



SLOVENSKI STANDARD

SIST ISO 5666-3:1997

01-januar-1997

Kakovost vode - Ugotavljanje skupnega živega srebra z atomsko absorpcijsko spektrometrijo (tehnika hladnih par) - 3. del: Metoda po razklopu z bromom

Water quality -- Determination of total mercury by flameless atomic absorption spectrometry -- Part 3: Method after digestion with bromine

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Qualité de l'eau -- Dosage du mercure total par spectrométrie d'absorption atomique sans flamme -- Partie 3: Méthode après minéralisation au brome

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Ta slovenski standard je istoveten z: **ISO 5666-3:1984**

ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
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International Standard



5666/3

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Water quality — Determination of total mercury by flameless atomic absorption spectrometry — Part 3 : Method after digestion with bromine

Qualité de l'eau — Dosage du mercure total par spectrométrie d'absorption atomique sans flamme — Partie 3 : Méthode après minéralisation au brome

ITEH STANDARD PREVIEW

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First edition — 1984-01-15

[SIST ISO 5666-3:1997](https://standards.iteh.ai/catalog/standards/sist/58b77b07-b06f-40ac-8311-06fc8ecd745a/sist-iso-5666-3-1997)

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UDC 614.777 : 543.422 : 546.49

Ref. No. ISO 5666/3-1984 (E)

Descriptors : water, quality, chemical analysis, determination of content, mercury, atomic absorption spectroscopic method.

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5666/3 was developed by Technical Committee ISO/TC 147, *Water quality*, and was circulated to the member bodies in February 1983.

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It has been approved by the member bodies of the following countries :

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Canada	Italy	South Africa, Rep. of
Chile	Korea, Dem. P. Rep. of	Spain
Czechoslovakia	Korea, Rep. of	Sweden
France	Mexico	Switzerland
Germany, F. R.	Netherlands	United Kingdom
Hungary	New Zealand	USSR
India	Norway	
Iran	Poland	

The member body of the following country expressed disapproval of the document on technical grounds :

Japan

Water quality — Determination of total mercury by flameless atomic absorption spectrometry — Part 3 : Method after digestion with bromine

0 Introduction

This document constitutes the third part of an International Standard specifying methods for the determination of total mercury in water by flameless atomic absorption spectrometry.

As various types of water may be tested for the presence of mercury, it has been considered preferable to standardize several methods of determination which, although they are all based on the same instrumental technique (atomic absorption spectrometry), involve, nevertheless, sufficiently important procedural differences that their respective fields of application differ significantly.

Thus, this part (part 3) specifies a method of determination after digestion with bromine and is applicable to fresh waters, soft waters and brines (saline waters), drinking waters and other types of water containing only small amounts of organic matter.

Part 1 specifies a method of determination after digestion with permanganate-persulfate and is applicable, in particular, to surface waters and domestic and industrial wastewaters.

Part 2 specifies a method of determination after pretreatment with ultraviolet radiation and is applicable to drinking water and to candidate drinking water.

Each of the three parts describes the method in its entirety and can therefore be used independently of the others.

1 Scope and field of application

This part of ISO 5666 specifies a flameless atomic absorption spectrometric method for the determination of total mercury in fresh waters, soft waters and brines (saline waters), drinking waters and other waters containing only small amounts of organic matter.

The method permits determination of mercury contents higher than 0,2 µg/l. However, under optimum conditions (minimum baseline noise of the apparatus, high spectral purity lamp, and reagents with very low mercury contents), the limit of detection which can be obtained is 0,05 µg/l.

The method is not applicable if the quantity of bromine added (see the note to 7.3.1) is insufficient to oxidize the organic matter in the test portion.

2 Reference

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Digestion of a test portion, using bromine at 45 °C, in order to convert all the mercury present to mercury(II).

Reduction of the excess of oxidant with hydroxylammonium chloride and reduction of mercury(II) to metallic mercury by tin(II) chloride.

Entrapment of the mercury in a current of gas at ambient temperature and determination of the mercury, as the monoatomic vapour, by flameless atomic absorption spectrometry at a wavelength of 253,7 nm.

4 Reagents

NOTE — Errors can be caused at low concentrations of mercury by absorption of mercury vapour from the laboratory atmosphere.

During the analysis, use only the water (4.1) and reagents of recognized analytical quality, the mercury contents of which are as low as possible.¹⁾

4.1 Demineralized distilled water, or water of equivalent purity, free from mercury.

4.2 Nitric acid, solution, $c(\text{HNO}_3) = 10 \text{ mol/l}$.

Dilute 67 ml of nitric acid ($\rho_{20} = 1,42 \text{ g/ml}$) to 100 ml with water.

