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Water quality — Determination of arsenic and antimony —

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

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

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

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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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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

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

- *Part 1: Method using hydride generation atomic fluorescence spectrometry (HG–AFS)*
- *Part 2: Method using hydride generation atomic absorption spectrometry (HG–AAS)*

Introduction

This part of ISO 17378 should be used by analysts experienced in the handling of trace elements at very low concentrations.

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

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

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

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

Water quality — Determination of arsenic and antimony —

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

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this document be carried out by suitably trained and experienced staff.

1 Scope

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

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

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-5, *Water quality — Sampling — Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems*

ISO 5667-6, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*

ISO 5667-8, *Water quality — Sampling — Part 8: Guidance on the sampling of wet deposition*

ISO 5667-11, *Water quality — Sampling — Part 11: Guidance on sampling of groundwaters*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

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

3 Principle

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

3.1 Arsenic

An aliquot of sample is acidified with hydrochloric acid (5.3). Potassium iodide–ascorbic acid reagent (5.9) is added to ensure quantified reduction of arsenic(V) to arsenic(III). The sample solutions are treated with sodium tetrahydroborate (5.5) to generate the covalent gaseous arsenic trihydride (arsine, AsH_3). The hydride and excess hydrogen are swept out of the generation vessel in case of batch mode and out of the gas/liquid separator in case of the continuous mode into a heated silica cell. After atomization, the absorbance of arsenic is determined at a wavelength λ = 193,7 nm. The procedure is automated by means of auto-sampler and control software.

3.2 Antimony

An aliquot of sample is digested with hydrochloric acid (5.3). Potassium iodide–ascorbic acid reagent (5.9) is added to ensure quantified reduction of the antimony(V) to antimony(III). The sample solutions are then treated with sodium tetrahydroborate (5.5) to generate the covalent gaseous antimony trihydride (stibane, SbH_3). The hydride and excess hydrogen are swept out of the generation vessel in case of batch mode and out of the gas/liquid separator in case of continuous mode. After atomization, the absorbance of antimony is determined at a wavelength λ = 217,6 nm. The procedure is automated by means of auto-sampler and control software.

4 Interferences

4.1 General

The hydride generation technique is prone to interferences by transition and easily reducible metals. For the majority of natural water samples, this type of interference shall not be significant. The user should carry out recovery tests on typical waters and also determine the maximum concentrations of potentially interfering elements, using appropriate methods. If such interferences are indicated, the level of interferences should be assessed by performing spike recoveries.

Metals which are readily reduced by sodium tetrahydroborate may also cause interferences. In particular, these include chromium, iron, copper, nickel, and lead. If the concentrations of these elements specified in Table 1 are exceeded, a significant decrease of absorption may occur.

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

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

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

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

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

4.2 Arsenic

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

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

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

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

4.3 Antimony

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

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

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

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

5 Reagents

5.1 General requirements

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

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

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

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

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

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

5.4 **Hydrochloric acid**, $c(\mathrm{HCl}) = 1$ 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 Figure B.1).

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

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

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

NOTE The concentration of $NaBH_4$ is dependent on the hybride generator manifold and flow-rate conditions. See recommendations of the manufacturer.

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

5.8 **Nitric acid**, $\rho(HNO_3)$ = 1,40 g/ml.

NOTE Nitric acid is available both as $\rho(HNO_3)$ = 1,40 g/ml [$w(HNO_3)$ = 650 g/kg] and $\rho(HNO_3)$ = 1,42 g/ml [$w(HNO_3)$ = 690 g/kg].

To prepare a nitric acid cleaning mixture, dilute nitric acid (1,40 g/ml) with an equal volume of water (5.2) by carefully adding the acid to the water.

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 and dilute to 500 ml.

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

5.10 **Reagent blank**.

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

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

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

5.11 Standard solutions (arsenic and antimony).

5.11.1 Arsenic solutions (standard, stock and calibration).

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

Use a quantitative stock solution with an 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 providing 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 stock solution D, 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.

5.11.1.5 Arsenic calibration solutions.

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

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

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

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

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

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

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

These calibration solutions contain 1 µg/l, 2 µg/l, 3 µg/l, 4 µg/l and 5 µg/l arsenic respectively.

They shall be prepared on the day of use.

