
**Water quality — Determination of
selenium —**

**Part 2:
Method using hydride generation
atomic absorption spectrometry (HG-
AAS)**

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Qualité de l'eau — Dosage du sélénium —

*Partie 2: Méthode par spectrométrie d'absorption atomique à
génération d'hydrures (HG-AAS)*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2, www.iso.org/directives.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received, www.iso.org/patents.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This first edition of ISO/TS 17379-2 cancels and replaces ISO 9965:1993, which has been technically revised.

ISO/TS 17379 consists of the following parts, under the general title *Water quality — Determination of selenium*:

- Part 1: Method using hydride generation atomic fluorescence spectrometry (HG-AFS)
- Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)

Introduction

This part of ISO/TS 17379 is intended for use by analysts experienced with the handling of trace elements at very low concentrations.

Inorganic selenium normally occurs in two oxidation states; Se(VI) and Se(IV). It is essential to convert all selenium species to the Se(IV) state prior to generating the hydrides. Selenium(VI) does not form a hydride.

In natural water sources, selenium compounds generally occur in very small quantities, typically less than 1 µg/l. Higher concentrations may be found, e.g. in industrial waste water. Selenium occurs naturally in organic and inorganic compounds and may have oxidation states –II, 0, IV, and VI.

In order to fully decompose all of the selenium compounds, a digestion procedure is necessary. Digestion can only be omitted if it is certain that the selenium in the sample can form a covalent hydride without the necessity of a pre-oxidation digestion step.

The user should be aware that particular problems could require the specification of additional marginal conditions.

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Water quality — Determination of selenium —

Part 2:

Method using hydride generation atomic absorption spectrometry (HG-AAS)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 document be carried out by suitably trained and experienced staff.

1 Scope

This part of ISO/TS 17379 specifies a method for the determination of selenium. The method is applicable to drinking water, surface water, ground water, and rain water. The dynamic range of this part of ISO/TS 17379 is approximately 0,5 µg/l to 20 µg/l. Samples containing selenium at higher concentrations than the application range can be analysed following appropriate dilution. The method is unlikely to detect organoselenium compounds.

The sensitivity of this method is dependent on the selected operating conditions.

It is important to use high purity reagents in all cases with minimum levels of selenium.

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 5667-5, *Water quality — Sampling — Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems*

ISO 5667-6, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*

ISO 5667-8, *Water quality — Sampling — Part 8: Guidance on the sampling of wet deposition*

ISO 5667-11, *Water quality — Sampling — Part 11: Guidance on sampling of groundwaters*

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

An aliquot of sample is treated with concentrated hydrochloric acid (5.2). Se(VI) is pre-reduced to Se(IV) by gently refluxing in 6 mol/l HCl for 1 h. Care is necessary to avoid any losses of volatile selenium components. A suitable apparatus is shown in Figure B.3. The sample solutions are then treated with sodium tetrahydroborate to generate the covalent gaseous hydride (SeH_2). The hydride and excess hydrogen are swept out of the generation vessel in the batch mode and out of the gas/liquid separator in the continuous mode into a heated silica cell. After atomization the absorbance of selenium is determined at a wavelength, $\lambda = 196,0$ nm. The procedure is automated by means of an auto sampler and control software.

Other measurement techniques may be applicable provided that the performance criteria can be adequately demonstrated or exceeded by the user laboratory (see Annex C).

4 Interferences

The hydride generation technique is prone to interferences by transition and easily reducible metals. For the majority of natural water samples, this type of interference should not be significant. The user should carry out recovery tests on typical waters and also determine the maximum concentrations of potentially interfering elements, using appropriate methods. If such interferences are indicated, the level of interferences should be assessed by performing spike recoveries.

The reaction conditions set out in this part of ISO/TS 17379 have been chosen so that any interferences are reduced to a minimum.

See References [1][2] for further information concerning these interferences and the technique.

These elements do not cause interferences provided the concentrations specified in Table 1 are not exceeded.

Table 1 — Maximum mass concentrations of hydride-forming or volatile elements causing no interferences

Element				
As	Sb	Sn	Te	Hg
Mass concentration of interfering elements in test solution mg/l				
1	1	0,1	1	0,1

If the concentrations in Table 1 are exceeded, it may be necessary to use the standard addition method (9.3). Assuming that the selenium content is high enough, an appropriate dilution of the water sample is preferred.

