
**Water quality — Determination of
selenium —**

Part 1:
**Method using hydride generation
atomic fluorescence spectrometry
(HG-AFS)**

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Qualité de l'eau — Dosage du sélénium —

*Partie 1: Méthode par spectrométrie de fluorescence atomique à
génération d'hydrures (HG-AFS)*

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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 standard will be in the Introduction and/or on the ISO list of patent declarations received, www.iso.org/patents.

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

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

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ISO/TS 17379-1:2013
- 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 can be found, e.g. in industrial waste water. Selenium occurs naturally in organic and inorganic compounds and can 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 1:

Method using hydride generation atomic fluorescence spectrometry (HG-AFS)

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 application range of this part of ISO/TS 17379 is from 0,02 µg/l to 100 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 operating conditions selected.

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2 Normative references

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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 15587-1, *Water quality — Digestion for the determination of selected elements in water — Part 1: Aqua regia digestion*

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 (SeH₂). 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 an atomizer suited for atomic fluorescence measurements (e.g. a chemically generated hydrogen diffusion flame). The hydride is atomized and the resulting atoms excited by an intense selenium light source, the resulting fluorescence is detected by atomic fluorescence spectrometry after isolation by an interference filter that transmits the selenium fluorescence at a wavelength, $\lambda = 196,0$ nm. The procedure is automated by means of an auto sampler and control software.

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. However, the atomic fluorescence technique has a high linear dynamic range and a very low detection limit. In most cases, any interferences can be removed by a simple dilution step.

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

It is important that the light source does not contain any significant amount of other hydride-forming elements (e.g. arsenic, antimony, tellurium) that emit fluorescent radiation over the bandpass of the interference filter used in the detector, if these elements are present in the sample.

Measurements carried out using the procedures in this part of ISO/TS 17379 do not generally suffer from interferences due to quenching within the ranges of interest.

Interference studies on a number of elements have been conducted and are shown in Table 1. It can be seen that tellurium causes a significant positive bias and that gold, silver and copper cause a significant negative bias. However, these elements are unlikely to be present at the tested levels in the vast majority of water samples.

Interferences can be indicated by the irregularity of the signal peak shape. Usually the interference can be removed by diluting the samples, this dilution should not reduce the concentration of the analyte lower than the limit of quantification.

Table 1 — Interference study for selenium

Interfering substance		Concentration of interfering substance	Se recovery	
		mg/l	2 µg/l Se	10 µg/l Se
Thallium nitrate	Tl(III)	20	98,4 ± 3,1	97,2 ± 1,6
Strontium nitrate	Sr(II)	20	101,6 ± 1,2	97,0 ± 1,5
Zinc nitrate	Zn(II)	1	99,9 ± 1,8	102,4 ± 0,8
Diammonium silicon hexafluoride	Si(IV)	1	96,7 ± 2,7	98,8 ± 1,82
Aluminium nitrate	Al(III)	1	95,2 ± 3,0	97,2 ± 0,5
Calcium chloride	Ca(II)	200	97,4 ± 0,9	97,0 ± 3,3
Sodium chloride	Na(I)	200	98,0 ± 1,0	95,0 ± 0,6

Table 1 (continued)

