
**Water quality — Determination of
arsenic and antimony —**

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

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Qualité de l'eau — Dosage de l'arsenic et de l'antimoine —

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

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Published in Switzerland

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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 (see 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 (see 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.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

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 17378-2 cancels and replaces ISO 11969:1996, which has been technically revised.

ISO 17378 consists of the following parts, under the general title *Water quality — Determination of arsenic and antimony*:

- *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 17378 should be used by analysts experienced in the handling of trace elements at very low concentrations.

Arsenic concentrations in natural waters are highly variable, from <10 µg/l to as high as several milligrams per litre in some parts of Asia, South America and the USA, notable in the Ganges delta where arsenic poisoning from contaminated tube wells is a serious problem. Antimony concentrations in natural waters are generally well below 10 µg/l. Arsenic and antimony occur naturally in organic and inorganic compounds and may have oxidation states -III, 0, III and V.

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

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

The method for determining arsenic or antimony is identical in all aspects except for the preparation of standard solutions to be tested. To avoid repetition or duplication the text refers to both arsenic and antimony where the text is equally applicable to both instances. The subclause dealing with preparation of standard solutions is divided into [5.11.1](#), which deals with solutions of arsenic, and [5.11.2](#), which deals with solutions of antimony.

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Water quality — Determination of arsenic and antimony —

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 according to this document be carried out by suitably trained and experienced staff.

1 Scope

This part of ISO 17378 specifies a method for the determination of arsenic and antimony. The method is applicable to drinking water, surface water, ground water, and rain water. The approximate linear application range of this part of ISO 17378 for both elements is from 0,5 µg/l to 20 µg/l. Samples containing higher concentrations than the application range can be analysed following appropriate dilution.

Generally sea water is outside the scope of this part of ISO 17378. Sea water samples can be analysed using a standard additions approach providing that this is validated for the samples under test. The method is unlikely to detect organo-arsenic and organo-antimony compounds.

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

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*

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

3 Principle

NOTE Other measurement techniques can be applicable providing the performance criteria are adequately demonstrated to be fulfilled or exceeded by the user laboratory. (See [Annex C](#).)

3.1 Arsenic

An aliquot of sample is acidified with hydrochloric acid (5.3). Potassium iodide–ascorbic acid reagent (5.9) is added to ensure quantified reduction of arsenic(V) to arsenic(III). The sample solutions are treated with sodium tetrahydroborate (5.5) to generate the covalent gaseous arsenic trihydride (arsine, AsH₃). The hydride and excess hydrogen are swept out of the generation vessel in case of batch mode and out of the gas/liquid separator in case of the continuous mode into a heated silica cell. After atomization, the absorbance of arsenic is determined at a wavelength $\lambda = 193,7$ nm. The procedure is automated by means of auto-sampler and control software.

3.2 Antimony

An aliquot of sample is digested with hydrochloric acid (5.3). Potassium iodide–ascorbic acid reagent (5.9) is added to ensure quantified reduction of the antimony(V) to antimony(III). The sample solutions are then treated with sodium tetrahydroborate (5.5) to generate the covalent gaseous antimony trihydride (stibane, SbH₃). The hydride and excess hydrogen are swept out of the generation vessel in case of batch mode and out of the gas/liquid separator in case of continuous mode. After atomization, the absorbance of antimony is determined at a wavelength $\lambda = 217,6$ nm. The procedure is automated by means of auto-sampler and control software.

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4 Interferences

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4.1 General

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 shall 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.

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 1](#) are exceeded, a significant decrease of absorption may occur.

Table 1 — Maximum mass concentration in test solution of interfering heavy metals (valid for flow systems)

Interfering element				
Cr	Fe	Cu	Ni	Pb
mg/l				
500	500	500	250	100

The reaction conditions in this part of ISO 17378 have been chosen to minimize these interferences.

Further information on these interferences and the technique are given in References.[1][2]

NOTE If batch systems are used, mass concentrations which are appreciably lower than those specified in [Table 1](#), [Table 2](#) and [Table 3](#) can cause interferences.

4.2 Arsenic

Elements such as antimony, selenium, tellurium, mercury, and tin are also volatilized by this procedure and may cause interferences. These elements do not cause interferences providing the concentrations specified in [Table 2](#) are not exceeded.