4.3 Bromine, solution approximately 15 g/l.

Dilute 0,5 ml of bromine ($\rho_{20} = 3,12 \text{ g/ml}$) to 100 ml with water. In general this solution can be kept for a week when stored in a closed bottle.

1) If the reagents used tend to high results in blank tests, it is necessary to use products of better quality.

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4.4 Bromine-nitric acid, solution containing 1,5 g of Br₂ per litre.

Add 10 ml of nitric acid solution (4.2) to 10 ml of the bromine solution (4.3) and dilute to 100 ml with water.

4.5 Hydroxylammonium chloride, 10 g/l solution.

Dissolve 1 g of hydroxylammonium chloride (NH₂OHCl) in water and dilute to 100 ml. Prepare this solution daily.

4.6 Tin(II) chloride, solution containing 100 g of SnCl₂·2H₂O per litre.

Prepare this solution on the day of use by one of the following two methods :

a) Dissolve 25 g of tin(II) chloride dihydrate (SnCl₂·2H₂O) in 50 ml of warm hydrochloric acid ($\rho_{20} = 1,19$ g/ml). If the solution is cloudy, filter and add a small granule of tin to the filtrate. Cool, transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

b) Dissolve, by heating in a boiling water-bath, 13,0 g of tin in 20 ml hydrochloric acid ($\rho_{20} = 1,19$ g/ml). Cool, transfer quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

Eliminate any mercury which may be present in this solution by bubbling nitrogen through it.

4.7 Mercury, standard solution corresponding to 1 g of Hg per litre.

Dry about 2,5 g of mercury(II) chloride (HgCl₂) for about 24 h over phosphorus pentoxide (P₂O₅).

Weigh, to the nearest 0,001 g, 1,354 g of dried HgCl₂, transfer to a 1 000 ml one-mark volumetric flask and dissolve in about 10 ml nitric acid (4.2). Dilute to the mark with water and mix.

This solution can be stored in borosilicate glass bottles for about 1 month.

1 ml of this standard solution contains 1 mg of Hg.

4.8 Mercury, standard solution corresponding to 10 mg of Hg per litre.

Dilute 10,0 ml of the standard mercury solution (4.7) with 10 ml of nitric acid solution (4.2) and dilute with water to the mark in a 1 000 ml one-mark volumetric flask.

1 ml of this standard solution contains 10 µg of Hg.

Prepare this solution on the day of use.

4.9 Mercury, standard solution corresponding to 0,1 mg of Hg per litre.

Dilute 10,0 ml of the standard mercury solution (4.8) with 10 ml of nitric acid solution (4.2) and dilute with water to the mark in a 1 000 ml one-mark volumetric flask.

1 ml of this standard solution contains 0,1 µg of Hg.

Prepare this solution on the day of use.

4.10 Entrainment gas, air, nitrogen or argon.

4.11 Absorbing solution, with 2,5 g/l iodine in 30 g/l potassium iodide solution, for absorbing mercury vapour.

5 Apparatus

Before use, all glassware shall be washed very carefully with bromine-nitric acid solution (4.4), and then rinsed several times with water (4.1).

Never dry the glassware between two determinations and keep the aeration flask (5.3) full of water (4.1). (See the note to clause 4.)

A schematic diagram of the apparatus is given in the figure.

Ordinary laboratory equipment and

5.1 Atomic absorption spectrometer, provided with a low pressure mercury lamp (or a hollow cathode mercury lamp), or a mercury vapour analyser.

The spectrometer shall be set up and operated according to the manufacturer's instructions.

NOTES

1 The apparatus should be provided with the capability to measure background absorption. This can be done simultaneously (for example by a deuterium continuum lamp), in which case the recorded absorption signal is already corrected for possible background absorption, or in a separate test sample, by leading the entrainment gas, after passing it through the aeration flask, through a mercury absorbing trap containing gold foil, silver foil or palladium chloride.

2 It is possible to use an aeration system based on a closed circuit in which the mercury vapour is recycled by means of a pump. In this case, a recorder is not required and it is possible to use a direct reading instrument or a maximum signal indicator. In this case, the aeration system described in note 1 cannot then be used.

