TECHNICAL SPECIFICATION

ISO/TS 17379-2

First edition
2013-07-15

Water quality — Determination of selenium —

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

Qualité de l'eau — Dosage du sélénium —

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

Reference number
ISO/TS 17379-2:2013(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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, www.iso.org/directives.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received, www.iso.org/patents.

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

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/TS 17379-2 cancels and replaces ISO 9965:1993, which has been technically revised.

ISO/TS 17379 consists of the following parts, under the general title *Water quality — Determination of selenium*:

- *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/TS 17379 is intended for use by analysts experienced with the handling of trace elements at very low concentrations.

Inorganic selenium normally occurs in two oxidation states; Se(VI) and Se(IV). It is essential to convert all selenium species to the Se(IV) state prior to generating the hydrides. Selenium(VI) does not form a hydride.

In natural water sources, selenium compounds generally occur in very small quantities, typically less than 1 µg/l. Higher concentrations may be found, e.g. in industrial waste water. Selenium occurs naturally in organic and inorganic compounds and may have oxidation states –II, 0, IV, and VI.

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

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

Water quality — Determination of selenium —

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 in accordance with this document be carried out by suitably trained and experienced staff.

1 Scope

This part of ISO/TS 17379 specifies a method for the determination of selenium. The method is applicable to drinking water, surface water, ground water, and rain water. The dynamic range of this part of ISO/TS 17379 is approximately 0,5 µg/l to 20 µg/l. Samples containing selenium at higher concentrations than the application range can be analysed following appropriate dilution. The method is unlikely to detect organoselenium compounds.

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

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

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

An aliquot of sample is treated with concentrated hydrochloric acid (5.2). Se(VI) is pre-reduced to Se(IV) by gently refluxing in 6 mol/l HCl for 1 h. Care is necessary to avoid any losses of volatile selenium components. A suitable apparatus is shown in Figure B.3. The sample solutions are then treated with sodium tetrahydroborate to generate the covalent gaseous hydride (SeH_2). The hydride and excess hydrogen are swept out of the generation vessel in the batch mode and out of the gas/liquid separator in the continuous mode into a heated silica cell. After atomization the absorbance of selenium is determined at a wavelength, $\lambda = 196,0$ nm. The procedure is automated by means of an auto sampler and control software.

Other measurement techniques may be applicable provided that the performance criteria can be adequately demonstrated or exceeded by the user laboratory (see Annex C).

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.

The reaction conditions set out in this part of ISO/TS 17379 have been chosen so that any interferences are reduced to a minimum.

See References [1][2] for further information concerning these interferences and the technique.

These elements do not cause interferences provided the concentrations specified in Table 1 are not exceeded.

Table 1 — Maximum mass concentrations of hydride-forming or volatile elements causing no interferences

Element				
As	Sb	Sn	Te	Hg
Mass concentration of interfering elements in test solution mg/l				
1	1	0,1	1	0,1

If the concentrations in Table 1 are exceeded, it may be necessary to use the standard addition method (9.3). Assuming that the selenium content is high enough, an appropriate dilution of the water sample is preferred.

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 2 are exceeded, a significant decrease of absorption may occur.

Table 2 — Maximum mass concentrations in test solution of interfering heavy metals (valid for flow systems)

Interfering element				
Cr	Fe	Cu	Ni	Pb
Mass concentration in test solution mg/l				
500	500	500	250	100

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

5 Reagents and standards

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

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

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

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

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

5.3 **Hydrochloric acid**, $c(\text{HCl}) = 1$ mol/l.

5.4 **Sodium hydroxide**, NaOH.

5.5 Sodium tetrahydroborate solution, $\rho(\text{NaBH}_4) = 13$ g/l.

Dissolve an appropriate amount of sodium tetrahydroborate (13 g has proven suitable for the system illustrated in Annex B) in 500 ml water (5.1) and add (4,0 ± 0,1) g of sodium hydroxide (5.4). Dilute to 1 000 ml with water (5.1). Prepare on day of use and do not keep in a closed container because of pressure build-up due to hydrogen evolution.

NOTE 1 The concentration of NaBH_4 is dependent on the hydride generator manifold and flow rate conditions. See recommendations of the manufacturer.

NOTE 2 Suitably stored sodium tetrahydroborate pellets have a shelf-life of 6 months.