The use of piston pipettes is permitted and enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed.

Once an established calibration pattern has been confirmed, the number of standards used routinely may be reduced. Any such change shall not alter the result obtained from tests or the ranking with other samples.

5.11.2 Antimony solutions (standard, stock and calibration).

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

Use a quantitative stock solution with an antimony(III) content of (1 000 ± 2) mg/l.

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

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

Place (2,743 ± 0,002) g of potassium antimony(III) oxide tartrate hemihydrate, $K(SbO)C_4H_4O_6 \cdot 0{,}5H_2O$ in a 1 000 ml volumetric flask.

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

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

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 ± 0,1) ml of potassium iodide–ascorbic acid solution (5.9) and fill up to the mark with water (5.2).

This solution shall be prepared weekly.

5.11.2.4 Antimony stock solution D, 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 should 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.

5.11.2.5 Antimony calibration solutions.

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

Prepare a minimum of five antimony calibration solutions from the antimony standard solution C (5.11.2.3) covering the working range of expected antimony concentrations.

For example, for an operating range from 1 µg/l to 5 µg/l proceed as follows.

Pipette into a series of five 100 ml volumetric flasks (1 ± 0,01) ml, (2 ± 0,02) ml, (3 ± 0,03) ml, (4 ± 0,04) ml, and (5 ± 0,05) ml, respectively, of antimony standard solution C (5.11.2.3).

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

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

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

These calibration solutions contain 1 µg/l, 2 µg/l, 3 µg/l, 4 µg/l, and 5 µg/l antimony, respectively.

They shall be prepared on the day of use.

The use of piston pipettes is permitted and enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed.

Once an established calibration pattern has been confirmed, the number of standards used routinely may be reduced. Any such change shall not alter the result obtained from tests or the ranking with other samples.

6 Apparatus

Usual laboratory equipment and in particular the following.

The following are set out as guidelines. In general, the manufacturer's instructions shall be followed.

6.1 Atomic absorption spectrometer, equipped with a hydride generation system and a heated silica tube atomizer or a graphite furnace atomizer (preferably equipped with a background correction system) is recommended. Automated flow systems [flow injection analysis (FIA) or continuous flow analysis (CFA)] for hydride generation are suitable and more usual, but batch systems are also adequate. The description below follows a continuous flow regime.

Use a radiation source which emits wavelength $\lambda = 193,7$ nm for arsenic and wavelength $\lambda = 217,6$ nm for antimony with an adequate spectral radiance.

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 absorption detector.

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

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

6.3 Laboratoryware.

6.3.1 General requirements.

For the determination of arsenic or antimony at very low concentrations, contamination and loss are of critical consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment. Use a clean laboratory work area, designated for trace element sample handling.

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, $c(\text{HCl}) = 1$ mol/l (5.4) and leave for 24 h.

Disposable (single-use) plastics laboratoryware does not require special cleaning, providing that negligible arsenic contamination in that material is demonstrated.

6.3.2 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.

6.3.3 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 adsorb nor desorb the analyte under test.

6.3.4 Auto-sampler vials.

Use vials constructed of materials as specified in 6.3.2.

6.4 Sample processing equipment.

6.4.1 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.

6.4.2 Balance.

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

6.4.3 Digestion apparatus.

Pre-digestion is not required for water samples within the scope of this part of ISO 17378.

7 Sampling and sample preparation

7.1 Sampling technique

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 6.3.2.

For the determination of arsenic or antimony in aqueous samples, acidify at time of sampling to pH < 2. Hydrochloric acid (5.3) (3 ± 0,1) ml per litre is sufficient for most samples. Ensure that the pH is less than 2; otherwise, add more hydrochloric acid as required.

On receipt in the laboratory, all samples shall be logged and processed in a timeframe that will not affect the integrity of the analyte.

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

NOTE Sample preservation using dilute nitric acid (5.8) is suitable, providing that 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) or antimony(III) prior to the step of hydride generation.

7.2.1 Standard procedure for water samples with no solid or organically bound arsenic or antimony

Pre-treat water samples free from solid materials and organically bound arsenic or antimony, 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) to arsenic(III) or of antimony(V) to antimony(III).

