PD ISO/TS 17379-1:2013

BSI Standards Publication

Water quality — Determination of selenium

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

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National foreword

This Published Document is the UK implementation of ISO/TS 17379-1:2013.

The UK participation in its preparation was entrusted to Technical Committee EH/3/2, Physical chemical and biochemical methods.

A list of organizations represented on this committee can be obtained on request to its secretary.

ISBN 978 0 580 70966 1

ICS 13.060.50

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 31 July 2013.

Amendments issued since publication

Date	Text affected

PD ISO/TS 17379-1:2013

TECHNICAL SPECIFICATION

ISO/TS 17379-1

First edition
2013-07-15

Water quality — Determination of selenium —

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

Qualité de l'eau — Dosage du sélénium —

Partie 1: Méthode par spectrométrie de fluorescence atomique à génération d'hydrures (HG-AFS)

Reference number
ISO/TS 17379-1:2013(E)

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Published in Switzerland

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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, www.iso.org/directives.

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

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 can be found, e.g. in industrial waste water. Selenium occurs naturally in organic and inorganic compounds and can 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 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 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 application range of this part of ISO/TS 17379 is from 0,02 µg/l to 100 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 operating conditions selected.

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 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 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 selenium light source, the resulting fluorescence is detected by atomic fluorescence spectrometry after isolation by an interference filter that transmits the selenium fluorescence at a wavelength, λ = 196,0 nm. The procedure is automated by means of an 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, any interferences can be removed by a simple dilution step.

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

It is important that the light source does not contain any significant amount of other hydride-forming elements (e.g. arsenic, antimony, tellurium) that emit fluorescent radiation over the bandpass 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/TS 17379 do not generally 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 Table 1. It can be seen that tellurium causes a significant positive bias and that gold, silver and copper cause a significant negative bias. However, these elements are unlikely to be present at the tested levels in the vast majority of water samples.

Interferences 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 limit of quantification.

Table 1 — Interference study for selenium

Interfering substance		**Concentration of interfering substance**	**Se recovery**	
		mg/l	2 µg/l Se	10 µg/l Se
Thallium nitrate	Tl(Ill)	20	98,4 ± 3,1	97,2 ± 1,6
Strontium nitrate	Sr(II)	20	101,6 ± 1,2	97,0 ± 1,5
Zinc nitrate	Zn(II)	1	99,9 ± 1,8	102,4 ± 0,8
Diammonium silicon hexafluoride	Si(IV)	1	96,7 ± 2,7	98,8 ± 1,82
Aluminium nitrate	Al(III)	1	95,2 ± 3,0	97,2 ± 0,5
Calcium chloride	Ca(II)	200	97,4 ± 0,9	97,0 ± 3,3
Sodium chloride	Na(I)	200	98,0 ± 1,0	95,0 ± 0,6