5.6 Nitric acid, $\rho(\text{HNO}_3) = 1{,}40$ g/ml.

NOTE Nitric acid is available both as $\rho(\text{HNO}_3) = 1{,}40$ g/ml [$w(\text{HNO}_3) = 650$ g/kg] and $\rho(\text{HNO}_3) = 1{,}42$ g/ml [$w(\text{HNO}_3) = 690$ g/kg].

Prepare a nitric acid cleaning mixture by diluting nitric acid [$\rho(\text{HNO}_3) = 1{,}40$ g/ml] with an equal volume of water (5.1) by carefully adding the acid to the water.

5.7 Reagent blank.

For each 1 000 ml, prepare a solution containing (300 ± 3) ml of hydrochloric acid (5.2). Dilute to volume with water (5.1).

On the continuous flow system, the reagent blank solution is run as background. Since the blank solution may contain detectable trace levels of selenium, it is important that the same reagents be used for both sample and standard preparation, as well as for preparation of the reagent blank. The analyte signal is superimposed on this signal once the sample is introduced into the measurement cycle. The selenium concentration of the blank solution should be less than the lower level of interest.

5.8 Selenium standard solutions.

5.8.1 Selenium stock solution A, ρ[Se(IV)] = 1 000 mg/l.

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

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

NOTE Other stock solutions may be available and can be used providing the uncertainty of the measurement is not compromised.

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

Place 1,094 g of sodium selenite (Na_2SeO_3) dried for 2 h at (105 ± 3) °C into a 500 ml volumetric flask.

Add 200 ml of water (5.1) and 200 ml of hydrochloric acid (5.3) and dissolve the sodium selenite completely by stirring.

Dilute to 500 ml with water (5.1) and mix thoroughly.

5.8.2 Selenium standard solution B, ρ[Se(IV)] = 10 mg/l.

Pipette (1 ± 0,01) ml of selenium stock solution A (5.8.1) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.2) and fill up to the mark with water (5.1).

This solution is stable for one month.

5.8.3 Selenium standard solution C, ρ[Se(IV)] = 100 µg/l.

Pipette (1 ± 0,01) ml of selenium standard solution B (5.8.2) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.2) and fill up to the mark with water (5.1).

This solution is stable for one week.

5.8.4 Selenium standard solution D, ρ[Se(IV)] = 10 µg/l.

Pipette (10 ± 0,1) ml of selenium standard solution C (5.8.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.7).

This solution shall be prepared freshly on the day of use.

5.8.5 Selenium stock solution E, ρ[Se(VI)] = 1 000 mg/l.

Dissolve (2,392 ± 0,002) g of sodium selenate (Na_2SeO_4) after drying at (105 ± 3) °C for 2 h in 500 ml water (5.1), then transfer the solution quantitatively to a 1 000 ml volumetric flask and fill up to the mark with water (5.1).

Use this standard to prepare a suitable selenium(VI) standard to check quantitative recovery of selenium(IV).

The solution is stable for at least six months.

5.8.6 Selenium calibration solutions.

A minimum of five independent calibration solutions shall be used. Perform the calibration in accordance with ISO 8466-1.

Prepare a minimum of five selenium calibration solutions from the selenium standard solution C (5.8.3) covering the working range of expected selenium concentrations.

For the operating range from 1 µg/l to 5 µg/l, for example, 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 selenium standard solution C (5.8.3).

Add 30 ml of hydrochloric acid (5.2).

Dilute to 100 ml with water (5.1) and mix thoroughly.

These calibration solutions contain 1 µg/l, 2 µg/l, 3 µg/l, 4 µg/l, and 5 µg/l selenium 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 a calibration pattern has been established, 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.

6.1.1 General. An 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.

6.1.2 Radiation source for the determination of selenium. Use a radiation source which emits at wavelength $\lambda = 196{,}0$ nm for selenium with an adequate spectral radiance.

6.2 Gas supply. Use argon with a grade specified by the manufacturer.

The gas supply shall be with a two stage regulator and the argon supplied at a pressure recommended by the manufacturer.

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

Nitrogen gas may also be used but has reduced sensitivity.

6.3 Laboratory-ware.

6.3.1 General requirements. For the determination of selenium 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. A clean laboratory work area, designated for trace element sample handling shall be used.

All re-usable laboratory-ware in contact with the sample shall be cleaned prior to use.

Laboratory-ware shall be soaked in the nitric acid cleaning mixture (5.6) for at least 24 h and rinsed five times with water (5.1).

