tin(II) chloride causes extensive contamination of the apparatus with tin. Considerable interferences occur if tin has to be determined afterwards on the same system.