Table 1 *(continued)*

Interfering substance		Concentration of interfering substance	Se recovery	
		mg/l	2 µg/l Se	10 µg/l Se
Potassium bromide	K(I)	200	94,9 ± 3,8	99,6 ± 1,1
Indium nitrate	In(III)	1	93,3 ± 1,7	98,9 ± 2,0
Barium nitrate	Ba(II)	1	96,6 ± 1,5	96,6 ± 1,6
Magnesium oxide	Mg(II)	1	98,9 ± 2,4	97,0 ± 0,9
Cadmium nitrate	Cd(II)	1	99,4 ± 0,5	90,1 ± 0,9
Ammonium dihydrogenphosphate	P(V)	1	98,0 ± 1,9	96,9 ± 3,4
Sodium fluoride	F(I)	1	97,4 ± 1,1	97,8 ± 2,7
Gold chloride	Au(Ill)	0,1	89,3 ± 3,1	83,1 ± 5,4
Gold chloride	Au(lII)	1	46,2 ± 4,1	76,8 ± 6,4
Ortho-boric acid	B(III)	1	99,1 ± 1,9	101,4 ± 2,1
Iron(II) nitrate	Fe(II)	1	96,9 ± 2,7	97,4 ± 4,9
Lead(II) nitrate	Pb(II)	1	99,2 ± 2,5	97,9 ± 0,9
Bismuth nitrate	Bi(III)	1	105,0 ± 4,8	95,6 ± 1,7
Tin nitrate	Sn(IV)	1	93,8 ± 6,1	97,8 ± 1,5
Ammonium molybdate	Mo(II)	1	95,7 ± 2,3	97,0 ± 1,3
Germanium chloride	Ge(IV)	1	100,7 ± 3,1	98,0 ± 0,6
Mercury nitrate	Hg(II)	1	99,4 ± 3,7	99,7 ± 3,9
Arsenic(III) oxide	As(III)	1	99,4 ± 2,5	97,7 ± 7,3
Chromium(III) nitrate	Cr(III)	1	95,9 ± 2,0	98,6 ± 1,5
Cobalt nitrate	Co(II)	1	93,2 ± 1,6	97,4 ± 1,7
Silver nitrate	Ag(I)	1	78,2 ± 6,5	72,0 ± 0,8
Nickel(II) nitrate	Ni(II)	1	95,0 ± 3,6	97,1 ± 1,9
Telluric acid	Te(IV)	0,01	104,0 ± 1,8	98,8 ± 1,8
Telluric acid	Te(IV)	0,1	110,0 ± 5,0	105,2 ± 1,0
Telluric acid	Te(IV)	1	123,5 ± 0,5	108,6 ± 1,0
Antimony oxide	Sb(III)	0,01	98,6 ± 0,8	99,1 ± 0,3
Antimony oxide	Sb(III)	0,05	89,3 ± 3,1	98,5 ± 2,1
Antimony oxide	Sb(III)	0,1	95,8 ± 2,2	100,4 ± 1,1
Copper sulfate	Cu(II)	0,1	98,5 ± 1,5	96,4 ± 0,0
Copper sulfate	Cu(II)	0,2	93,4 ± 1,9	100,8 ± 2,5
Copper sulfate	Cu(II)	0,5	94,5 ± 0,5	98,3 ± 1,9
Copper sulfate	Cu(II)	1	82,2 ± 2,3	85,1 ± 5,4
Copper sulfate	Cu(II)	2	79,8 ± 2,4	98,8 ± 1,8
Gold chloride	Au(I)	0,1	89,3 ± 3,1	83,1 ± 5,4

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 should have selenium concentrations below that which would result in a selenium blank value for the method being above the lowest level of interest.

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

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

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

5.4 **Sodium tetrahydroborate**, $NaBH_4$, available as pellets.

5.5 **Sodium hydroxide**, NaOH.

5.6 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) 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.

NOTE 3 See Clause 8.

5.7 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].

Prepare a nitric acid cleaning mixture by diluting nitric acid [$\rho(HNO_3) = 1{,}40$ g/ml] with an equal volume of water (5.1) by carefully adding the acid to the water.

5.8 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.

5.9 **Selenium standard solutions**.

5.9.1 Selenium stock solution A, $\rho[\mathrm{Se(IV)}] = 1\,000$ mg/l.

Use a quantitative stock solution with a traceable Se(IV) 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 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.

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

Pipette (1 ± 0,01) ml of selenium stock solution A (5.9.1) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.2) and fill up to the mark with reagent blank solution (5.8).

Prepare this solution monthly.

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

Pipette (1 ± 0,01) ml of selenium standard solution B (5.9.2) into a 100 ml volumetric flask, add (30 ± 0,5) ml of hydrochloric acid (5.2) and fill up to the mark with reagent blank solution (5.8).

Prepare this solution weekly.

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

Pipette (10 ± 0,1) ml of selenium standard solution C (5.9.3) into a 100 ml borosilicate volumetric flask. Fill up to the mark with reagent blank solution (5.8).

Prepare this solution weekly.

5.9.5 **Selenium standard solution E**, ρ[Se(VI)] = 1 000 mg/l.

Dissolve (1,000 ± 0,002) g of pure selenium powder in (10 ± 0,1) ml of concentrated nitric acid (5.7).

Heat the solution to boiling and evaporate off the excess nitric acid.

Perform this procedure carefully under the chemical hood.

Cool and then take up the hydrated oxide in (50 ± 0,5) ml of cold hydrochloric acid (5.2).

Transfer the solution quantitatively to a 1 000 ml volumetric flask and fill up to the mark with reagent blank solution (5.8).