Following this, refill laboratory-ware with hydrochloric acid, $c(\text{HCl}) = 1$ mol/l (5.3) and leave for 24 h.

Disposable (single-use) plastics laboratory-ware does not require special cleaning, provided that negligible selenium contamination in that material is demonstrated.

6.3.2 Storage and sample processing bottles. Use sampling vessels constructed of silica, borosilicate glass or suitable plastics materials] e.g. polytetrafluorethylene (PTFE), perfluoro (ethene-propene) (FEP)] that neither absorb nor desorb the analyte under test.

6.3.3 Instrument reagent reservoir. The reagents are delivered via a peristaltic pump from glass 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 of polystyrene or materials specified in 6.3.2.

6.4 Sample processing equipment.

6.4.1 Air displacement pipette. Use a micropipette system capable of delivering volumes from 10 µl to 1 000 µl with an assortment of metal-free, disposable pipette tips.

6.4.2 Balances. Analytical balance, capable of accurately weighing (standards) to ±0,1 mg; and a top-pan balance, for preparation of solutions, accurate to ±0,1 g.

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 selenium in aqueous samples, acidify at time of sampling to <pH 2. Hydrochloric acid (5.2) (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.

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.

7.2 Pre-reduction

7.2.1 General

Since only Se(IV) reacts quickly and quantitatively under the conditions used in the hydride technique, Se(VI) has to be reduced to Se(IV) prior to the hydride generation step.

7.2.2 Standard procedure for water samples with no solid or organically bound selenium

Pre-treat water samples, free from solid materials and organically bound selenium, 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 (5.2).

Reflux gently for 1 h.

Transfer to a volumetric flask and dilute to 100 ml with water (5.1).

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

For greater accuracy, the sample can also be dispensed by mass. In this case, calculate the volume from the density and the mass and record the volume.

7.2.3 Samples requiring additional digestion

Samples that contain significant amounts of solid material and/or organically bound selenium require an additional digestion step as specified in ISO 15587-1. This is outside the scope of this part of ISO/TS 17379, but samples may be analysed using a similar procedure provided that correctly matrix-matched reagents are prepared using the correct proportion of nitric acid (5.6) and hydrochloric acid (5.2). Blanks and standard solutions shall also be matrix matched.

8 Instrumental set-up

Configure the instrumentation as described in the instrument manufacturer’s manual. 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 length.

Fill the reagent reservoirs with reagent blank solution (5.7) and sodium tetrahydroborate solution (5.5), respectively.

Set up the continuous flow vapour generator according to the manufacturer’s instructions. Ensure that the reagent flows are within the accepted tolerances. 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 for a given range setting, re-analyse after dilution of the sample into the calibration range. If the sample is diluted, then the dilutent shall be the reagent blank (5.7), 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 $\lambda = 196{,}0$ nm).

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

If a flow system is used, hydrochloric acid (5.3) shall be used as carrier solution. See recommendations of the manufacturer.

The sodium tetrahydroborate solution (5.5) and all pre-reduced test solutions (reagent blank solution (5.7), calibration solutions (5.8.6) 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.

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 selenium 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 selenium calibration solutions as described in 5.8.6.

Determine the absorbance references of the selenium calibration solutions (5.8.6) and of the undigested, but pre-reduced reagent blank solution (5.7).

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

Measure the absorbance of the test solutions and of the pre-reduced reagent blank solution (5.7). If the selenium content of the test solution is 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 (5.7) and a calibration solution of average concentration to check whether the measured values still agrees with the calibration graph.

Measure the absorbance of each solution at least twice.

Calculate the selenium 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, provided 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 3.

Table 3 — Example of standard addition method (volumes adapted for 10 ml volumetric flasks)

Test solution	Test solution	Selenium standard solution C (5.8.3)	Concentration of selenium in solution added
	ml	ml	µg/l
Test solution according to 7.2	5	0	0
Reference solution 1	5	0,1	2
Reference solution 2	5	0,2	4
Reference solution 3	5	0,3	6

Fill up all volumetric flasks to the mark with water (5.1).

NOTE The filling of the volumetric flasks to 10 ml is not to be considered as a dilution step in the subsequent calculation.

Treat and measure the reagent blank solution (5.7) in the same way.

Measure the absorbance of each solution at least twice.