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 using the correct proportion of nitric acid (5.8) and hydrochloric acid (5.4). This requires attention to detail.

8 Instrumental set up

Configure the instrumentation as described in the instrument manufacturer's manual. It is recommended that automatic background correction be employed. The following relates to continuous flow systems, for details on flow injection instruments or batch analysers refer to manufacturer's instruction manual.

Check tubing for wear and pumping reliability each day that 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. See manufacturer's instructions.

Set up the continuous flow vapour generator according to the manufacturer's instructions. Ensure that the reagent flows are within the accepted balances or ratios. Once stable conditions are established analysis can proceed. Both standards and samples shall be quantified using the same flow characteristics.

For samples which are above the calibration at a given range setting, reanalyse after dilution of the sample into the calibration range. If the sample is diluted, then the diluent shall be the reagent blank (5.10) i.e. matrix-matched. Samples which are digested shall be matrix-matched against standards and blanks to provide reliable data.

9 Procedure

9.1 General requirements

Before beginning the measurement procedure, set the instrument parameters according to the manufacturer's instructions (wavelength λ = 193,7 nm for arsenic and wavelength λ = 217,6 nm for antimony).

Align the silica tube atomizer or if using the graphite furnace atomization condition an iridium-coated graphite tube according to the manufacturer's instructions.

Set the argon or nitrogen flow until a constant signal has been reached.

If a flow system is used, hydrochloric acid (5.4) shall be used as carrier solution. See recommendations of the manufacturer.

The sodium tetrahydroborate solution (5.7) and all pre-reduced test solutions (reagent blank solution 5.10), calibration solutions (5.11.1.5 for arsenic and 5.11.2.5 for antimony) and samples (7.2) are introduced to the flow system according to the manufacturer's instructions and measurements are carried out.

Measure the absorbance of each solution at least twice.

NOTE 1 Inorganic arsenic occurs in two oxidation states, As(V) and As(III), and inorganic antimony occurs in two oxidation states, Sb(V) and Sb(III). It is essential to convert all arsenic or antimony species to the As(III) or Sb(III) state prior to generating the hydrides. Arsenic(V) or antimony(V) gives a significantly lower response than arsenic(III) or antimony(III).

NOTE 2 See Clause 4.

NOTE 3 For arsenic and antimony, prepare As(V) or Sb(V) standards from stock solution D (5.11.1.4 or 5.11.2.4) at known concentrations and analyse after pre-reduction to validate the pre-reduction stage of this procedure.

9.2 Analysis using the method of standard calibration

A standard calibration shall only be applied if matrix effects can be excluded. Otherwise samples can be diluted, assuming that the arsenic content is high enough. If not, use the standard addition method (9.3).

Plot a calibration graph for the analysis using the following procedure.

Prepare calibration solutions as specified in 5.11.1.5 or 5.11.2.5.

Determine the absorbance references of the arsenic calibration solutions (5.11.1.5 or 5.11.2.5) and of the undigested, but pre-reduced reagent blank solution (5.10).

Establish a calibration graph using the series of results thus obtained.

Measure the absorbances of the test solutions and of the pre-reduced reagent blank solution (5.10). If the arsenic or antimony contents of any of test solutions are not within the range of the calibration graph, dilute the original sample and repeat the analysis.

After each series of samples, and in any case after about 10 to 20 measurements, use the reagent blank solution (5.10) and a calibration solution of average concentration to check whether the measured values still agree with the calibration graph.

Measure the absorbance of each solution at least twice.

Calculate the arsenic or antimony content of the measured solutions according to 10.2.

9.3 Analysis using the standard addition method of calibration

The use of the method of standard addition can compensate for errors due to matrix effects, providing that no additive errors occur and that the absorbance references of the spiked measurement solutions are within the working range of the calibration function.

Prepare and measure at least two test solutions containing each standard addition. An example for the preparation of 10 ml test portions (10 ml volumetric flasks) is shown in Table 4.

Table 4 — Example of standard addition method (volumes adapted for 10 ml volumetric flasks)

Test solution	**Volume**	**KI–ascorbic-acid-solution (5.9)**	**Standard solution C (5.11.1.3 or 5.11.2.3)**	**Concentration of arsenic or antimony in solution added**
	ml	ml	ml	µg/l
Test solution according to 7.2	5	0,5	0	0
Reference solution 1	5	0,5	0,1	2
Reference solution 2	5	0,5	0,2	4
Reference solution 3	5	0,5	0,3	6

Fill up all volumetric flasks to the mark with water (5.2).

