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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)

Reference number
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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(Ill) 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, ρ(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.

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 (stock, standard and calibration).

5.11.1.1 Arsenic stock solution A, ρ[As(III)] = 1 000 mg/l.

Use a quantitative stock solution with a traceable arsenic(III) content of (1 000 ± 2) 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 providng the uncertainty of the measurement is not compromised.

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

Place (1,734 ± 0,002) g of sodium metaarsenite $NaAsO_2$ in a 1 000 ml volumetric flask.

Add (50 ± 0,5) 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, ρ[As(III)] = 10 mg/l.

Pipette (1 ± 0,01) ml of arsenic stock solution A (5.11.1.1) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.3) and (2 ± 0,1) 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, ρ[As(III)] = 100 µg/l.

Pipette (1 ± 0,01) ml of arsenic standard solution B (5.11.1.2) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.3) and (2 ± 0,1) 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 standard solution D, ρ[As(III)] = 10 µg/l.

Pipette (10 ± 0,1) ml of arsenic standard solution C (5.11.1.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.10).

This solution should be prepared on the day of use.

5.11.1.5 Arsenic standard solution E, ρ[As(V)] = 1 000 mg/l.

Dissolve (1,000 ± 0,002) g of pure arsenic powder in (10 ± 0,1) 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 ± 0,5) 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.

5.11.1.6 Arsenic calibration solutions.

Use a minimum of five independent calibration solutions. Carry out the calibration as specified in ISO 8466-1. The calibration solutions are prepared by suitable dilution of the arsenic standard C (5.11.1.3) or D (5.11.1.4).

Each calibration solution shall contain (30 ± 0,5) ml of hydrochloric acid (5.3) and (2 ± 0,01) ml of potassium iodide–ascorbic acid solution (5.9) per 100 ml in borosilicate volumetric flasks.

This solution should be prepared on the day of use.

For example, for a calibration range from 0,2 µg/l to 1 µg/l, proceed as follows.

Pipette into a series of five 100 ml volumetric flasks (2 ± 0,02) ml, (4 ± 0,04) ml, (6 ± 0,06) ml, (8 ± 0,08) ml, and (10 ± 0,1) ml, respectively, of arsenic standard solution D (5.11.1.4). Fill up to the mark with reagent blank solution (5.10) and mix thoroughly.

These calibration solutions contain 0,2 µg/l, 0,4 µg/l, 0,6 µg/l, 0,8 µg/l and 1 µg/l arsenic respectively.

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

These solutions 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.

5.11.2 Antimony solutions (stock, standard and calibration).

5.11.2.1 Antimony stock solution A, ρ[Sb(III)] = 1 000 mg/l.

Use a quantitative stock solution with a traceable 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, $K(SbO)C_4H_4O_6 \cdot 0{,}5H_2O$ in a 1 000 ml volumetric flask.

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

Dilute to 1 l with water (5.2).

5.11.2.2 Antimony standard solution B, ρ[Sb(III)] = 10 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.

5.11.2.3 Antimony standard solution C, ρ[Sb(III)] = 100 µg/l.

Pipette (1 ± 0,01) ml of antimony standard solution B (5.11.2.2) 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 should be prepared weekly.

5.11.2.4 Antimony standard solution D, ρ[Sb(III)] = 10 µg/l.

Pipette (10 ± 0,01) ml of antimony standard solution C (5.11.2.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.10).

This solution should be prepared on the day of use.

5.11.2.5 Antimony stock solution E, ρ[Sb(V)] = 1 000 mg/l.

Dissolve (1,000 ± 0,002) g of pure antimony powder in (10 ± 0,1) 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 antimony(V) oxide in (50 ± 0,5) 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 should be used to prepare a suitable antimony(V) standard to check quantitative recovery of antimony(V).

The solution is stable for at least six months.

Dilute antimony(V) standard solutions shall be prepared on the day of use and checked for turbidity which is evidence that hydrolysis has occurred. Discard any solution that exhibits any visible turbidity.

5.11.2.6 Antimony calibration solutions.

Use a minimum of five independent calibration solutions. Carry out the calibration as specified in ISO 8466-1. The calibration solutions are prepared by suitable dilution of the antimony standard C (5.11.2.3) or D (5.11.2.4).