Interfering substance		Concentration of interfering substance	Se recovery	
		mg/l	2 µg/l Se	10 µg/l Se
Potassium bromide	K(I)	200	94,9 ± 3,8	99,6 ± 1,1
Indium nitrate	In(III)	1	93,3 ± 1,7	98,9 ± 2,0
Barium nitrate	Ba(II)	1	96,6 ± 1,5	96,6 ± 1,6
Magnesium oxide	Mg(II)	1	98,9 ± 2,4	97,0 ± 0,9
Cadmium nitrate	Cd(II)	1	99,4 ± 0,5	90,1 ± 0,9
Ammonium dihydrogenphosphate	P(V)	1	98,0 ± 1,9	96,9 ± 3,4
Sodium fluoride	F(I)	1	97,4 ± 1,1	97,8 ± 2,7
Gold chloride	Au(III)	0,1	89,3 ± 3,1	83,1 ± 5,4
Gold chloride	Au(III)	1	46,2 ± 4,1	76,8 ± 6,4
Ortho-boric acid	B(III)	1	99,1 ± 1,9	101,4 ± 2,1
Iron(II) nitrate	Fe(II)	1	96,9 ± 2,7	97,4 ± 4,9
Lead(II) nitrate	Pb(II)	1	99,2 ± 2,5	97,9 ± 0,9
Bismuth nitrate	Bi(III)	1	105,0 ± 4,8	95,6 ± 1,7
Tin nitrate	Sn(IV)	1	93,8 ± 6,1	97,8 ± 1,5
Ammonium molybdate	Mo(II)	1	95,7 ± 2,3	97,0 ± 1,3
Germanium chloride	Ge(IV)	1	100,7 ± 3,1	98,0 ± 0,6
Mercury nitrate	Hg(II)	1	99,4 ± 3,7	99,7 ± 3,9
Arsenic(III) oxide	As(III)	1	99,4 ± 2,5	97,7 ± 7,3
Chromium(III) nitrate	Cr(III)	1	95,9 ± 2,0	98,6 ± 1,5
Cobalt nitrate	Co(II)	1	93,2 ± 1,6	97,4 ± 1,7
Silver nitrate	Ag(I)	1	78,2 ± 6,5	72,0 ± 0,8
Nickel(II) nitrate	Ni(II)	1	95,0 ± 3,6	97,1 ± 1,9
Telluric acid	Te(IV)	0,01	104,0 ± 1,8	98,8 ± 1,8
Telluric acid	Te(IV)	0,1	110,0 ± 5,0	105,2 ± 1,0
Telluric acid	Te(IV)	1	123,5 ± 0,5	108,6 ± 1,0
Antimony oxide	Sb(III)	0,01	98,6 ± 0,8	99,1 ± 0,3
Antimony oxide	Sb(III)	0,05	89,3 ± 3,1	98,5 ± 2,1
Antimony oxide	Sb(III)	0,1	95,8 ± 2,2	100,4 ± 1,1
Copper sulfate	Cu(II)	0,1	98,5 ± 1,5	96,4 ± 0,0
Copper sulfate	Cu(II)	0,2	93,4 ± 1,9	100,8 ± 2,5
Copper sulfate	Cu(II)	0,5	94,5 ± 0,5	98,3 ± 1,9
Copper sulfate	Cu(II)	1	82,2 ± 2,3	85,1 ± 5,4
Copper sulfate	Cu(II)	2	79,8 ± 2,4	98,8 ± 1,8
Gold chloride	Au(I)	0,1	89,3 ± 3,1	83,1 ± 5,4

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 should have selenium concentrations below that which would result in a selenium blank value for the method being above the lowest level of interest.

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 tetrahydroborate, NaBH_4 , available as pellets.

5.5 Sodium hydroxide, NaOH .

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

Prepare appropriate quantities on day of use (13 g/l has proven suitable for the system illustrated in [Annex B](#)) 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.

NOTE 3 See [Clause 8](#).

5.7 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.

5.8 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.

5.9 Selenium standard solutions.

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

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

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

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 $(105 \pm 3) \text{ }^\circ\text{C}$ 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.

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

Pipette $(1 \pm 0,01)$ ml of selenium stock solution A (5.9.1) into a 100 ml volumetric flask, add $(30 \pm 0,5)$ ml of hydrochloric acid (5.2) and fill up to the mark with reagent blank solution (5.8).

Prepare this solution monthly.

5.9.3 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 (5.9.2) into a 100 ml volumetric flask, add $(30 \pm 0,5)$ ml of hydrochloric acid (5.2) and fill up to the mark with reagent blank solution (5.8).

Prepare this solution weekly.

5.9.4 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 (5.9.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.8).

Prepare this solution weekly.

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

Dissolve $(1,000 \pm 0,002)$ g of pure selenium powder in $(10 \pm 0,1)$ ml of concentrated nitric acid (5.7).

Heat the solution to boiling and evaporate off the excess nitric acid.

Perform this procedure carefully under the chemical hood.

Cool and then take up the hydrated oxide in $(50 \pm 0,5)$ ml of cold hydrochloric acid (5.2).

Transfer the solution quantitatively to a 1 000 ml volumetric flask and fill up to the mark with reagent blank solution (5.8).

Alternatively, dissolve $(2,392 \pm 0,002)$ g of sodium selenate (Na_2SeO_4) after drying at $(105 \pm 3) \text{ }^\circ\text{C}$ 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 reagent blank solution (5.8).

Use this standard to check quantitative recovery of Se(VI).

The solution is stable for at least six months.

5.9.6 Selenium calibration solutions.

A minimum of five independent calibration solutions shall be used. Perform the calibration in accordance with ISO 8466-1. The calibration solutions are prepared by suitable dilution of the selenium standard solution C (5.9.3) or D (5.9.4).

Each calibration solution shall contain $(30 \pm 0,5)$ ml of hydrochloric acid (5.2) per 100 ml.

Prepare on the day of use.

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

Pipette into a series of five 100 ml volumetric flasks $(2 \pm 0,02)$ ml, $(4 \pm 0,04)$ ml, $(6 \pm 0,06)$ ml, $(8 \pm 0,08)$ ml, and $(10 \pm 0,1)$ ml, respectively, of selenium standard solution D (5.9.4).

Fill up to the mark with reagent blank solution (5.8) and mix thoroughly.

These calibration solutions contain $0,2 \text{ }\mu\text{g/l}$, $0,4 \text{ }\mu\text{g/l}$, $0,6 \text{ }\mu\text{g/l}$, $0,8 \text{ }\mu\text{g/l}$, and $1 \text{ }\mu\text{g/l}$ selenium respectively.

They should be prepared on the day of use.