Table 2 — Maximum mass concentration of hydride-forming or volatile elements causing no interferences

Element				
Sb	Se	Sn	Te	Hg
mg/l				
1	1	0,1	1	0,1

If these concentrations are exceeded, it may be necessary to use the standard addition method ([9.3](#)). Assuming that the arsenic content is high enough, an appropriate dilution of the water sample is preferred.

4.3 Antimony

Elements such as arsenic, selenium, tellurium, mercury, and tin are also volatilized by this procedure and may cause interferences. These elements do not cause interferences providing the concentrations specified in [Table 3](#) are not exceeded.

Table 3 — Maximum mass concentration of hydride-forming or volatile elements causing no interferences

Element				
As	Se	Sn	Te	Hg
mg/l				
1	1	0,1	1	0,1

If these concentrations are exceeded, it may be necessary to use the standard addition method ([9.3](#)). Assuming that the antimony content is high enough, an appropriate dilution of the water sample is preferred.

5 Reagents

5.1 General requirements

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

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

Use only reagents of recognized analytical grade, unless otherwise specified.

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

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

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

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

5.5 Sodium tetrahydroborate, NaBH₄.

Available as pellets. Keep the pellets dry and store in a cool, dark place.

5.6 Sodium hydroxide, NaOH.

5.7 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 [Figure B.1](#)).

Dissolve 0,4 g sodium hydroxide ([5.6](#)) and the appropriate quantity of sodium tetrahydroborate ([5.5](#)) in 800 ml of water and dilute to 1 000 ml.

Do not keep in a closed container because of potential pressure build-up due to hydrogen evolution.

Excess sodium borohydride solution should be slowly poured to drain with copious quantities of water. Do not allow the solution to come into contact with acid during disposal.

NOTE The concentration of NaBH₄ is dependent on the hydride generator manifold and flow-rate conditions. See recommendations of the manufacturer.

Alternatively smaller volumes can be prepared on a pro rata basis.

5.8 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 $\rho(\text{HNO}_3) = 1,42 \text{ g/ml}$ [$w(\text{HNO}_3) = 690 \text{ g/kg}$].

To prepare a nitric acid cleaning mixture, dilute nitric acid (1,40 g/ml) with an equal volume of water ([5.2](#)) by carefully adding the acid to the water. [ISO 17378-2:2014](#)

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5.9 Potassium iodide–ascorbic acid solution.

Dissolve (250 ± 0,1) g of potassium iodide (KI) and (50 ± 0,1) g of ascorbic acid (C₆H₈O₆) in approximately 400 ml water and dilute to 500 ml.

Prepare freshly on day of use. See Note to ([5.7](#)).

5.10 Reagent blank.

For each 1 000 ml, prepare a solution containing (300 ± 3) ml of hydrochloric acid ([5.3](#)) and (20 ± 0,5) ml of potassium iodide–ascorbic acid solution ([5.9](#)). Dilute to volume with water ([5.2](#)).

IMPORTANT — On the continuous flow system, the reagent blank solution is run as background. Since the blank solution can contain trace level detectable amounts of arsenic or antimony, ensure that the same reagents are used for both sample and standard preparation as well as for the preparation of the reagent blank.

The analyte signal is superimposed on the top of this signal once the sample is introduced into the measurement cycle. Arsenic and antimony concentrations in the reagent blank solution should be less than the lower levels of interest.

5.11 Standard solutions (arsenic and antimony).

5.11.1 Arsenic solutions (standard, stock and calibration).

5.11.1.1 Arsenic stock solution A, $\rho[\text{As(III)}] = 1\,000\text{ mg/l}$.

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

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

NOTE If other stock solutions are available, they can be used providing the uncertainty of the measurement is not compromised.

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

Place $(1,734 \pm 0,002)\text{ g}$ of sodium metaarsenite NaAsO_2 in a 1 000 ml volumetric flask.

Add $(50 \pm 0,5)\text{ ml}$ of hydrochloric acid (5.3) and dissolve the sodium metaarsenite completely by stirring.

Dilute to 1 l with water (5.2).