Each calibration solution shall contain (30 ± 0,5) ml of hydrochloric acid (5.3) and (2 ± 0,01) ml of potassium iodide–ascorbic acid solution (5.9) per 100 ml in borosilicate volumetric flasks.

Prepare on the day of use.

For example, for a calibration range from 0,2 µg/l to 1 µg/l, proceed as follows.

Pipette into a series of five 100 ml volumetric flasks (2 ± 0,02) ml, (4 ± 0,04) ml, (6 ± 0,06) ml, (8 ± 0,08) ml, and (10 ± 0,1) ml respectively of antimony standard solution D (5.11.2.4). Fill up to the mark with reagent blank solution (5.10) and mix thoroughly.

These calibration solutions contain 0,2 µg/l, 0,4 µg/l, 0,6 µg/l, 0,8 µg/l and 1 µg/l antimony respectively.

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

These solutions should 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.

6 Apparatus

Usual laboratory equipment and in particular the following.

Atomic fluorescence systems should be set up to the manufacturer's recommendations. The following specification is typical of an atomic fluorescence system suitable for these measurements.

6.1 Atomic fluorescence system.

6.1.1 General.

A schematic block diagram of an example of an automated analysis system (for use with arsenic or antimony) is shown in Figure B.1. The system consists of 6.1.2 to 6.1.6.

6.1.2 Auto-sampler, where operated in an automatic regime.

6.1.3 Continuous flow vapour generator.

6.1.4 Gas/liquid separator, a moisture removal system.

6.1.5 Atomic fluorescence spectrometer, with appropriate interference filter and electronic controller.

6.1.6 Appropriate calculation and reporting software.

A typical signal response from a continuous flow vapour generator atomic fluorescence system is also shown in Figure B.2.

The background level is the summation of the instrumental blank, the reagent blank and the flame blank. Additional background levels may be contributed if a mixture of argon and hydrogen is used.

6.2 Gas supply.

For maximum performance of this part of ISO 17378, pure argon (99,9 % purity) is recommended.

The gas supply should be fitted with a two stage regulator and the argon supplied at a sufficient pressure to purge the arsenic or antimony hydrides from the gas/liquid separator and transfer the gas to the atomic fluorescence detector.

The use of a gas purifier consisting of activated charcoal is recommended.

Nitrogen gas may also be used but results in a significantly reduced sensitivity.

Compressed air from a cylinder or oil-free compressor can be used as the dryer gas.

6.3 Moisture removal.

Moisture removal is provided using a Nafion[1)] hygroscopic membrane which continuously removes moisture present. Details of a suitable unit are provided in Annex B. Air, argon or nitrogen can be used as the dryer gas.

NOTE Nafion[1)] hygroscopic membranes for moisture removal are commercially available.

6.4 Laboratoryware.

6.4.1 General requirements.

Clean all re-usable laboratoryware that comes into contact with the sample prior to use.

Immerse laboratoryware in the nitric acid cleaning mixture (5.8) for at least 24 h and rinse five times with water (5.2).

Following this, refill laboratoryware with hydrochloric acid, c(HCl) = 1 mol/l (5.4) and leave for 24 h.

6.4.2 Storage and sample processing bottles.

Use sampling vessels constructed of silica, borosilicate glass, plastics materials [e.g. polytetrafluoroethene (PTFE), perfluoro (ethene–propene) (FEP)] or other material that neither adsorbs nor desorbs the analyte under test.

6.4.3 Instrument reagent reservoir.

The reagents are delivered via a peristaltic pump from reagent bottles through PTFE transfer lines. All pump tubing shall be compatible with reagents in use and neither absorb or desorb the analyte under test.

6.4.4 Auto-sampler vials.

Use vials constructed of materials specified in 6.4.2.

6.5 Sample processing equipment.

6.5.1 Air displacement pipette.

Micro-pipette system capable of delivering volumes from 10 µl to 1 000 µl with an assortment of metal-free, disposable pipette tips.

6.5.2 Balance.

A balance, accurate to 0,001 g for preparation of reagent solutions and standards.