Calculate the selenium 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 selenium, $\rho(\text{Se})$ in the samples using Formula (1):

$$\rho(\text{Se}) = \frac{(A_\text{s} - A_{\text{s}0})V_\text{M}}{bV_\text{P}} \tag{1}$$

where

$\rho(\text{Se})$ is the concentration of selenium in the sample in micrograms per litre, µg/l;

A_s is the absorbance response of the water sample;

$A_{\text{s}0}$ is the absorbance response of the reagent blank solution;

b is the slope 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, the calculations shall be carried out as specified in 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 stepwise with increasing selenium concentrations.

Obtain the concentration of selenium in the sample by extrapolation of the calibration line to absorbance $A = 0$. Similarly, determine the selenium concentration 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 micrograms per litre, µg/l, and round them to the nearest 0,1 µg/l. Do not use more than two significant figures.

EXAMPLES

Selenium (Se)	2,3 µg/l
Selenium (Se)	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/TS 17379 (ISO/TS 17379-2:2013);

b) complete identification of the laboratory;

c) complete identification of the sample;

d) expression of results as indicated in Clause 11;

e) sample pre-treatment;

f) any deviations from this part of ISO/TS 17379 and details of all circumstances which could have affected the result.

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 as a carrier gas because of the explosion risk.

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.

---

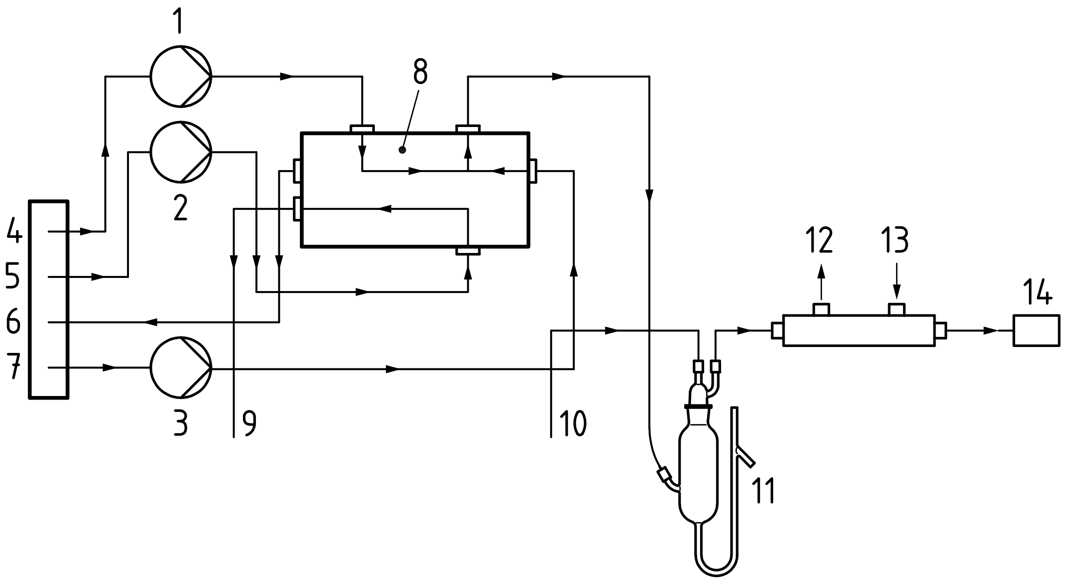
1) Nafion is the trade name of a product supplied by DuPont. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex B

(informative)

Schematic flow diagram and signal response

Figure B.1 shows an example. Any other suitable system may be used subject to satisfactory performance data.



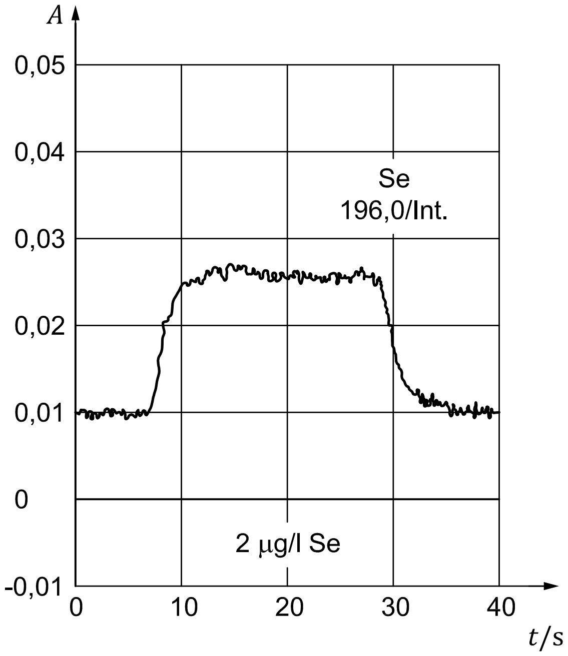
Key

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

Argon or nitrogen can be used.

