BRITISH STANDARD

BS EN ISO 11969:1996
BS 6068-2.55: 1996

Water quality —

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

The European Standard EN ISO 11969:1996 has the status of a British Standard

ICS 13.060

Confirmed July 2008

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods, upon which the following bodies were represented:

British Agrochemicals Association Ltd.
British Ceramic Research
British Gas plc
British Soft Drinks Association Ltd.
Chemical Industries' Association
Convention of Scottish Local Authorities
Department of the Environment (Her Majesty's Inspectorate of Pollution)
Department of the Environment (Water Directorate)
Department of Trade and Industry (Laboratory of the Government Chemist)
GAMBICA (BEAMA) Ltd.
Industrial Water Society
National Rivers Authority
Royal Society of Chemistry
Soap and Detergent Industry Association
Society of Chemical Industry
Swimming Pool and Allied Trades Association Ltd.
Water Companies Association
Water Research Centre
Water Services Association of England and Wales

This British Standard, having been prepared under the direction of the Health and Environment Sector Board, was published under the authority of the Standards Board and comes into effect on 15 November 1996

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Contents

National foreword

This British Standard has been prepared by Subcommittee EH/3/2. It is the English language version of EN ISO 11969:1996 *Water quality — Determination of arsenic — Atomic absorption spectrometric method (hydride technique)* published by the European Committee for Standardization (CEN). It is identical with ISO 11969:1996 published by the International Organization for Standardization (ISO).

NOTE The tests described in this British Standard should only be carried out by suitably qualified persons with an appropriate level of chemical expertise. Standard chemical procedures should be followed throughout.

Cross-references

Publication referred to	Corresponding British Standard
	BS EN 25667 *Water quality. Sampling*
ISO 5667-1:1980	Part 1:1994 *Guidance on the design of sampling programmes*
ISO 5667-2:1991	Part 2:1993 *Guidance on sampling techniques*
ISO 5667-3:1994	BS 6068 *Water quality* Part 6: *Sampling* Section 6.3:1996 *Guidance on the preservation and handling of samples*

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN ISO title page, pages 2 to 8, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN ISO 11969

July 1996

ICS: 13.060.00

Descriptors: Water, quality, water pollution, water tests, chemical analysis, determination of content, arsenic, atomic absorption spectrometric method.

English version

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

(ISO 11969:1996)

Qualité de l'eau — Dosage de l'arsenic — Méthode par spectrométrie d'absorption atomique (technique hydrure)
(ISO 11969:1996)

Wasserbeschaffenheit — Bestimmung von Arsen — Atomabsorptionspektrometrie (Hydridverfahren)
(ISO 11969:1996)

This European Standard was approved by CEN on 1996-06-28. CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Foreword

The text of the International Standard ISO 11969:1996 has been prepared by Technical Committee ISO/TC 147, Water quality, in collaboration with Technical Committee CEN/TC 230, Water analysis, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 1997 and conflicting national standards shall be withdrawn at the latest by January 1997.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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), ρ = 1,84 g/ml.

4.2 *Hydrochloric acid* (HCl), ρ = 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.

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

NOTE 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.

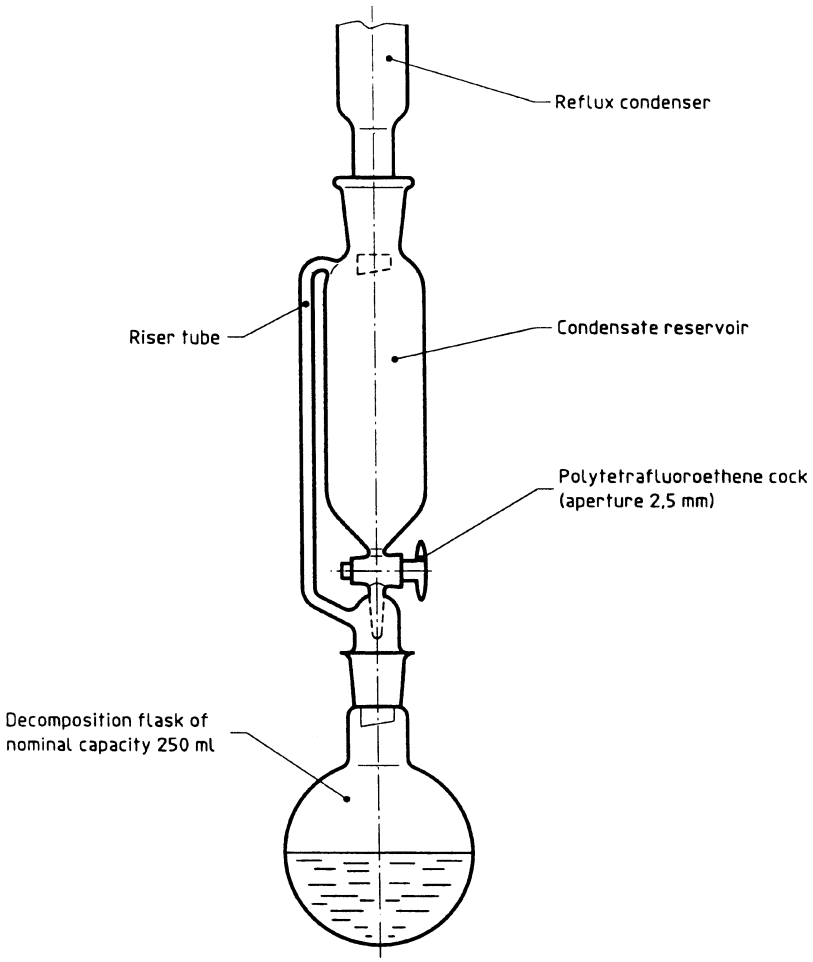

Figure 1 — Example of decomposition apparatus

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[a]	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[a]	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

[a] 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.

Annex B (informative)
Precision data

Samples	n	o	n_a %	$\bar{x}$ µg/l	x_{theor} µg/l	RR %	s_r µg/l	VC_r %	s_R µg/l	VC_R %
1	60	1	2	1,40	1,30	108	0,084	6,0	0,268	19
2	60	1	2	4,38	4,00	109	0,172	3,9	0,509	12
3	60	—	0	7,99	7,50	107	0,572	7,1	0,919	12

n	is the valid number of measured values	RR	is the recovery rate
o	is the number of outliers	s_r	is the repeatability standard deviation
n_a	is the percentage of outliers	VC_r	is the repeatability variation coefficient
$\bar{x}$	is the overall mean	s_R	is the reproducibility standard deviation
x_{theor}	is the theoretical value	VC_R	is the reproducibility variation coefficient

List of references

See national foreword.

BSI — British Standards Institution

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