INTERNATIONAL STANDARD

# ISO 11969

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# Water quality — Determination of arsenic — Atomic absorption spectrometric method (hydride technique)



*Qualité de l'eau — Dosage de l'arsenic — Méthode par spectrométrie d'absorption atomique (technique hydrure)*



Reference number
ISO 11969:1996(E)

## 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.



International Standard ISO 11969 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods*.



Annexes A and B of this International Standard are for information only.



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# Water quality — Determination of arsenic — Atomic absorption spectrometric method (hydride technique)

**WARNING — Arsenic and arsenic compounds are toxic and are recognized as human carcinogens. Avoid any exposure by inhalation. Personal protection must be used in all cases where exposure to arsenic or arsenic compounds is possible.**

## 1 Scope

This International Standard specifies a method for the determination of arsenic including organically bound arsenic in drinking waters, ground waters and surface waters, in a concentration range from 1 µg/l to 10 µg/l.

Higher concentrations can be determined by using a suitable dilution of the water sample.



## 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

## 3 Principle

The method is based on the atomic absorption measurement of arsenic generated by the thermal decomposition of arsenic(III) hydride.

Under the conditions of this method, only As(III) is quantitatively converted to the hydride. To avoid errors in determination, other oxidation states need to be converted to As(III) prior to the determination.

As(III) is reduced to gaseous arsenic(III) hydride ($AsH_3$) by reaction with sodium tetrahydroborate in a hydrochloric acid medium.

The absorbance is determined at a wavelength of 193,7 nm.

## 4 Reagents

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

The arsenic content of the water and the reagents shall be negligible, compared with the lowest concentration to be determined.

**4.1 Sulfuric acid** ($H_2SO_4$), $\rho$ = 1,84 g/ml.

**4.2 Hydrochloric acid** (HCl), $\rho$ = 1,15 g/ml.

**4.3 Hydrogen peroxide** ($H_2O_2$), $w$ = 30 % $(m/m)$.

**4.4 Sodium hydroxide** (NaOH).

**4.5 Sodium tetrahydroborate solution.**

Dissolve 1 g of sodium hydroxide (4.4) in about 20 ml of water. Add 3 g of sodium tetrahydroborate ($NaBH_4$). Dilute to 100 ml with water.

Prepare the solution on the day of use.

NOTE 1 For flow-through systems, it is recommended to follow the instructions of the manufacturer. A solution containing 0,5 % of sodium tetrahydroborate and 0,5 % of sodium hydroxide is suitable. This solution is stable for at least one week.

**4.6 Potassium iodide-ascorbic acid solution.**

Dissolve 3 g of potassium iodide (KI) and 5 g of L(+)–ascorbic acid ($C_6H_8O_6$) in 100 ml of water.

Prepare the solution on the day of use.

NOTE 2 It is unnecessary to use ascorbic acid if a 20 % solution of potassium iodide is used.

**4.7 Arsenic stock solution,** corresponding to 1 000 mg of As per litre.

Place 1,320 g of arsenic(III) oxide ($As_2O_3$), in a volumetric flask of nominal capacity 1 000 ml. Add 2 g of sodium hydroxide (4.4) and dissolve in a small quantity of water. Dilute to volume with water.

This solution is stable for at least 1 year.

Arsenic stock solutions are commercially available. If the stock solution contains As(V), the standard solutions shall be treated in the same way as the sample for the reduction step (8.3.2).

**4.8 Arsenic standard solution 1,** corresponding to 10 mg of As per litre.

Pipette 10 ml of arsenic stock solution (4.7) into a volumetric flask of nominal capacity 1 000 ml. Add 20 ml of hydrochloric acid (4.2) and dilute to volume with water.

The solution is stable for about 1 month.

If a stock solution of arsenic(V) is used, arsenic(V) shall be reduced to arsenic(III) according to 8.3.2, before dilution to 1 000 ml.

**4.9 Arsenic standard solution 2,** corresponding to 0,1 mg of As per litre.

Pipette 10 ml of arsenic standard solution 1 (4.8) into a volumetric flask of nominal capacity 1 000 ml. Add 20 ml of hydrochloric acid (4.2) and dilute to volume with water.

Prepare the solution on the day of use.

## 5 Apparatus

Usual laboratory apparatus and

**5.1 Atomic absorption spectrometer**, fitted with a hydride system, and a suitable radiation source for the determination of arsenic, for example electrodeless discharge lamp or a hollow cathode lamp with a background correction facility, if necessary.

**5.2 Gas supply**, with argon or nitrogen.

**5.3 Glassware**, to be cleaned immediately before use with warm, dilute nitric acid [10 % (*V*/*V*)] and rinsed with water.

## 6 Sampling

Take samples according to ISO 5667-1 and ISO 5667-2.