6.6 Digestion apparatus.

Pre-digestion is not normally required for water samples within the scope of this part of ISO 17378. Should this part of ISO 17378 be extended to samples requiring digestion, use apparatus similar to that specified in ISO 15587-1.

1) Nafion is the trade name of a product supplied by Dupont. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

7 Sampling and sample preparation

7.1 Sampling techniques

Carry out the sampling as specified in ISO 5667-1, ISO 5667-3, ISO 5667-5, ISO 5667-6, ISO 5667-8 and ISO 5667-11 using sampling vessels as specified in 6.4.2.

For the determination of arsenic or antimony in aqueous samples, acidify at time of sampling to pH < 2. Hydrochloric acid (5.3) (3 ± 0,5) ml per litre is sufficient for most samples. Ensure that the pH is less than 2; otherwise, add more hydrochloric acid as required.

For all types of samples, prepare an appropriate blank and analyse as required. Use the same type of vessel and quantity of acid as used in the sample.

A continuous flow procedure is described in this part of ISO 17378. All samples, blanks and standards shall be prepared in the same matrix: i.e. matrix-matched. This is a fundamental principle of continuous flow techniques.

NOTE Sample preservation using nitric acid (5.8) is suitable, providing it is shown that arsenic or antimony determinations are unaffected by using this reagent.

7.2 Pre-reduction

Since only arsenic(III) and antimony(III) react quickly and quantitatively under the conditions used in the hydride technique, arsenic(V) and antimony(V) have to be reduced to arsenic(III) and antimony(III) prior to the step of hydride generation.

7.2.1 Standard procedure for water samples

Pre-treat water samples, field blanks, and blank solutions in the following way.

Accurately transfer an aliquot of the sample (40 ml to 50 ml) to a 100 ml volumetric flask.

Add (30 ± 0,5) ml of hydrochloric acid (5.3).

Add (2 ± 0,1) ml of potassium iodide–ascorbic acid solution (5.9), mix, and allow to stand for at least 2 h. This ensures quantitative reduction of arsenic(V) or antimony(V) to arsenic(III) or antimony(III).

Transfer to a volumetric flask and dilute to 100 ml with water (5.2).

If other sample volumes are applied, use reagents and equipment adequate for the chosen volumes.

NOTE For greater accuracy, the sample can also be dispensed by mass using a tared flask. In this case, it is necessary to calculate the volume from the density and the mass and record the volume.

7.2.2 Samples requiring additional digestion

For samples that contain significant amounts of solid material and/or organically bound arsenic or antimony, perform an additional digestion step as specified in ISO 15587-1. This is outside the scope of this part of ISO 17378, but samples may be analysed using a similar procedure, providing correctly matrix-matched reagents are prepared using the correct proportion of nitric acid (5.8) and hydrochloric acid (5.4). Blanks and standard solutions shall also be matrix matched.

8 Instrumental set-up

Configure the instrumentation as described in the instrument manufacturer's manual. It is recommended that automatic background correction be employed. An example of the configuration is given in Annex B.

Check tubing for wear and pumping reliability each day the system is used and replace if necessary. All tube distances between the auto-sampler, vapour generator, and detector shall be kept to a minimum.

Fill the reagent reservoirs with reagent blank solution (5.10) and sodium tetrahydroborate solution (5.7), respectively.

Set up the continuous flow vapour generator system according to the manufacturer's recommendations. Ensure that reagent flows are within the accepted tolerances and that the atomizer is set up correctly, e.g. if the system has a hydrogen flame that it has ignited. Once stable conditions are established, analysis can proceed.

Where the manufacturer's instrument uses a hydrogen flame the reagent (5.7) has a twofold function:

a) to reduce the arsenic or antimony to its hydride; and

b) to generate hydrogen for the atomization source.

The latter may require that the concentration of $NaBH_4$ (5.7) be optimized to suit the pumping and gas flow rates used on the instrumentation and to obtain noise levels consistent with the detection levels required by this part of ISO 17378.

Both standards and samples shall be quantified using the same flow characteristics.