Alternatively, 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 reagent blank solution (5.8).

Use this standard to check quantitative recovery of Se(VI).

The solution is stable for at least six months.

5.9.6 **Selenium calibration solutions.**

A minimum of five independent calibration solutions shall be used. Perform the calibration in accordance with ISO 8466-1. The calibration solutions are prepared by suitable dilution of the selenium standard solution C (5.9.3) or D (5.9.4)

Each calibration solution shall contain (30 ± 0,5) ml of hydrochloric acid (5.2) per 100 ml.

Prepare on the day of use.

For example, for the concentration range from 0,1 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 selenium standard solution D (5.9.4).

Fill up to the mark with reagent blank solution (5.8) 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 selenium respectively.

They 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 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.

6.1 Atomic fluorescence system.

6.1.1 General. Atomic fluorescence systems should be set up to the manufacturer's recommendations. The following example shows a typical example of a system specific for these measurements.

A schematic flow diagram of an example of an automated hydride generation system for selenium analysis is shown in Figure B.1. This consists of the components specified in 6.1.2 to 6.1.5.

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.

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

The gas supply should 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 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 Nafion1) hygroscopic membrane which continuously removes moisture present. Details are provided in Annex B. Air, argon or nitrogen can be used as the dryer gas.

6.4 Laboratory-ware.

6.4.1 General requirements. 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 (5.7) for at least 24 h and rinsed five times with water (5.1).

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

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

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1) Nafion is the trade name of a product supplied by DuPont. Nafion hygroscopic membranes for moisture removal are commercially available from Perma Pure Inc. 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.

6.4.3 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 absorb nor desorb the analyte under test.

6.4.4 Auto-sampler vials. Use vials of polystyrene or materials specified in (6.4.2).

6.5 Sample processing equipment.

6.5.1 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.

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

A continuous flow procedure is used for this part of ISO/TS 17379, accordingly prepare and analyse an appropriate blank as required. Prepare all samples, blanks, and standards in the same matrix: i.e. matrix matched.

NOTE Sample preservation using dilute nitric acid (5.7) is suitable, provided it can be shown that the selenium determinations are unaffected by using this reagent.

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

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 container.

Add (30 ± 0,5) ml of hydrochloric acid (5.2).

Mix and reflux gently for 1 h. This ensures quantitative reduction of Se(VI) to Se(IV).

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 using a tared flask. 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 (5.7) and hydrochloric acid (5.3). 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 Figure B.1.

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.

Fill the reagent reservoirs with reagent blank solution (5.8) and sodium tetrahydroborate solution (5.6), 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 (5.6) has a twofold function:

a) to reduce the selenium to its hydride;

b) to generate hydrogen for the atomization source.

The latter may require optimization of the concentration of $NaBH_4$ (5.6) 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/TS 17379.

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

Turn on the argon (6.2) to provide carrier gas. Use a suitable dryer (moisture removal) system (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 detector range selected is appropriate to the sample concentration being determined.

For samples which are above the calibration for a given range setting, either re-analyse 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 (5.8), 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 (5.8) and the sodium tetrahydroborate solution (5.6) 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 (5.9.6), samples (see Clause 7), and blanks (5.8) sequentially in the manner required or else run automatically in the following manner.

Load the auto-sampler with the calibration solutions (5.9.6), samples (see Clause 7), and blanks (5.8); then start the auto-sampler programme. Analysis of a field blank within a sample run establishes whether contamination has occurred. Should significant level of contamination be established, the analytical results are brought into question.

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

Prepare Se(VI) standards (5.9.5) at known concentrations and analyse after pre-reduction 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 selenium, ρ(Se) in the samples using Formula (1):

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

where

ρ(Se) is the concentration of selenium 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 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.