Collect samples in polyethylene or borosilicate glass containers which have been previously cleaned with nitric acid [e.g. 10 % (*V*/*V*)] and then rinsed with water.



On site, add 20 ml of hydrochloric acid (4.2) to each 1 000 ml of the water sample.

If the pH of the sample is still greater than 2, add more hydrochloric acid until the pH is 2 or less.

For sample conservation, see ISO 5667-3.

## 7 Interferences

Most organic materials interfere with the arsenic determination. They shall be removed prior to the analysis by the digestion procedure described in 8.3.1. Samples forming foams when tetrahydroborate is added shall be pretreated (e.g. with an anti-foaming agent or by complete digestion). When an anti-foaming agent is added, it is also necessary to add it to the blank and calibration solutions.

Annex A gives details of the effect of potential interfering substances on the determination of arsenic. These results were obtained at the Laboratory of the Government Chemist (UK). Of the substances tested, only concentrations of copper greater than 2,0 mg/l, antimony greater than 0,2 mg/l, selenium greater than 0,05 mg/l and nitrate greater than 100 mg/l interfere at arsenic concentration levels of 1,0 µg/l.

The noble metals, for example platinium and palladium, may supress the response of the arsenic(III) hydride.

## 8 Procedure

### 8.1 Blank solution

Pipette 2 ml of hydrochloric acid (4.2) into a volumetric flask of nominal capacity 100 ml and dilute to volume with water.

Treat the blank in exactly the same way as the sample.

### 8.2 Calibration solutions

Using arsenic standard solution 2 (4.9), prepare at least five calibration solutions covering the expected working range.

For example, for the range 1 µg/l to 10 µg/l, pipette 1 ml, 3 ml, 5 ml, 8 ml and 10 ml of arsenic standard solution 2 into a series of 100 ml volumetric flasks. To each of these flasks, add 2 ml of hydrochloric acid (4.2) and dilute to volume with water. These solutions correspond to arsenic concentrations of 1 µg/l, 3 µg/l, 5 µg/l, 8 µg/l and 10 µg/l, respectively.



Prepare the calibration solutions daily.

Treat the calibration solutions in exactly the same way as the sample.

### 8.3 Pretreatment

Most of the organically bound arsenic compounds are decomposed by the digestion procedure described in 8.3.1. If it is known that the sample to be analysed does not contain organic arsenic compounds, it is permissible to omit the digestion process. In this case, proceed to 8.3.2.

Place 50 ml of the sample (see clause 6) in a round-bottomed flask (see example in figure 1).

#### 8.3.1 Method of digestion

**WARNING — Fumes produced by heating concentrated sulfuric acid are irritant and this operation must therefore be carried out in a fume chamber.**

Add 5 ml of sulfuric acid (4.1) and 5 ml of hydrogen peroxide (4.3) to the round-bottomed flask (see 8.3).

Add some anti-bumping beads and connect the flask to the apparatus as shown in figure 1. Heat the contents of the flask to boiling and collect the condensate in the condensate reservoir.

Continue heating until fumes of sulfuric acid appear. Examine the appearance of the sample. If it is turbid and almost colourless, add a further 5 ml portion of hydrogen peroxide (4.3) and continue boiling as described in the previous paragraph.

When the appearance of the sample is colourless and not turbid, cool the flask and contents, return the condensate to the round-bottomed flask and proceed to 8.3.2.

Take care to ensure that the sample is never evaporated to complete dryness.

#### 8.3.2 Reduction from As(V) to As(III)

Add 20 ml of hydrochloric acid (4.2) and 4 ml of potassium iodide-ascorbic acid solution (4.6) to the round-bottomed flask containing the digested sample (see 8.3.1) or non-digested sample (see 8.3).

Heat gently for 15 min at 50 °C.

Cool the sample solution and transfer it quantitatively to a volumetric flask of nominal capacity 100 ml. Dilute to volume with water.

### 8.4 Calibration and determination

Depending on the hydride system used, greater or smaller volumes than those described below are permitted. However, the quantity ratios defined shall be maintained.

Set all instrumental parameters of the atomic absorption spectrometer (5.1) in accordance with the manufacturer's operating manual (wavelength: 193,7 nm) and optimize the position of the absorption cell in order to obtain maximum transmission of the light beam.

Pass a stream of argon or nitrogen (5.2) through the system and set the instrument to zero.

Measure the absorption given by the solutions in the following order:

— blank solution,

— calibration solutions,

— samples, prepared as follows.

Transfer an appropriate volume of the sample solution (see 8.3.2) to the reaction vessel.

Connect the reaction vessel to the hydride system.

Pass argon or nitrogen through the solution until the absorption signal of the atomic absorption spectrometer returns to zero.

For 20 ml of the sample solution (8.3.2), add 5 ml ± 0,1 ml of sodium tetrahydroborate solution (4.5) to the solution and record the signal.