Turn on the argon (6.2) to provide carrier gas. A suitable dryer (moisture removal) system shall be used (6.3). Turn on the dryer gas (6.2). Flow rates shall be set according to the instrument manufacturer's recommendations.

Select the required amplification for the atomic fluorescence detector. Ensure that the selected detector range is appropriate to the sample concentration being determined.

For samples which are above the calibration for a given range setting, either reanalyse at a lower sensitivity or dilute the sample into the calibration range. If the sample is diluted, then the diluent shall be the reagent blank solution (5.10), i.e. matrix matched.

Samples which are digested shall be matrix matched against standards and blanks using the same acid concentrations to provide reliable data.

9 Procedure

Follow the manufacturer's instructions to set up instrumental conditions and software procedures to establish quantitative analysis.

With the reagent blank (5.10) and the sodium tetrahydroborate solution (5.7) flowing to the gas/liquid separator, ensure that the system is equilibrated by monitoring for a stable fluorescence detector background. If sufficient warm up time is not allowed the detector baseline can change during an analytical cycle.

Analyse calibration solutions (5.11), samples (see Clause 7) and blanks (5.10) sequentially in the manner required or else run automatically in the following manner.

Load the auto-sampler with the calibration solutions (5.11.1.6 or 5.11.2.6), samples (see Clause 7) and blanks (5.10) and start the auto-sampler programme. Analysis of a field blank within a sample run establishes whether contamination has occurred. Should a significant level of contamination be established, the analytical results are brought into question.

Inorganic arsenic occurs in two oxidation states; As(V) and As(III) and inorganic antimony occurs in two oxidation states as Sb(V) and Sb(III). It is essential to convert all arsenic or antimony species to the As(III) or Sb(III) states prior to generating the hydrides. Arsenic(V) or antimony(V) give a significantly lower response than arsenic(III) or antimony(III).

Prepare As(V) or Sb(V) standards (5.11.1.5 or 5.11.2.5) at known concentrations and analyse after pre-reduction (7.2) to validate the pre-reduction stage of this procedure.

10 Calibration and data analysis

10.1 General requirements

The dilution factor of each sample shall be applied. If additional dilutions were made to any samples, the appropriate factor shall be applied to the calculated sample concentrations. Concentrations of samples where additional reagents were added to preserve the sample shall be corrected with the corresponding blank subtraction. Care shall be exercised to correctly matrix match these solutions.

10.2 Calculation using the calibration curve

Determine the calibration curve from the data measured for the calibration solutions, e.g. by using the method of linear regression.

Calculate the concentration of arsenic, $\rho(\mathrm{As})$, or antimony, $\rho(\mathrm{Sb})$, in the samples using Formulae (1) or (2):

$$\rho(\mathrm{As}) = \frac{(F_\mathrm{s} - F_\mathrm{b})V_\mathrm{M}}{b_\mathrm{As} V_\mathrm{P}} \tag{1}$$

$$\rho(\mathrm{Sb}) = \frac{(F_\mathrm{s} - F_\mathrm{b})V_\mathrm{M}}{b_\mathrm{Sb} V_\mathrm{P}} \tag{2}$$

where

$\rho(\mathrm{As})$ is the concentration of arsenic in the sample in micrograms per litre, µg/l;

$\rho(\mathrm{Sb})$ is the concentration of antimony in the sample in micrograms per litre, µg/l;

F_s is the fluorescence response of the water sample;

F_b is the fluorescence response of the blank solution;

b_As is the slope of the calibration curve for arsenic and a measure of the sensitivity in litres per microgram, l/µg;

b_Sb is the slope of the calibration curve for antimony and a measure of the sensitivity in litres per microgram, l/µg;

V_M is the volume of measurement solution in millilitres, ml;

V_P is the volume of sample used to prepare the measurement solution in millilitres, ml.

11 Expression of results

Report the results in µg/l and round them to the nearest 0,01 µg/l. Do not use more than two significant figures.

EXAMPLES

Arsenic (As) 0,04 µg/l

Arsenic (As) 14 µg/l

Antimony (Sb) 0,04 µg/l

Antimony (Sb) 14 µg/l

12 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this part of ISO 17378 (ISO 17378-1:2014);

b) complete identification of the sample;

c) expression of results as indicated in Clause 11;

d) sample pre-treatment;

e) any deviations from this part of ISO 17378 and details of all circumstances which could have affected the result.