11 Expression of results

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

EXAMPLES

Selenium (Se) 0,04 µg/l

Selenium (Se) 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/TS 17379 (ISO/TS 17379-1:2013);

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

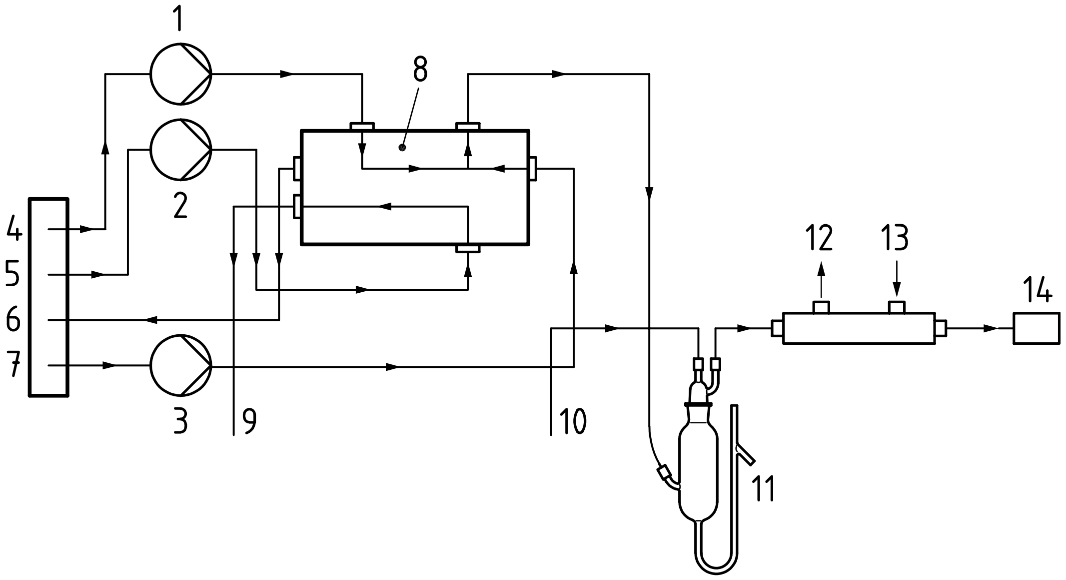
A.2 While any inert gas may be used to purge the selenium from the gas/liquid separator, the optimum signal response is provided using argon. Nitrogen can be used but quenches the fluorescence signal, reducing sensitivity. Air should not be used because of the explosion risk.

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

Annex B
(informative)

Figures

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

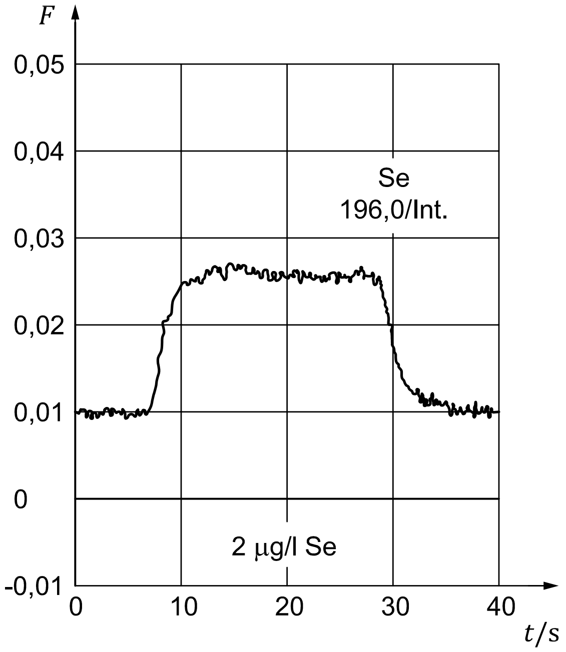


Key

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 Nafion[1)] dryer system (6.3)
6	recycle	13	dryer gas in to Nafion[1)] dryer system (6.3)
7	reductant	14	atomic fluorescence spectrometer (AFS)

NOTE This continuous flow vapour generator consists of a constant speed peristaltic pump to deliver sodium tetrahydroborate solution (5.6), reagent blank, and sample. A switching valve alternates between the reagent blank and sample or standard solutions. The vapour generator switches between reagent blank (5.8) and sample solution in a prescribed sequence so that the measured signal is directly related to the background levels of selenium in the sample. The signal response is shown in Figure B.2.