NOTE This continuous flow vapour generator consists of a constant speed peristaltic pump to deliver sodium tetrahydroborate solution (5.5), 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 selenium in the sample. The typical signal response is shown below in Figure B.2.

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



Key

A	absorbance signal	*t*	time

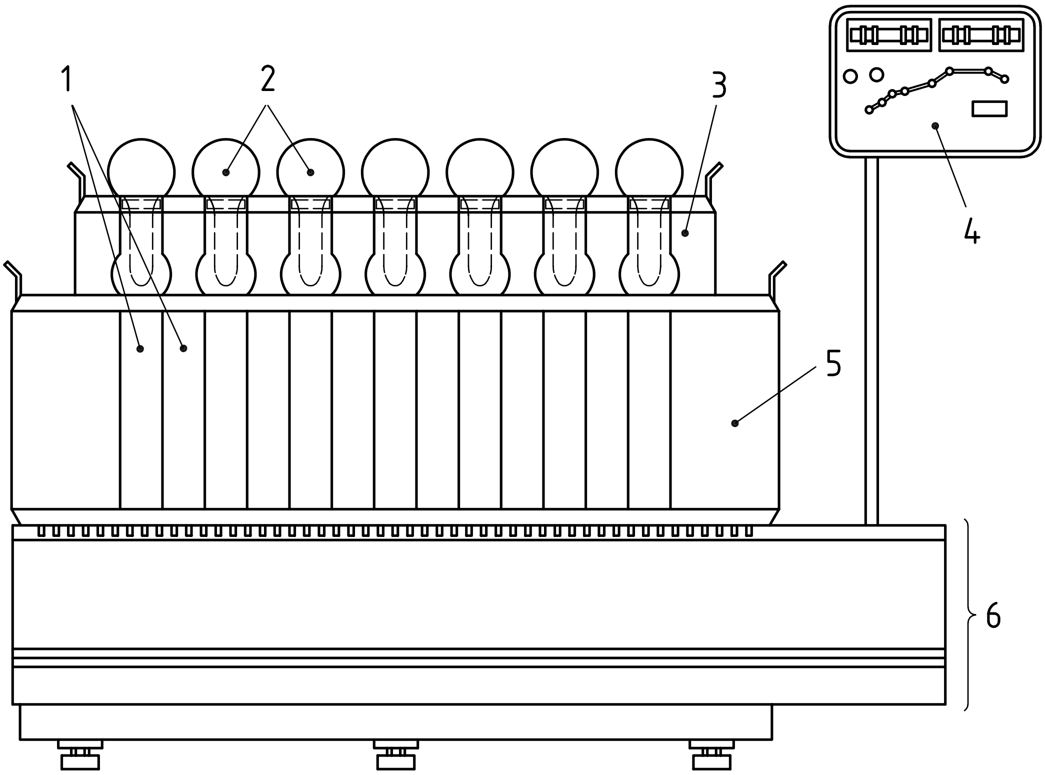
NOTE Background signal is made up of instrumental blank and reagent blank. When a sample is analysed, the signal from selenium in the sample is superimposed on the background level.

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

Samples, standards, and blank shall be matrix matched.

Figure B.2 — Representation of typical signal response from selenium in water sample by continuous flow hydride generation atomic absorption spectrometry

The distillation may be implemented following the use of a block digestion with a “cold finger” device to prevent vaporization losses. See Figure B.3. Control standards should be used to check the transfer of Se(VI) to Se(IV) and that losses are not occurring.



Key

1	sample tubes	3	cold finger rack	5	tube rack
2	cold fingers	4	controller panel	6	block digester/power module

Figure B.3 — An example of a suitable block digester with the cold finger arrangement

Annex C
(informative)

Example of enrichment technique

C.1 Introduction

If selenium is enriched in an iridium-coated graphite tube prior to atomization and measurement by AAS, the lower limit of the working range is 10 ng/l within the scope of this part of ISO/TS 17379. The concentration of the selenium in the blank solution shall not exceed 10 ng/l.