5.2 Recorder.

5.3 Aeration flasks, tall form, of volume appropriate to the size of the test portion and compatible with the rest of the apparatus, bearing a calibration mark corresponding to the optimum filling level, the dead volume of which has been reduced to a minimum and through which the gas flows under the optimum conditions. For this, the aeration tube shall be fitted either with a finely drawn out point, a sphere pierced with holes, or a fritted end (pores of 100 to 250 µm). It is necessary to confirm that each in a series of different flasks gives the same result.

Ensure that the dead volume is the same if the flasks are changed.

After each use, treat the aeration flasks with the bromine-nitric acid solution (4.4) to oxidize any traces of Sn(II) that they may contain.

5.4 Measuring cell, with windows (for example of quartz) transparent to ultraviolet radiation (253,7 nm), the optical pathlength of which should be appropriate to the spectrometer being used, but not less than 10 cm.

5.5 Equipment, to prevent any condensation of water vapour in the measuring cell. Any appropriate system may be used for this purpose (an infra-red lamp, black electrical heating element, rod heater and desiccant trap).

NOTE — If it is difficult or impossible to install a heating device, it may be useful to use a device for dividing the flow of the entrainment gas (4.10) (2,8 l/min) into two portions. A flow of about 2,1 l/min is led through the aeration flask (5.3) and is then mixed with the remaining flow of gas (about 0,7 l/min) before it reaches the measuring cell (see the figure).

5.6 Equipment for absorption of mercury vapour, as it leaves the measuring cell.

5.7 Magnetic stirrer, with a bar coated with an inert material.

The magnetic stirrer should be capable of stirring the test solution (7.3.2) in the aeration flask vigorously enough to make the air above the liquid reach the bottom of the vessel.

6 Samples

Immediately after collection, adjust the pH of each sample to 1 or less by adding nitric acid solution (4.2) (see note 1). If the determination cannot be carried out immediately after sampling, add 10 ml of the bromine solution (4.3) per litre of sample.

Store samples in borosilicate glass bottles which have been cleaned according to the procedure described in clause 5.

NOTES

1 If it is desired to measure dissolved and suspended mercury separately, carry out an appropriate separation (filtration through a 0,45 μm membrane filter or centrifugation) of the sample immediately after collection, then add the bromine-nitric acid solution (4.4) to the clear solution.

2 Record the volume of the sample and also the volumes of reagents added, so that allowance can be made for these in the blank test and in the calculation of results. Take care to use the same reagents for both the sample and in the blank test.

7 Procedure

7.1 Test portion

Take a test portion of 100 ml from the previously mixed sample (clause 6) containing not more than 0,5 μg of mercury. If necessary take a volume less than 100 ml and dilute to 100 ml with water (4.1).

7.2 Calibration

Prepare, just before use, using the standard mercury solutions (4.8 and 4.9), at least five calibration solutions, covering the

range of concentrations which can be measured with the apparatus to be used (depending on the circumstances, this range may cover a part or the whole of the range 0,05 to 5,0 μg of mercury per litre).

Treat each of these solutions immediately after their preparation in exactly the same way as the test portion on which the determination is to be carried out (see 7.3.1 and 7.3.2). Also proceed in exactly the same way, on a solution (the zero member) in which the standard mercury solution is replaced with water (4.1).

Express the peak height in centimetres or the peak areas in square centimetres and plot a calibration graph.

7.3 Determination

7.3.1 Digestion

Introduce the test portion (7.1), or a measured aliquot portion diluted to 100 ml, into a volumetric flask. Add 1 ml of the bromine solution (4.3) unless it has been added already directly after sampling (see clause 6). Stopper the flask and mix. Heat for at least 4 h at 45 °C (for example in an incubator). Mix and cool to room temperature.

Allow suspended matter, if any, to settle.

NOTE — At this moment the solution should contain free bromine. This can be established either by the colour or, if this is difficult because of the original colour of the sample, by using potassium iodide and starch paper. If there is no free bromine, another type of digestion should be considered (for example digestion with potassium permanganate and persulfate, see ISO 5666/1).

7.3.2 Entrainment and determination

Transfer 50 ml of the digested solution (7.3.1) into the aeration flask (5.3) containing a magnetic stirring bar (5.7) and add 1 ml of hydroxylammonium chloride solution (4.5). Keep the other 50 ml for a second test if necessary.

Add 1 ml of tin(II) chloride solution (4.6) and stopper the flask immediately. Stir vigorously for 3 min. The tip or the glass frit of the aeration tube should stay immersed in the liquid during the stirring.

Switch on the entrainment gas (4.10) supply and let the developed mercury vapour flow through the absorption cell and measure the instrument response.

