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Water quality — Determination of arsenic and antimony —

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

Qualité de l'eau — Dosage de l'arsenic et de l'antimoine —
Partie 1: Méthode par spectrométrie de fluorescence atomique à génération d'hydrures (HG-AFS)

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Foreword

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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).

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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*.

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, notably 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 or antimony occur naturally in organic and inorganic compounds, and can 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 can 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.

Water quality — Determination of arsenic and antimony —

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 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 linear application range of this part of ISO 17378 is from 0,02 µg/l to 100 µg/l. Samples containing arsenic or antimony at 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 compounds or 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 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 acidified with hydrochloric acid (7.2.1). Potassium iodide–ascorbic acid reagent (5.9) is added to ensure quantified reduction of the arsenic(V) to arsenic(III) and antimony(V) to antimony(III). The subsequent sample solutions are then treated with sodium tetrahydroborate (5.7) to generate the covalent gaseous hydride (AsH_3) or (SbH_3). The hydride and excess hydrogen are swept out of the generation vessel in case of the batch mode and out of the gas/liquid separator in the case of 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 arsenic or antimony light source, the resulting fluorescence is detected by atomic fluorescence spectrometry after isolation by an interference filter that transmits the arsenic or antimony resonance line at 193,7 nm (for arsenic) or 206,8 nm and 217,6 nm (for antimony). The procedure is automated by means of 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, many interferences can be removed by a simple dilution step as long as the final antimony and arsenic concentrations are above the LOQ.

The reaction conditions set out in this part of ISO 17378 have been chosen so that any interference is reduced to a minimum.

It is important that the light source does not contain any significant amount of other hydride-forming elements (e.g. antimony when analysing for arsenic or arsenic when analysing for antimony) that emit fluorescent radiation over the band pass 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 17378 generally do not 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 Tables 1 and 2 for arsenic and antimony, respectively. Easily reducible elements such as gold and mercury cause a significant negative bias, especially for antimony. A significant positive bias is caused by bismuth for both arsenic and low levels of antimony. However, these elements are unlikely to be present at the tested levels in the vast majority of water samples. Arsenic causes a large positive bias for antimony.

Interference 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 LOQ.

Table 1 — Interference study for arsenic

Interfering substance		Concentration of interfering substance	As recovery, %	
		mg/l	2 µg/l As	10 µg/l As
Thallium nitrate	Tl(III)	20	94,8 ± 0,9	89,9 ± 2,8
Strontium nitrate	Sr(II)	20	107,3 ± 5,9	100,0 ± 2,5
Zinc nitrate	Zn(II)	1	101,7 ± 5,5	91,0 ± 3,1
di(Ammonium)silicon hexafluoride	Si(IV)	1	94,4 ± 3,7	102,4 ± 1,7
Aluminium nitrate	Al(III)	1	104,6 ± 0,8	98,9 ± 0,8
Calcium chloride	Ca(II)	200	101,8 ± 1,3	103,3 ± 1,3
Sodium chloride	Na(I)	200	104,2 ± 1,6	100,6 ± 1,8
Potassium bromide	K(I)	200	96,3 ± 0,7	97,6 ± 0,7
Indium nitrate	In(III)	1	99,4 ± 1,4	99,1 ± 1,5
Barium nitrate	Ba(II)	1	95,2 ± 3,1	105,9 ± 1,4
Magnesium oxide	Mg(II)	1	99,7 ± 3,5	97,2 ± 1,5
Cadmium nitrate	Cd(II)	1	100,4 ± 0,9	97,2 ± 0,2
Ammonium dihydrogenphosphate	P(V)	1	100,3 ± 1,3	100,5 ± 2,1
Sodium fluoride	F(I)	1	113,3 ± 2,6	109,4 ± 1,0
Gold chloride	Au(III)	0,1	97,8 ± 6,4	103,2 ± 1,4
Gold chloride	Au(III)	1	80,9 ± 1,9	93,8 ± 1,5
Orthoboric acid	B(III)	1	99,5 ± 3,0	99,7 ± 3,4
Iron(II) nitrate	Fe(II)	1	99,0 ± 0,9	100,2 ± 0,7
Lead(II) nitrate	Pb(II)	1	87,0 ± 4,1	95,3 ± 0,7
Bismuth nitrate	Bi(III)	1	121,4 ± 0,9	107,0 ± 0,2
Tin nitrate	Sn(IV)	1	95,1 ± 1,9	104,8 ± 1,8
Germanium chloride	Ge(IV)	1	104,4 ± 3,0	102,1 ± 1,1
Mercury	Hg(II)	1	100,7 ± 0,7	98,1 ± 0,4
Chromium(III) nitrate	Cr(III)	1	101,0 ± 1,2	98,4 ± 0,6
Cobalt nitrate	Co(II)	1	103,1 ± 0,7	99,9 ± 2,0
Silver nitrate	Ag(I)	1	97,9 ± 1,8	95,9 ± 2,3
Nickel(II) nitrate	Ni(II)	1	100,2 ± 0,4	98,8 ± 1,2
Telluric acid	Te(IV)	0,01	90,7 ± 2,9	99,3 ± 0,7
Telluric acid	Te(IV)	0,1	100,1 ± 1,2	98,0 ± 0,9
Telluric acid	Te(IV)	1	101,5 ± 0,6	100,3 ± 1,0
Antimony oxide	Sb(III)	0,01	101,0 ± 0,8	102,1 ± 1,1
Antimony oxide	Sb(III)	0,05	107,3 ± 1,8	97,5 ± 1,7
Antimony oxide	Sb(III)	0,1	118,3 ± 1,0	96,7 ± 2,7
Copper(II) sulfate	Cu(II)	0,1	101,8 ± 1,9	102,7 ± 2,4
Copper(II) sulfate	Cu(II)	0,2	100,5 ± 2,8	101,4 ± 0,1
Copper(II) sulfate	Cu(II)	0,5	99,8 ± 1,1	99,0 ± 1,0
Copper(II) sulfate	Cu(II)	1	94,0 ± 4,7	100,7 ± 1,9
Copper(II) sulfate	Cu(II)	2	98,8 ± 1,1	99,0 ± 1,0
Iron(III) nitrate	Fe(III)	200	114,3 ± 0,7	105,0 ± 0,6