C.2 Principles involved in this technique

An aliquot of the sample is digested with concentrated hydrochloric acid which ensures quantified reduction of the selenium(VI) to selenium(IV). The subsequent sample solutions are then treated with sodium tetrahydroborate to generate the covalent gaseous selenium dihydride (SeH_2). The hydride and excess hydrogen are swept out of a generation vessel in the batch mode and out of a gas/liquid separator in the continuous mode, and transferred and sequestrated in an iridium-coated graphite tube. After atomization, the absorbance of selenium is determined at a wavelength λ = 196,0 nm. The procedure is automated by means of an auto-sampler 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 with reference to guaranteed 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 hydride generated is guided with the help of the furnace auto-sampler into the graphite tube. The tube requires heating to about 300 °C to decompose the hydrides. The analyte selenium is trapped on the activated graphite surface. The auto-sampler capillary shall be equipped with 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 length.

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, pyrolyse, and heat up according to the manufacturers' 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 require reactivation.

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

Fill the reagent reservoirs with reagent blank solution (5.7) and sodium tetrahydroborate solution (5.5), respectively.

C.6 Procedure

C.6.1 General requirements

Before beginning the measurement procedure, set the instrument parameters according to the manufacturer's instructions (wavelength λ = 196,0 nm).

If trapping analyte in the graphite tube, the process of hydride generation is similar to the silica atomizer procedure. The hydride generated, however, is preconcentrated in the graphite tube. The sensitivity and the detection limits are therefore a function of the preconcentration time. A preconcentration time of between 10 s to 30 s is usually required to obtain detection limits below 0,05 µg/l.

Follow the manufacturer's recommendations for the hydride generator programme. The trapped selenium 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 (5.3) shall be used as carrier solution. See recommendations of the manufacturer.

Introduce the sodium tetrahydroborate solution (5.5) and all pre-reduced test solutions (reagent blank solution (5.7), calibration solutions (5.8.6), and samples (7.2) into the flow system according to the manufacturer's instructions, and perform measurements.

Measure the absorbance of each solution at least twice. The user shall confirm that the operation of the above procedures 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 P S 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 Table D.1) were analysed in accordance with the standard method. Each of the 13 sets of samples contains As, Se, and Sb in oxidation states V/III/VI. 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 Table D.1 after removal of outliers, identified by inconsistency in the data set when compared to both standard measurements and peer laboratory results.

Table D.1 — Performance data

Sample	**Matrix**	l	n	o	X	$\overline{\overline{x}}$	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	7	20	0,0	18,0	14,5	80,4	9,67	66,8	0,73	5,1
2	Rotherham interm. water 15 %	6	17	15,0	3,0	3,39	113,0	0,466	13,7	0,370	10,9
3	Bradford soft water 60 % spike	5	14	30,0	12,0	11,9	99,5	0,48	4,0	0,45	3,8
4	Low standard 20 %	6	17	15,0	4,0	4,29	107,4	0,288	6,7	0,150	3,5
5	Blank	—	—	—	—	—	—	—	—	—	—
6	High standard 80 %	7	20	0,0	16,0	12,1	75,4	7,38	61,2	1,11	9,2
7	Blank	—	—	—	—	—	—	—	—	—	—
8	Rotherham interm. water 15 %	7	20	0,0	3,0	3,27	109,0	0,620	19,0	0,321	9,8
9	Low standard 20 %	6	17	15,0	4,0	4,02	100,6	0,441	11,0	0,172	4,3
10	High standard 80 %	7	20	0,0	16,0	12,2	76,4	7,83	64,1	0,59	4,8
11	Nutwell hard water 90 % spike	7	20	0,0	18,0	14,3	79,7	9,05	63,1	0,61	4,2
12	Bradford soft water 60 % spike	6	17	15,0	12,0	12,4	103,2	0,97	7,9	0,42	3,4
13	Standard 30 µg/l	7	20	0,0	30,0	29,3	97,7	3,70	12,6	1,49	5,1

l number of laboratories after outlier rejection

n number of analytical results after outlier rejection

o percentage of outliers

X assigned value

$\overline{\overline{x}}$ 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

Bibliography

[1] Dedina J., & Tsalav D.L. *Hydride generation atomic absorption spectrometry*. Chichester: Wiley, 1995. 544 p.

[2] Welz B., & Sperling M. *Atomic absorption spectrometry*. Weinheim: Wiley-VCH, Third Edition, 1998. 965 p.

ICS 13.060.50

Price based on 18 pages