NOTE The filling of the volumetric flasks to 10 ml is not to be considered as a dilution step in the subsequent calculation since the dilution factor is already included in the calculation of the concentration of arsenic and antimony in the solutions added in Table 4.

Treat and measure the reagent blank solution (5.10) in the same way.

Measure the absorbance of each solution at least twice.

Calculate the arsenic and antimony content of the measured solutions according to (10.3).

If volumetric flasks of other nominal volumes are used, adapt volumes of test, reagent and standard solution accordingly and maintain the quantitative ratios.

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):

$$\rho(\mathrm{As}) = \frac{(A_\mathrm{s} - A_\mathrm{s0})V_\mathrm{M}}{b_\mathrm{As}V_\mathrm{P}} \quad (1)$$

$$\rho(\mathrm{Sb}) = \frac{(A_\mathrm{s} - A_\mathrm{s0})V_\mathrm{M}}{b_\mathrm{Sb}V_\mathrm{P}} \quad (2)$$

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;
A_s	is the absorbance response of the water sample;
A_s0	is the absorbance of the reagent blank solution;
b_As, b_Sb	are the slopes of the calibration curve 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.

If dilutions deviating from the above mentioned steps are used, the calculation shall be modified accordingly.

A second order calibration function is allowed. In this case, carry out the calculations according to ISO 8466-2.

The use of appropriate instrument software for the calculations is also allowed.

10.3 Calculation using the standard addition method

Prepare a calibration line with concentration as abscissa and absorbance as ordinate. Use the measured absorbance references of the unspiked and spiked measurement solutions step-wise with increasing arsenic and antimony concentrations.

Obtain the concentration of arsenic and antimony in the sample by extrapolation of the calibration line to absorbance $A = 0$. Similarly, determine the arsenic and antimony concentrations of the reagent blank solution and subtract from the result obtained for the sample.

Alternatively, carry out the evaluation by an automated method of linear regression.

11 Expression of results

Report the results in µg/l and round them to the nearest 0,1 µg/l. Do not use more than two significant figures.

EXAMPLES

Arsenic (As)	2,3 µg/l	Antimony (Sb)	2,3 µg/l
Arsenic (As)	13 µg/l	Antimony (Sb)	13 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 17378-2:2014);

b) complete identification of the sample;

c) date of sampling and date of analysis;

d) expression of results as indicated in Clause 11;

e) sample pre-treatment;

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

g) identification of laboratory and experience of these measurements.

Annex A
(informative)

Additional information

A.1 The method requires proper attention to detail to attain the low levels of measurement. Other stabilization strategies have been proven particularly the addition of high purity nitric acid.

A.2 The method and any variation from it shall be rigorously checked for performance using statistical data and analytical quality control sample materials, including certified reference materials.

A.3 Air shall not be used because of the risk of explosion.

A.4 Although water vapour is not normally a problem with atomic absorption methods in automated instruments moisture could condense in the transfer lines. A Nafion[1] dryer system can alleviate this potential problem; these are commercially available.