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



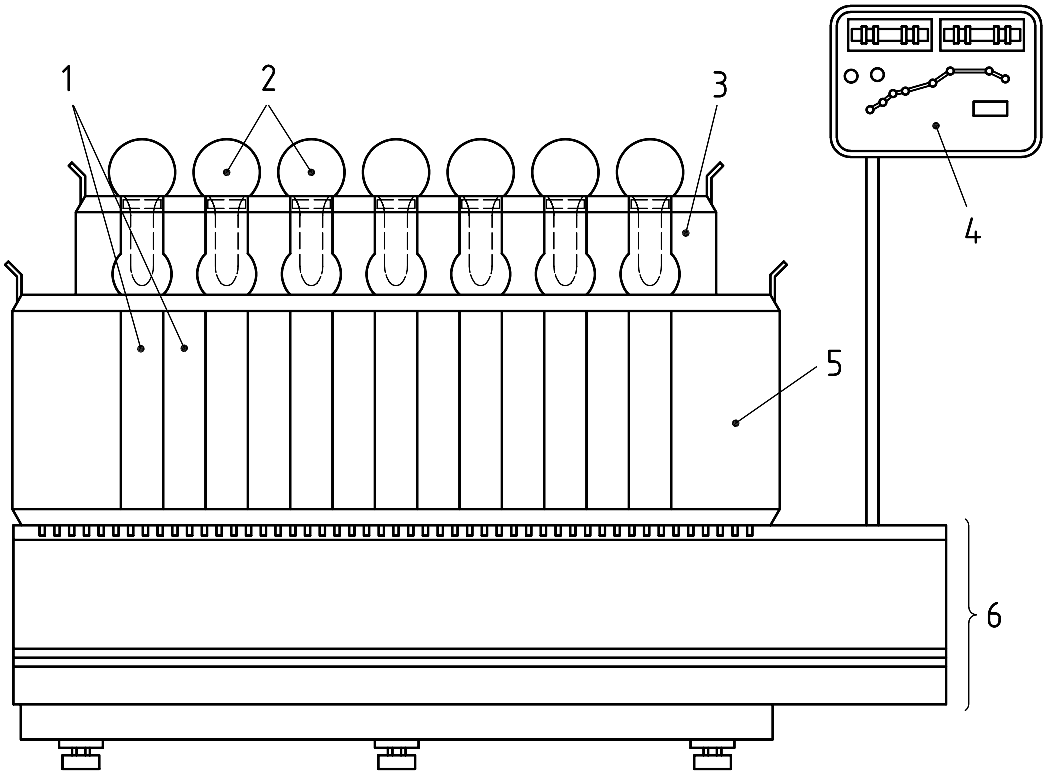
Key

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 (5.8). 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 fluorescence 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 conversion 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)

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 C.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 C.1 after removal of outliers, identified by inconsistency in the data set when compared to both standard measurements and peer laboratory results.

Table C.1 — Performance data

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	20	0,0	18,0	18,8	104,7	1,45	7,7	0,48	2,5
2	Rotherham interm. water 15 %	9	20	0,0	3,0	3,18	106,0	0,436	13,7	0,186	5,9
3	Bradford soft water 60 % spike	8	17	15,0	12,0	12,0	100,4	0,40	3,3	0,16	1,3
4	Low standard 20 %	8	18	10,0	4,0	3,98	99,6	0,378	9,5	0,153	3,9
5	Blank	—	—	—	—	—	—	—	—	—	—
6	High standard 80 %	8	18	10,0	16,0	15,8	98,9	1,68	10,6	0,82	5,2
7	Blank	—	—	—	—	—	—	—	—	—	—
8	Rotherham interm. water 15 %	8	19	0,0	3,0	3,08	102,8	0,215	7,0	0,077	2,5
9	Low standard 20 %	7	17	0,0	4,0	4,03	100,8	0,276	6,8	0,161	4,0
10	High standard 80 %	7	17	10,5	16,0	16,1	100,5	1,54	9,6	0,38	2,3
11	Nutwell hard water 90 % spike	8	19	0,0	18,0	18,9	104,8	1,39	7,4	0,33	1,8
12	Bradford soft water 60 % spike	7	16	15,8	12,0	12,2	101,4	0,50	4,1	0,28	2,3
13	Standard 30 µg/l	7	16	15,8	30,0	28,6	95,4	1,76	6,1	0,35	1,2

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

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