Repeat the procedure using separate portions of each solution. Use the mean of these results.

Establish the calibration curve using means of values obtained with the blank and calibration solutions.

NOTES

3 It is good practice to check the blank and calibration points from time to time.

4 With unknown samples, it is recommended to check the validity of the method by adding a known volume of arsenic to at least one sample. If recovery tests are not satisfactory, the procedure of standard additions should be used.

## 9 Calculation of the results using the standard calibration method

Calculate the arsenic concentration in the solution by comparing the absorption response of the sample solution with those of known standard concentrations obtained from the calibration procedure (8.4).

All dilution steps shall be taken into account.



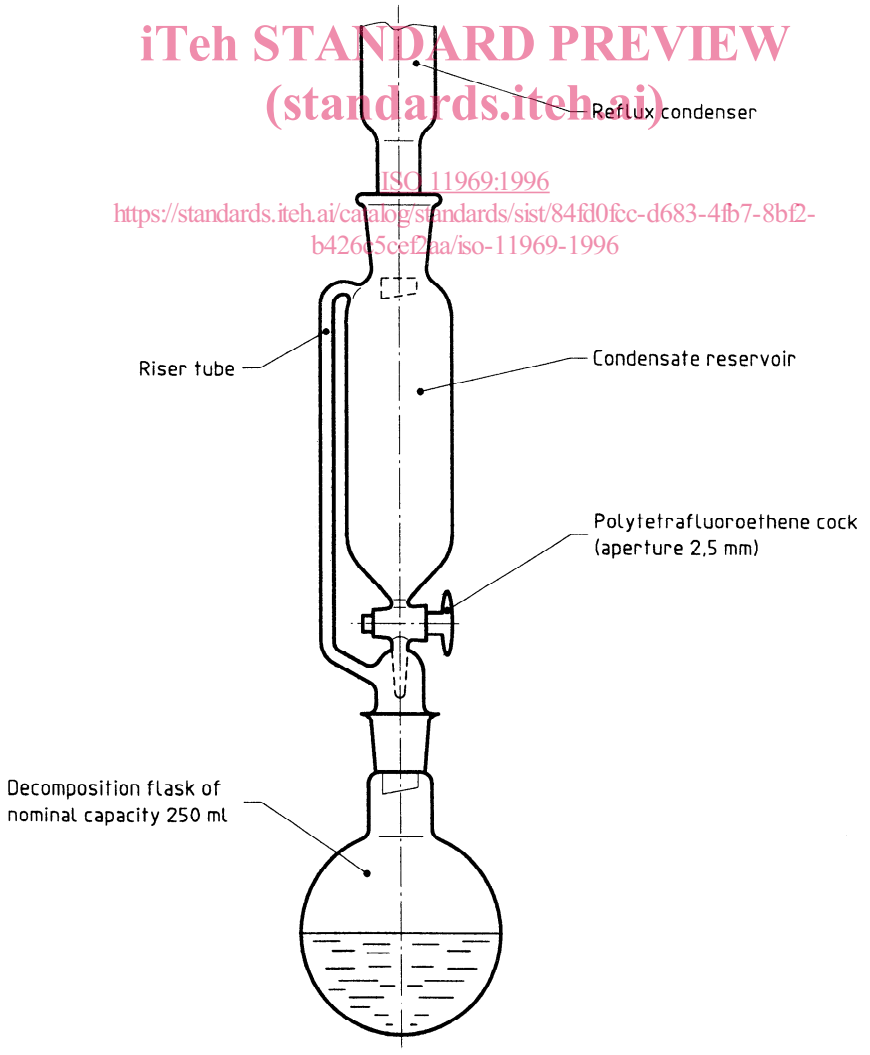


**Figure 1 — Example of decomposition apparatus**

## 10 Expression of results

Express the results, in micrograms per litre, to two significant figures and one decimal place.

## 11 Precision

An interlaboratory trial, carried out in 1982, with a method based on the same principle on drinking water samples, topped up with water of known arsenic concentration, yielded the results given in annex B.

## 12 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) complete identification of the sample;

c) expression of the results as indicated in clause 10;

d) any details not specified in this International Standard or which are optional, as well as any factor which may have affected the results.