Annex A
(informative)

Additional information

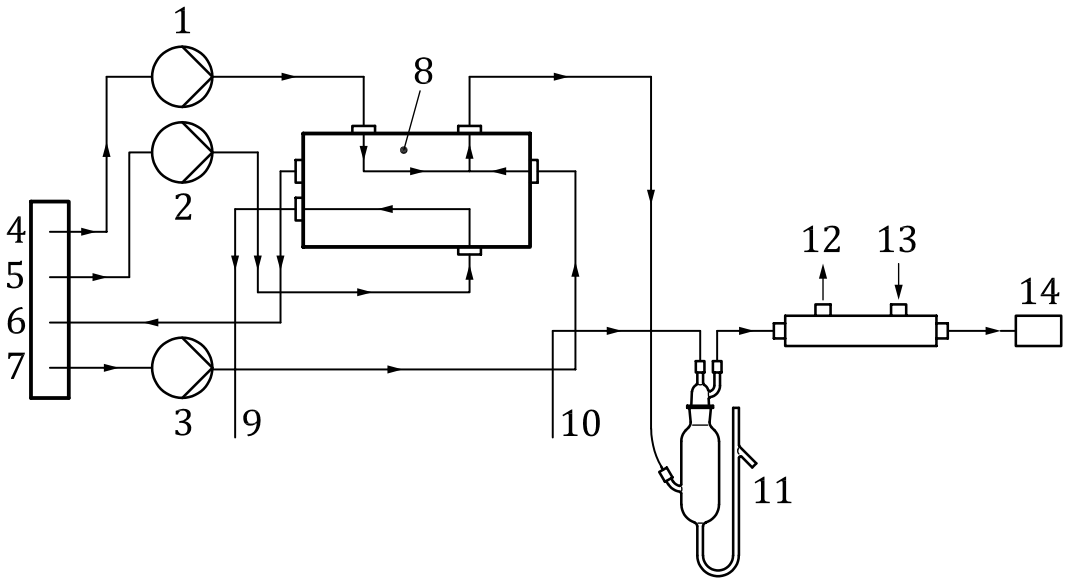
A.1 The method and any variation from it should be rigorously checked for performance using statistical data and analytical quality control sample materials, including certified reference materials.

A.2 While any inert gas may be used to purge the arsenic or antimony from the gas/liquid separator, the optimum signal response is provided using argon. Nitrogen can be used but quenches the fluorescence signal reducing sensitivity. Air should not be used because of the risk of explosion.

A.3 Water vapour may also be removed using a desiccant tube. Care shall be taken using this approach to avoid trapping arsenic or antimony in the trap due to excess moisture retention.

Annex B
(informative)