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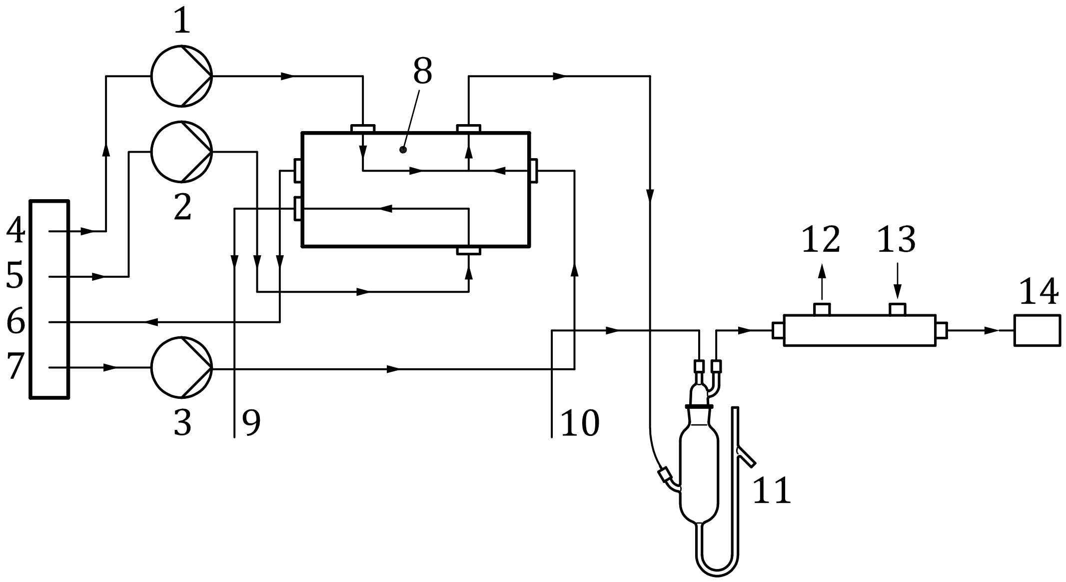
[1] Nafion is the trade name of a product supplied by Dupont. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex B
(informative)

Schematic flow diagram and signal response



Key

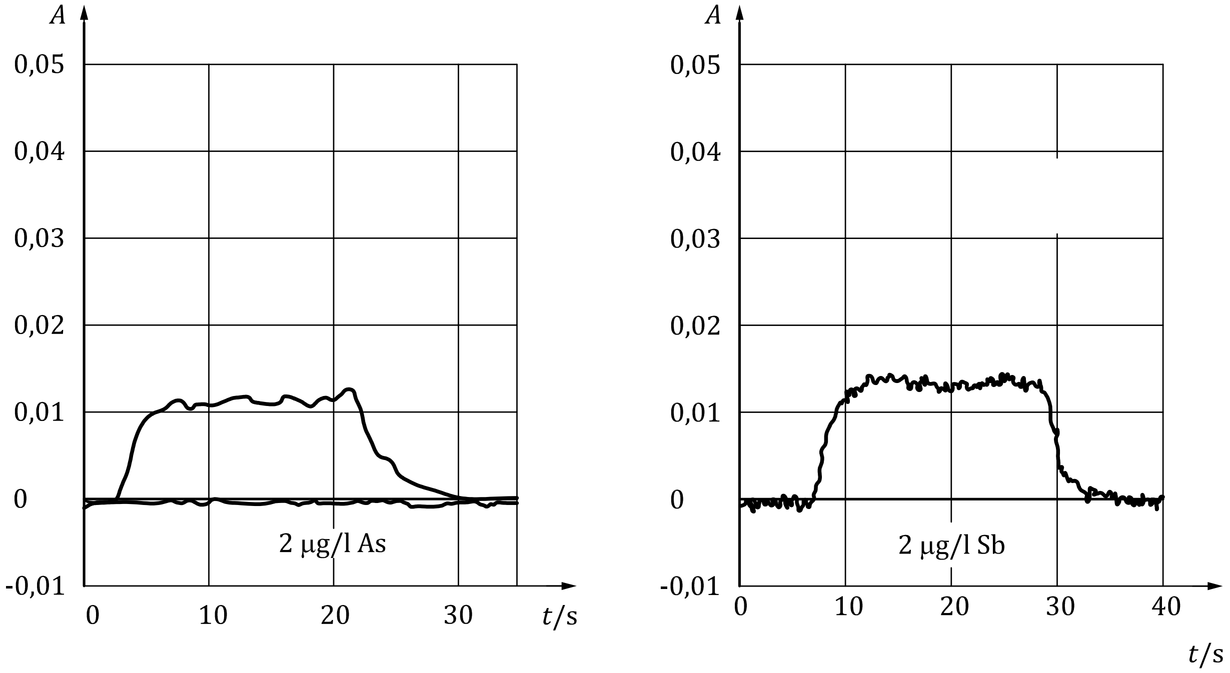
1	pump 1	6	recycle	11	gas/liquid separator
2	pump 2	7	reductant	12	dryer gas out from Nafion1) dryer system (A.4)
3	pump 3	8	sample valve	13	dryer gas in to Nafion1) dryer system (A.4)
4	blank	9	waste	14	atomic absorption spectrometer (AAS)
5	sample	10	argon carrier gas		

Argon or nitrogen can be used.