Metals which are readily reduced by sodium tetrahydroborate may also cause interferences. In particular, these include chromium, iron, copper, nickel, and lead. If the concentrations of these elements specified in Table 2 are exceeded, a significant decrease of absorption may occur.

Table 2 — Maximum mass concentrations in test solution of interfering heavy metals (valid for flow systems)

Interfering element				
Cr	Fe	Cu	Ni	Pb
Mass concentration in test solution mg/l				
500	500	500	250	100

NOTE If batch systems are used, mass concentrations which are appreciably lower than those specified in [Table 1](#) and [Table 2](#) can cause interferences.

5 Reagents and standards

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

Reagents may contain selenium as an impurity. All reagents shall have selenium concentrations below that which would result in a selenium blank value for the method being above the lowest level of interest.

Reagents shall be prepared to manufacturer's recommendations using the following series as an example.

5.1 Water, complying with grade 1 as defined in ISO 3696, for all sample preparation and dilutions.

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

5.3 Hydrochloric acid, $c(\text{HCl}) = 1 \text{ mol/l}$.

5.4 Sodium hydroxide, NaOH.

5.5 Sodium tetrahydroborate solution, $\rho(\text{NaBH}_4) = 13 \text{ g/l}$.

Dissolve an appropriate amount of sodium tetrahydroborate (13 g has proven suitable for the system illustrated in [Annex B](#)) in 500 ml water ([5.1](#)) and add $(4,0 \pm 0,1) \text{ g}$ of sodium hydroxide ([5.4](#)). Dilute to 1 000 ml with water ([5.1](#)). Prepare on day of use and do not keep in a closed container because of pressure build-up due to hydrogen evolution.

NOTE 1 The concentration of NaBH_4 is dependent on the hydride generator manifold and flow rate conditions. See recommendations of the manufacturer.

NOTE 2 Suitably stored sodium tetrahydroborate pellets have a shelf-life of 6 months.

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

NOTE Nitric acid is available both as $\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$ [$w(\text{HNO}_3) = 650 \text{ g/kg}$] and $\rho(\text{HNO}_3) = 1,42 \text{ g/ml}$ [$w(\text{HNO}_3) = 690 \text{ g/kg}$].

Prepare a nitric acid cleaning mixture by diluting nitric acid [$\rho(\text{HNO}_3) = 1,40 \text{ g/ml}$] with an equal volume of water ([5.1](#)) by carefully adding the acid to the water.

5.7 Reagent blank.

For each 1 000 ml, prepare a solution containing $(300 \pm 3) \text{ ml}$ of hydrochloric acid ([5.2](#)). Dilute to volume with water ([5.1](#)).

On the continuous flow system, the reagent blank solution is run as background. Since the blank solution may contain detectable trace levels of selenium, it is important that the same reagents be used for both sample and standard preparation, as well as for preparation of the reagent blank. The analyte signal is superimposed on this signal once the sample is introduced into the measurement cycle. The selenium concentration of the blank solution should be less than the lower level of interest.

5.8 Selenium standard solutions.

5.8.1 Selenium stock solution A, $\rho[\text{Se(IV)}] = 1\,000\text{ mg/l}$.

Use a quantitative stock solution with a selenium content of $(1\,000 \pm 2)\text{ mg/l}$.

This solution is considered to be stable for at least one year.

NOTE Other stock solutions may be available and can be used providing the uncertainty of the measurement is not compromised.

Alternatively, use a stock solution prepared from high purity grade chemicals:

Place 1,094 g of sodium selenite (Na_2SeO_3) dried for 2 h at $(105 \pm 3)^\circ\text{C}$ into a 500 ml volumetric flask.

Add 200 ml of water (5.1) and 200 ml of hydrochloric acid (5.3) and dissolve the sodium selenite completely by stirring.

Dilute to 500 ml with water (5.1) and mix thoroughly.

5.8.2 Selenium standard solution B, $\rho[\text{Se(IV)}] = 10\text{ mg/l}$.

Pipette $(1 \pm 0,01)$ ml of selenium stock solution A (5.8.1) into a 100 ml volumetric flask, add $(30 \pm 0,5)$ ml of hydrochloric acid (5.2) and fill up to the mark with water (5.1).