Table 2 — Interference study for antimony

Interfering substance		Concentration of interfering substance	Sb recovery, %	
		mg/l	2 µg/l Sb	10 µg/l Sb
Thallium nitrate	Tl(lll)	20	100,9 ± 1,6	93,5 ± 2,1
Strontium nitrate	Sr(II)	20	99,7 ± 4,5	99,6 ± 3,3
Zinc nitrate	Zn(II)	1	98,2 ± 3,4	94,4 ± 3,4
di(Ammonium)silicon hexafluoride	Si(IV)	1	95,9 ± 1,4	100,8 ± 2,7
Aluminium nitrate	Al(III)	1	96,4 ± 1,0	99,1 ± 2,0
Calcium chloride	Ca(II)	200	92,4 ± 4,1	98,5 ± 2,3
Sodium chloride	Na(I)	200	98,7 ± 2,8	97,8 ± 3,0
Potassium bromide	K(I)	200	94,5 ± 2,5	101,3 ± 2,1
Indium nitrate	In(III)	1	97,4 ± 2,0	95,2 ± 3,5
Barium nitrate	Ba(II)	1	99,7 ± 0,6	97,7 ± 1,0
Magnesium oxide	Mg(II)	1	95,9 ± 4,1	100,6 ± 1,7
Cadmium nitrate	Cd(II)	1	96,0 ± 1,1	94,5 ± 0,7
Ammonium dihydrogenphosphate	P(V)	1	102,7 ± 2,7	100,2 ± 3,1
Sodium fluoride	F(−I)	1	108,0 ± 10,6	100,2 ± 5,0
Gold chloride	Au(III)	0,1	101,4 ± 2,6	98,0 ± 3,1
Gold chloride	Au(III)	1	46,1 ± 3,6	47,6 ± 4,4
Orthoboric acid	B(III)	1	91,2 ± 2,4	95,8 ± 3,3
Iron(II) nitrate	Fe(II)	1	96,6 ± 2,6	94,4 ± 2,2
Lead(II) nitrate	Pb(II)	1	97,6 ± 4,6	103,5 ± 1,2
Bismuth nitrate	Bi(III)	1	122,7 ± 5,1	95,7 ± 2,7
Tin nitrate	Sn(IV)	1	97,6 ± 4,2	97,1 ± 2,0
Mercury nitrate	Hg(II)	1	87,8 ± 0,7	97,8 ± 2,3
Arsenic(III) oxide (see NOTE)	As(III)	1	230,0 ± 0,8	136,3 ± 2,4
Chromium(III) nitrate	Cr(III)	1	98,5 ± 4,1	97,6 ± 0,5
Cobalt nitrate	Co(II)	1	99,4 ± 5,1	100,5 ± 2,8
Silver nitrate	Ag(I)	1	97,0 ± 3,1	94,0 ± 0,4
Nickel(II) nitrate	Ni(II)	1	97,8 ± 1,5	95,2 ± 3,0
Telluric acid	Te(IV)	1	95,4 ± 1,1	95,5 ± 0,8
Selenic acid	Se(IV)	1	99,3 ± 1,8	104,5 ± 1,5
Copper(II) sulfate	Cu(II)	1	96,9 ± 1,6	100,2 ± 1,0
Copper(II) sulfate	Cu(II)	2	95,0 ± 6,0	92,6 ± 0,9
Ammonium molybdate	Mo(VI)	1	100,3 ± 2,9	97,6 ± 1,3
Manganese sulfate	Mn(II)	1	97,0 ± 1,6	93,2 ± 0,7

NOTE The results for arsenic(III) oxide are attributable to the presence of trace levels of arsenic in the cathode of the boosted hollow cathode lamp used in these experiments.

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 can contain arsenic or antimony as an impurity. All reagents should 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.

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

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

5.4 Hydrochloric acid, $c(HCl)$ = 1 mol/l.

5.5 Sodium tetrahydroborate, $NaBH_4$.

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

5.6 Sodium hydroxide, NaOH.

5.7 Sodium tetrahydroborate solution, $\rho(NaBH_4)$ = 13 g/l.

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

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 $NaBH_4$ 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, $w(HNO_3)$ = 650 g/kg.

NOTE Nitric acid is available both as purity of HNO_3 = 650 g/kg or purity of HNO_3 = 690 g/kg.

To prepare a nitric acid cleaning mixture, dilute nitric acid (650 g/kg) with an equal volume of water (5.2) by carefully adding the acid to the water.

5.9 Potassium iodide–ascorbic acid solution.

Dissolve (250 ± 0,1) g of potassium iodide (KI) and (50 ± 0,1) g of ascorbic acid ($C_6H_8O_6$) in approximately 400 ml water (5.2) and dilute to 500 ml.

This solution should be prepared on the day of use.

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 levels of detectable amounts of arsenic or antimony, ensure that the same reagents are used for both sample and standard preparation as well as for preparation of the reagent blank.