NOTE This continuous flow vapour generator consists of a constant speed peristaltic pump to deliver sodium tetrahydroborate solution (5.7), reagent blank and sample. A switching valve alternates between the reagent blank and sample or standard solutions. The vapour generator switches between reagent 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 typical 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.



a) As 193,7/Int.

b) Sb 217,6/Int.

Key

A absorbance signal

t time in seconds

NOTE Background signal is made up of instrumental blank and reagent blank. When a sample is analysed the signal from arsenic or antimony in the sample is super imposed on the background level.

Peak rises to its maximum as sample is introduced and returns to baseline when sample is replaced with reagent blank.

Sample/standards and blank shall be matrix-matched.

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

Annex C
(informative)

Example of enrichment technique

C.1 Introduction

If arsenic or antimony is enriched in an iridium-coated graphite tube prior to atomization and measurement by AAS, the lower limit of the working range is 0,02 µg/l within the scope of this part of ISO 17378. The concentration of the arsenic or antimony in the blank solution shall not exceed 10 ng/l. If the concentration of the blank is controlled, then the levels of detection achieved with the enrichment techniques exceed the requirement set out in the scope of this method.

C.2 Principles involved in this technique

An aliquot of the sample is digested with concentrated hydrochloric acid. Potassium iodide–ascorbic acid reagent 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 to generate the covalent gaseous arsenic trihydride (AsH_3) and covalent gaseous antimony trihydride (SbH_3). The hydride and excess hydrogen are swept out of the generation vessel and transferred and sequestrated in an iridium-coated graphite tube. After atomization, the absorbance of arsenic is determined at a wavelength $\lambda = 193,7$ nm and of antimony at a wavelength of $\lambda = 217,6$ nm. The procedure is automated by means of an autosampler and control software.

C.3 Additional reagents and standards

Use a commercially available quantitative stock solution with an iridium content of 1 000 mg/l. This solution is considered to be stable for at least one year, but in reference to stability, see the recommendations of the manufacturer.

C.4 Graphite furnace atomic absorption spectrometer

An atomic absorption spectrometer equipped with a hydride system and a graphite furnace atomizer (preferably equipped with a background correction system) is recommended. Automated flow systems [flow injection analysis (FIA) or continuous flow analysis (CFA)] for hydride generation are suitable and more usual but batch systems are also adequate.

If trapping analyte on the graphite tube, the generated hydride is guided into the tube with the help of the furnace auto-sampler. The tube requires heating to about 300 °C to decompose the hydrides. The analyte arsenic or antimony is trapped on the activated graphite surface. The auto-sampler capillary requires a silica or titanium tip. The auto-sampler graphite furnace and hydride generator require synchronization, normally by computer control.

C.5 Instrumental set up

Configure the instrumentation as described in the instrument manufacturer's manual.

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.

Prior to trapping the analyte in a graphite tube, the electrothermal atomizer shall first be activated. Introduce the recommended volume of iridium chloride solution (C.3) into the graphite tube. Dry, pyrolyze and heat out according to the manufacturer's recommendations. The process of tube activation is repeated twice and requires about 10 min. The activated tubes can be used for at least 300 measurement cycles before they have to be reactivated.

The programmes for furnace and hydride generator are set according to the recommendations of the manufacturer.

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

C.6 Procedure

Before beginning the measurement procedure, set the instrument parameters according to the manufacturer's instructions (wavelength λ = 193,7 nm for arsenic and wavelength λ = 217,6 nm for antimony).

If trapping analyte in the graphite tube, the process of hydride generation is similar to the silica atomizer procedure. The generated hydride, however, is pre-concentrated in the graphite tube. The sensitivity and the detection limits are therefore a function of the preconcentration time. A pre-concentration time of between 10 s to 30 s is usually required to obtain detection limits required by this part of ISO 17378.

Follow the manufacturer's recommendations for the hydride generator programme. The trapped arsenic or antimony is atomized using a short graphite furnace programme consisting of a step to remove excess hydrogen from the graphite tube (approximately 10 s at 300 °C), an atomization step (approximately 5 s at 2 200 °C) and a cleaning step (approximately 5 s at 2 300 °C). For more detailed information, follow the manufacturer's recommendations.