This solution is stable for one month.

5.8.3 Selenium standard solution C, $\rho[\text{Se(IV)}] = 100\text{ }\mu\text{g/l}$.

Pipette $(1 \pm 0,01)$ ml of selenium standard solution B (5.8.2) into a 100 ml volumetric flask, add $(30 \pm 0,5)$ ml of hydrochloric acid (5.2) and fill up to the mark with water (5.1).

This solution is stable for one week.

5.8.4 Selenium standard solution D, $\rho[\text{Se(IV)}] = 10\text{ }\mu\text{g/l}$.

Pipette $(10 \pm 0,1)$ ml of selenium standard solution C (5.8.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.7).

This solution shall be prepared freshly on the day of use.

5.8.5 Selenium stock solution E, $\rho[\text{Se(VI)}] = 1\,000\text{ mg/l}$.

Dissolve $(2,392 \pm 0,002)$ g of sodium selenate (Na_2SeO_4) after drying at $(105 \pm 3)^\circ\text{C}$ for 2 h in 500 ml water (5.1), then transfer the solution quantitatively to a 1 000 ml volumetric flask and fill up to the mark with water (5.1).

Use this standard to prepare a suitable selenium(VI) standard to check quantitative recovery of selenium(IV).

The solution is stable for at least six months.

5.8.6 Selenium calibration solutions.

A minimum of five independent calibration solutions shall be used. Perform the calibration in accordance with ISO 8466-1.

Prepare a minimum of five selenium calibration solutions from the selenium standard solution C (5.8.3) covering the working range of expected selenium concentrations.

For the operating range from $1\text{ }\mu\text{g/l}$ to $5\text{ }\mu\text{g/l}$, for example, proceed as follows.

Pipette into a series of five 100 ml volumetric flasks ($1 \pm 0,01$) ml, ($2 \pm 0,02$) ml, ($3 \pm 0,03$) ml, ($4 \pm 0,04$) ml, and ($5 \pm 0,05$) ml, respectively, of selenium standard solution C (5.8.3).

Add 30 ml of hydrochloric acid (5.2).

Dilute to 100 ml with water (5.1) and mix thoroughly.

These calibration solutions contain 1 µg/l, 2 µg/l, 3 µg/l, 4 µg/l, and 5 µg/l selenium respectively.

They shall be prepared on the day of use.

The use of piston pipettes is permitted and enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed.

Once a calibration pattern has been established, the number of standards used routinely may be reduced. Any such change shall not alter the result obtained from tests or the ranking with other samples.

6 Apparatus

Usual laboratory equipment and in particular the following.

The following are set out as guidelines. In general, the manufacturer's instructions shall be followed.

6.1 Atomic absorption spectrometer.

6.1.1 General. An atomic absorption spectrometer equipped with a hydride generation system and a heated silica tube atomizer or a graphite furnace atomizer (preferably equipped with a background correction system) is recommended. Automated flow systems [flow injection analysis (FIA) or continuous flow analysis (CFA)] for hydride generation are suitable and more usual but batch systems are also adequate. The description below follows a continuous flow regime.

6.1.2 Radiation source for the determination of selenium. Use a radiation source which emits at wavelength $\lambda = 196,0$ nm for selenium with an adequate spectral radiance.

6.2 Gas supply. Use argon with a grade specified by the manufacturer.

The gas supply shall be with a two stage regulator and the argon supplied at a pressure recommended by the manufacturer.

The use of a gas purifier consisting of activated carbon is recommended.

Nitrogen gas may also be used but has reduced sensitivity.

6.3 Laboratory-ware.

6.3.1 General requirements. For the determination of selenium at very low concentrations, contamination and loss are of critical consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area, designated for trace element sample handling shall be used.

All re-usable laboratory-ware in contact with the sample shall be cleaned prior to use.

Laboratory-ware shall be soaked in the nitric acid cleaning mixture (5.6) for at least 24 h and rinsed five times with water (5.1).

Following this, refill laboratory-ware with hydrochloric acid, $c(\text{HCl}) = 1$ mol/l (5.3) and leave for 24 h.

Disposable (single-use) plastics laboratory-ware does not require special cleaning, provided that negligible selenium contamination in that material is demonstrated.