Figures



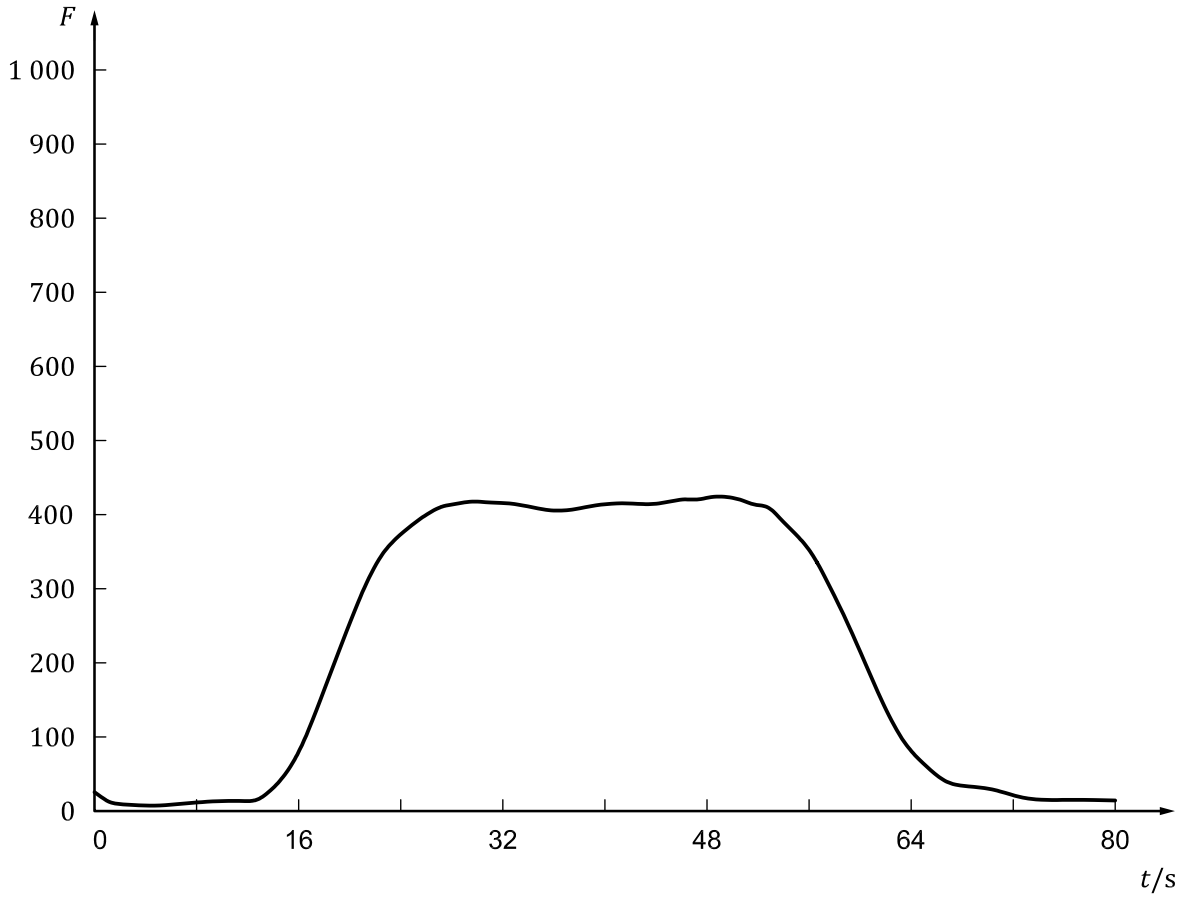
Key

1	pump 1	6	recycle	11	gas/liquid separator
2	pump 2	7	reductant	12	dryer gas out of Nafion[1)] dryer system (6.3)
3	pump 3	8	sample valve	13	dryer gas into Nafion[1)] dryer system (6.3)
4	blank	9	waste	14	atomic fluorescence spectrometer (AFS)
5	sample	10	argon carrier gas		

NOTE This continuous flow vapour generator consists of a constant speed peristaltic pump to deliver sodium tetrahydroborate solution (5.7), reagent blank (5.10) and sample. A switching valve alternates between the reagent blank and sample or standard solutions. The vapour generator switches between reagent blank and sample solution on a prescribed sequence, so that the measured signal is directly related to the background levels of arsenic or antimony in the sample. The signal response is shown in Figure B.2.

Figure B.1 — Schematic flow diagram of hydride generation system

This is only an example; any other suitable system may be used subject to satisfactory performance data.



Key

F fluorescence signal

t time

NOTE Signal rises to a plateau as the sample is introduced and returns back to the baseline once the sample is replaced by the reagent blank (5.10). Samples, standards and blank shall be matrix matched.

Figure B.2 — Representation of typical signal response from arsenic or antimony in water sample by continuous flow hydride generation atomic fluorescence spectrometry

Annex C
(informative)

Performance data

An interlaboratory trial was organized by Professor Peter B Stockwell, Convenor of WG52, with the assistance of Professor K. Clive Thompson and performed in October 2006 by PS Analytical, Orpington, UK and ALcontrol Laboratories, Rotherham, UK. A total of 17 laboratories from 7 countries took part (UK: 5, France: 5, Germany: 3, Italy: 1, The Netherlands: 1, Slovakia: 1 and USA: 1).