While passing argon or nitrogen, adjust the zero point after a steady baseline signal has been reached.

If a flow system is used, hydrochloric acid (5.4) shall be used as carrier solution. See the recommendations of the manufacturer.

The sodium tetrahydroborate solution (5.7) and all pre-reduced test solutions [reagent blank solution (5.10), calibration solutions (5.11.1.5 or 5.11.2.5) and samples (7.2)] are introduced to the flow system according to the manufacturer's instructions and measurements are carried out.

Measure the absorbance of each solution at least twice. The user shall confirm that the operation of the procedures in the preceding provides data in the range of detection and repeatability required. The results shall be traceable to international standards.

Annex D
(informative)

Performance data

An international laboratory 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 D.1 and D.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 D.1 and D.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 D.1 — Performance data for arsenic

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	8	22	0,0	18,0	18,4	102,1	1,38	7,5	0,95	5,2
2	Rotherham interm. water 15 %	8	22	0,0	3,0	2,81	93,7	0,389	13,8	0,174	6,2
3	Bradford soft water 60 % spike	8	23	0,0	12,0	11,8	98,4	0,83	7,1	0,59	5,0
4	Low standard 20 %	8	22	0,0	4,0	3,82	95,4	0,479	12,6	0,181	4,7
5	Blank	—	—	—	—	—	—	—	—	—	—
6	High standard 80 %	8	23	0,0	16,0	15,6	97,3	1,09	7,0	0,90	5,8
7	Blank	—	—	—	—	—	—	—	—	—	—
8	Rotherham interm. water 15 %	8	22	0,0	3,0	3,07	102,3	0,263	8,6	0,145	4,7
9	Low standard 20 %	8	22	0,0	4,0	3,98	99,5	0,301	7,6	0,217	5,5
10	High standard 80 %	8	22	0,0	16,0	15,0	94,0	1,27	8,4	0,99	6,6
11	Nutwell hard water 90 % spike	8	22	0,0	18,0	18,4	102,2	1,30	7,1	0,78	4,2
12	Bradford soft water 60 % spike	8	22	0,0	12,0	11,8	98,4	0,96	8,1	0,36	3,1
13	Standard 30 µg/l	7	19	13,6	30,0	28,4	94,6	1,96	6,9	0,87	3,1

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 D.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	8	23	0,0	18,0	19,3	107,3	2,22	11,5	0,91	4,7
2	Rotherham interm. water 15 %	7	20	0,0	3,0	3,05	101,7	0,299	9,8	0,234	7,7
3	Bradford soft water 60 % spike	8	23	0,0	12,0	12,5	103,8	1,13	9,1	0,55	4,4
4	Low standard 20 %	7	20	0,0	4,0	3,94	98,4	0,274	7,0	0,203	5,2
5	Blank	—	—	—	—	—	—	—	—	—	—
6	High standard 80 %	8	23	0,0	16,0	15,5	96,7	1,18	7,6	0,90	5,8
7	Blank	—	—	—	—	—	—	—	—	—	—
8	Rotherham interm. water 15 %	7	20	0,0	3,0	2,88	96,1	0,309	10,7	0,163	5,7
9	Low standard 20 %	8	21	0,0	4,0	3,99	99,8	0,374	9,4	0,242	6,1
10	High standard 80 %	8	22	0,0	16,0	15,7	98,1	1,85	11,8	1,10	7,0
11	Nutwell hard water 90 % spike	7	19	13,6	18,0	18,7	103,8	1,20	6,4	0,85	4,5
12	Bradford soft water 60 % spike	7	19	13,6	12,0	11,9	98,8	0,78	6,5	0,61	5,1
13	Standard 30 µg/l	6	17	26,1	30,0	29,2	97,2	1,40	4,8	1,10	3,8
Explanation of symbols, see Table D.1											

Bibliography

[1] Dedina J., & Tsalav D.L. *Hydride generation atomic absorption spectrometry*. Chichester: Wiley, 1995. 526 p.

[2] Welz B., & Sperling M. *Atomic absorption spectrometry*. Weinheim: Wiley-VCH, Fourth Edition, 1997

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