# Annex A
(informative)

## Effect of other substances on the determination of arsenic

| Other substance | | Other substance added as | Concentration of other substance | Effect of other substance (in µg/l) at an arsenic concentration of | |
|---|---|---|---|---|---|
| | | | mg/l | 0,0 µg/l [1] | 1,0 µg/l |
| Silver | (as $Ag^{+}$) | Perchlorate | 10,0 | + 0,06 | + 0,02 |
| Aluminium | (as $Al^{3+}$) | Perchlorate | 10,0 | 0,00 | − 0,03 |
| Cadmium | (as $Cd^{2+}$) | Perchlorate | 10,0 | + 0,12 | + 0,03 |
| Chromium | (as $Cr^{3+}$) | Perchlorate | 10,0 | 0,00 | − 0,01 |
| Copper | (as $Cu^{2+}$) | Perchlorate | 0,5 | | − 0,04 |
| Copper | (as $Cu^{2+}$) | Perchlorate | 1,0 | | − 0,06 |
| Copper | (as $Cu^{2+}$) | Perchlorate | 2,0 | | − 0,06 |
| Copper | (as $Cu^{2+}$) | Perchlorate | 5,0 | | − 0,15 |
| Copper | (as $Cu^{2+}$) | Perchlorate | 10,0 | | − 0,19 |
| Copper | (as $Cu^{2+}$) | Perchlorate | 20,0 | 0,00 | − 0,30 |
| Iron | (as $Fe^{3+}$) | Perchlorate | 10,0 | 0,00 | 0,00 |
| Mercury | (as $Hg^{2+}$) | Perchlorate | 10,0 | + 0,13 | − 0,04 |
| Manganese | (as $Mn^{2+}$) | Perchlorate | 10,0 | + 0,09 | + 0,04 |
| Nickel | (as $Ni^{2+}$) | Perchlorate | 0,5 | | − 0,02 |
| Nickel | (as $Ni^{2+}$) | Perchlorate | 1,0 | | − 0,03 |
| Nickel | (as $Ni^{2+}$) | Perchlorate | 2,0 | | − 0,03 |
| Nickel | (as $Ni^{2+}$) | Perchlorate | 10,0 | 0,00 | − 0,10 |
| Lead | (as $Pb^{2+}$) | Perchlorate | 10,0 | 0,00 | − 0,05 |
| Antimony | (as $Sb^{5+}$) | Chloride | 0,2 | 0,00 | − 0,04 |
| Antimony | (as $Sb^{5+}$) | Chloride | 0,5 | | − 0,12 |
| Antimony | (as $Sb^{5+}$) | Chloride | 1,0 | | − 0,23 |
| Antimony | (as $Sb^{5+}$) | Chloride | 2,0 | | − 0,26 |
| Antimony | (as $Sb^{5+}$) | Chloride | 5,0 | | − 0,28 |
| Antimony | (as $Sb^{5+}$) | Chloride | 10,0 | + 0,24 | − 0,57 |
| Selenium | (as $Se^{4+}$) | Nitrate | 0,01 | | + 0,03 |
| Selenium | (as $Se^{4+}$) | Nitrate | 0,02 | | + 0,01 |
| Selenium | (as $Se^{4+}$) | Nitrate | 0,05 | | − 0,07 |
| Selenium | (as $Se^{4+}$) | Nitrate | 0,1 | | − 0,28 |
| Selenium | (as $Se^{4+}$) | Nitrate | 0,2 | | − 0,42 |
| Selenium | (as $Se^{4+}$) | Nitrate | 0,5 | 0,00 | − 0,81 |
| Tin | (as $Sn^{4+}$) | Chloride | 0,5 | | 0,00 |
| Tin | (as $Sn^{4+}$) | Chloride | 1,0 | | − 0,05 |
| Tin | (as $Sn^{4+}$) | Chloride | 2,0 | | − 0,04 |

| Other substance | | Other substance added as | Concentration of other substance | Effect of other substance (in µg/l) at an arsenic concentration of | |
|---|---|---|---|---|---|
| | | | mg/l | 0,0 µg/l [1] | 1,0 µg/l |
| Tin | (as $Sn^{4+}$) | Chloride | 5,0 | | − 0,05 |
| Tin | (as $Sn^{4+}$) | Chloride | 10,0 | + 0,09 | − 0,08 |
| Zinc | (as $Zn^{2+}$) | Chloride | 10,0 | + 0,04 | + 0,01 |
| Nitrate | (as $NO_3^-$) | Nitric acid | 10,0 | | − 0,04 |
| Nitrate | (as $NO_3^-$) | Nitric acid | 50,0 | | 0,00 |
| Nitrate | (as $NO_3^-$) | Nitric acid | 100,0 | | − 0,09 |
| Nitrate | (as $NO_3^-$) | Nitric acid | 250,0 | 0,00 | − 0,21 |
| Perchlorate | (as $ClO_4^-$) | Perchloric acid | 10,0 | + 0,09 | − 0,07 |
| Phosphate | (as $PO_4^{3-}$) | Potassium dihydrogen | 10,0 | 0,00 | + 0,02 |
| Sulfate | (as $SO_4^{2-}$) | Sulfuric acid | 250,0 | + 0,04 | + 0,01 |

1) If the other substances did not interfere, the effect would be expected to be within 0,00 µg/l ± 0,02 µg/l and 0,00 µg/l ± 0,08 µg/l at arsenic concentrations of 0,0 µg/l and 1,0 µg/l, respectively.