A set of 12 samples containing drinking water, surface water and waste water plus a representative standard solution (shown in Tables C.1 and C.2) were analysed in accordance with the standard method.

a) Each of the 13 sets of samples contains As, Sb and Se in oxidation states V/III and VI.

b) Within the set of 13 samples there are duplicate samples of high and low standards and a further reference standard at 30 µg/l.

The performance data are shown in Tables C.1 and C.2 after outlying data have been removed, primarily due to inconsistency of the data set in comparison to both standard measurement and peer laboratory results.

Table C.1 — Performance data for arsenic

Sample	Matrix	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
				%	µg/l	µg/l	%	µg/l	%	µg/l	%
1	Nutwell hard water 90 % spike	9	21	0,0	18,0	19,0	105,8	1,18	6,2	0,56	2,9
2	Rotherham interm. water 15 %	9	21	0,0	3,0	2,90	96,7	0,333	11,5	0,130	4,5
3	Bradford soft water 60 % spike	9	21	0,0	12,0	11,9	98,8	0,68	5,7	0,34	2,9
4	Low standard 20 %	9	21	0,0	4,0	3,95	98,9	0,405	10,2	0,163	4,1
5	Blank	—	—	—	—	—	—	—	—	—	—
6	High standard 80 %	9	21	0,0	16,0	15,7	98,3	1,31	8,3	0,79	5,0
7	Blank	—	—	—	—	—	—	—	—	—	—
8	Rotherham interm. water 15 %	9	21	0,0	3,0	2,94	97,9	0,375	12,8	0,165	5,6
9	Low standard 20 %	9	21	0,0	4,0	3,88	97,1	0,389	10,0	0,147	3,8
10	High standard 80 %	9	21	0,0	16,0	15,5	97,0	1,61	10,4	0,31	2,0
11	Nutwell hard water 90 % spike	9	21	0,0	18,0	18,9	105,0	0,97	5,1	0,33	1,8
12	Bradford soft water 60 % spike	9	21	0,0	12,0	11,9	99,2	0,92	7,7	0,28	2,3
13	Standard 30 µg/l	7	17	15,0	30,0	29,4	98,0	2,04	6,9	0,72	2,5

l number of laboratories after outlier rejection

n number of analytical results after outlier rejection

o percentage of outliers

X assigned value

$\bar{\bar{x}}$ overall mean of results (without outliers)

η recovery rate

s_R reproducibility standard deviation

$C_{V,R}$ coefficient of variation of reproducibility

s_r repeatability standard deviation

$C_{V,r}$ coefficient of variation of repeatability

Table C.2 — Performance data for antimony

Sample	Matrix	l	n	o %	X µg/l	$\bar{\bar{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
1	Nutwell hard water 90 % spike	9	21	0,0	18,0	18,8	104,6	2,06	10,9	0,43	2,3
2	Rotherham interm. water 15 %	9	21	0,0	3,0	2,94	97,9	0,296	10,1	0,126	4,3
3	Bradford soft water 60 % spike	9	21	0,0	12,0	12,2	101,3	0,91	7,5	0,35	2,9
4	Low standard 20 %	9	21	0,0	4,0	4,00	99,9	0,370	9,3	0,130	3,3
5	Blank	—	—	—	—	—	—	—	—	—	—
6	High standard 80 %	9	21	0,0	16,0	15,8	99,0	1,16	7,3	0,40	2,6
7	Blank	—	—	—	—	—	—	—	—	—	—
8	Rotherham interm. water 15 %	8	20	0,0	3,0	2,88	96,1	0,344	12,0	0,073	2,5
9	Low standard 20 %	7	19	5,0	4,0	3,97	99,2	0,382	9,6	0,133	3,3
10	High standard 80 %	8	20	0,0	16,0	16,0	100,2	1,27	7,9	0,42	2,6
11	Nutwell hard water 90 % spike	7	18	10,0	18,0	19,1	106,0	1,24	6,5	0,44	2,3
12	Bradford soft water 60 % spike	7	18	10,0	12,0	12,3	102,2	0,95	7,8	0,39	3,2
13	Standard 30 µg/l	7	17	15,0	30,0	29,1	97,1	2,20	7,5	0,58	2,0
Explanation of symbols see Table C.1											

ICS 13.060.50

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