5.11.1.2 Arsenic standard solution B, $\rho[\text{As(III)}] = 10\text{ mg/l}$.

Pipette $(1 \pm 0,01)\text{ ml}$ of arsenic stock solution A (5.11.1.1) into a 100 ml volumetric flask, add $(30 \pm 0,5)\text{ ml}$ of hydrochloric acid (5.3) and $(2 \pm 0,1)\text{ ml}$ of potassium iodide–ascorbic acid solution (5.9) and fill up to the mark with water (5.2).

This solution is stable for one month.

5.11.1.3 Arsenic standard solution C, $\rho[\text{As(III)}] = 100\text{ }\mu\text{g/l}$.

Pipette $(1 \pm 0,01)\text{ ml}$ of arsenic standard solution B (5.11.1.2) into a 100 ml volumetric flask, add $(30 \pm 0,5)\text{ ml}$ of hydrochloric acid (5.3) and $(2 \pm 0,1)\text{ ml}$ of potassium iodide–ascorbic acid solution (5.9) and fill up to the mark with water (5.2).

This solution is stable for one week.

5.11.1.4 Arsenic stock solution D, $\rho[\text{As(V)}] = 1\,000\text{ mg/l}$.

Dissolve $(1,000 \pm 0,002)\text{ g}$ of pure arsenic powder in $(10 \pm 0,1)\text{ ml}$ of concentrated nitric acid (5.8).

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

Perform this procedure carefully under a chemical hood.

Cool and then take up the hydrated arsenic(V) oxide in $(50 \pm 0,5)\text{ ml}$ of cold hydrochloric acid (5.3).

Transfer the solution quantitatively to a 1 000 ml volumetric flask and fill up to the mark with water (5.2).

This standard shall be used to prepare a suitable arsenic(V) standard to check quantitative recovery of arsenic(V). Should the presence of arsenic(V) in the samples be suspected, use this standard to check recovery of this analyte.

The solution is stable for at least six months.

NOTE If other stock solutions are available, they can be used providing the uncertainty of the measurement is not compromised.

5.11.1.5 Arsenic calibration solutions.

Use a minimum of five independent calibration solutions. Carry out the calibration as specified in ISO 8466-1.

Prepare a minimum of five arsenic calibration solutions from the arsenic standard solution C (5.11.1.3) covering the working range of expected arsenic concentrations.

For the operating range from 1 µg/l to 5 µg/l, for example, proceed e.g. as follows:

Pipette into a series of five 100 ml volumetric flasks (1 ± 0,01) ml, (2 ± 0,02) ml, (3 ± 0,03) ml, (4 ± 0,04) ml and (5 ± 0,05) ml, respectively, of arsenic standard solution C (5.11.1.3).

Add 30 ml of hydrochloric acid (5.3) and 2 ml of potassium iodide–ascorbic acid solution (5.9).

Dilute to 100 ml with water (5.2) and mix thoroughly.

Allow to stand for at least 2 h before using to ensure quantitative reduction of arsenic(V) to arsenic(III).

These calibration solutions contain 1 µg/l, 2 µg/l, 3 µg/l, 4 µg/l and 5 µg/l arsenic 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 an established calibration pattern has been confirmed, 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.

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5.11.2 Antimony solutions (standard, stock and calibration).

5.11.2.1 Antimony stock solution A, $\rho[\text{Sb(III)}] = 1\,000\text{ mg/l}$.

Use a quantitative stock solution with an antimony(III) content of (1 000 ± 2) 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 (2,743 ± 0,002) g of potassium antimony(III) oxide tartrate hemihydrate, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 0,5\text{H}_2\text{O}$ in a 1 000 ml volumetric flask.

Add (50 ± 0,5) ml of hydrochloric acid (5.3) and dissolve the potassium antimony(III) oxide tartrate hemihydrate by stirring.

Dilute to 1 l with water (5.2).

5.11.2.2 Antimony standard solution B, $\rho[\text{Sb(III)}] = 10\text{ mg/l}$.

Pipette (1 ± 0,01) ml of antimony stock solution A (5.11.2.1) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.3) and (2 ± 0,01) ml of potassium iodide–ascorbic acid solution (5.9) and fill up to the mark with water (5.2).

This solution is stable for one week.

NOTE If a suitable commercial standard is available, it can be used if performance validated.