After each test, purge the aeration flask as indicated in 5.3.

NOTES

1 If a peak obtained during a determination does not have the same shape as that obtained from a standard solution, it is recommended that peak areas be measured and not peak heights. In all cases the absence of interferences should be verified by means of the control test (7.5).

2 If background measurements are made separately (see note 1 to 5.1), the test portion signal has to be corrected for the background signal by subtraction.

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7.4 Blank test

Carry out a blank test with each batch of samples, according to 7.3.1 and 7.3.2, but replacing the test portion with water (4.1), and using the same volume of reagent(s) as for the determination proper. Make allowance for the volumes of reagent added during the collection of the samples (see note 2 to clause 6).

Determine the blank value (see the annex).

7.5 Control test

In waters with low contents of organic matter, interferences are unlikely to occur. In cases of doubt, carry out a control test by repeating the operations specified in 7.3.1 and 7.3.2 using a new test portion taken from the sample (clause 6) or using an aliquot portion of it to which a known quantity of the standard mercury solution (4.9) has been added.

Work only within the linear portion of the calibration graph.

8 Expression of results

From the height, in centimetres, or area, in square centimetres, of the peak obtained in the determination, determine, by reference to the calibration graph and making allowance for the blank test, the mercury content of the test portion.

In the case of an apparatus with a digital read-out, or a maximum response indicator, prepare a graph of mass of mercury against the corresponding instrument read-out.

From this value, compute the total mercury content of the sample, allowing for the volumes of reagents introduced during

sampling and the treatment (7.1) of the sample. Express this content in micrograms per litre.

9 Precision

An ISO interlaboratory test was carried out in January 1979, on

- a first sample A, containing 2,272 µg of mercury per litre as mercury(II) chloride (HgCl₂);
- a second sample B, containing 2,033 µg of mercury per litre as phenyl mercury(II) acetate (HgC₈H₈O₂); and
- a third sample C, containing 2,168 µg of mercury per litre as phenyl mercury(II) acetate (HgC₈H₈O₂) and 150 mg of iodide ions per litre.

Statistical analysis of the results in accordance with ISO 5725 has led to the information given in the table.

10 Test report

The test report shall contain the following information :

- a) all information necessary for complete identification of the sample;
- b) the method used;
- c) the results obtained;
- d) the conditions of test;
- e) details of any operations not included in this part of ISO 5666, or regarded as optional, together with any incidents likely to have had an influence upon the results.

Table

Sample	Number of participating laboratories	Number of eliminated laboratories	Mean µg/l	Standard deviation			
				Repeatability		Reproducibility	
				Absolute	Relative %	Absolute	Relative %
A	47	5	2,418	0,121	5,0	0,259	10,7
B	48	6	2,018	0,097	4,8	0,231	11,5
C	48	7	2,205	0,077	3,5	0,235	10,7

Annex

Control of blank values

A.1 General

When carrying out determinations at concentrations close to the lower limit of detection, it is essential to control the blank values in order to ensure that the results obtained are meaningful; a realistic value for the limit of detection can then be established by each laboratory according to the results obtained in their own blank tests.

A.2 Evaluation and control of blank values

Several techniques, based on a statistical approach, can be applied for checking the blank values.

The following technique is given as an indication.

For the method of analysis being used, carry out a series of 10 blank tests following the appropriate procedure (7.4).

Compute the standard deviation and use the value obtained to compute the confidence interval (CI) from the expression

$$CI = \bar{x} \pm s \frac{t_{(P, f)}}{\sqrt{n}}$$

where

\bar{x} is the mean of the blank values;

s is the standard deviation;

t is the Student's coefficient (2,26 in this case);

P is the bilateral confidence level chosen (95 % in this case);

f is the number of degrees of freedom (9 in this case);

n is the number of measurements (10 in this case).

Carry out a blank test daily. The result should be within the confidence interval CI. If it is significantly greater than $\bar{x} + st (n-1/2)$, check the reagents used and replace those that have mercury contents that are too high. If the blank value still exceeds the upper limit, or if it is significantly less than $\bar{x} - st (n-1/2)$, redetermine the confidence interval and deduct the limit of detection.

As an indication, the average value and the confidence interval CI (at a confidence level of 95 %) of the blanks obtained in an ISO interlaboratory trial January 1979 in which from 41 laboratories participated, is

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CI = 0,004 2 ± 0,000 2 µg of mercury (for a blank test of 50 ml)

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