

BS EN 12926:2015



BSI Standards Publication

Chemicals used for treatment of water intended for human consumption — Sodium peroxodisulfate

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National foreword

This British Standard is the UK implementation of EN 12926:2015. It supersedes BS EN 12926:2008 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/59, Chemicals for drinking water treatment.

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

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Compliance with a British Standard cannot confer immunity from legal obligations.

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Date	Text affected
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English Version

Chemicals used for treatment of water intended for human consumption - Sodium peroxodisulfate

Produits chimiques pour le traitement de l'eau destinée à la consommation humaine - Peroxodisulfate de sodium

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Natriumperoxodisulfat

This European Standard was approved by CEN on 20 December 2014.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (EN 12926:2015) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2015, and conflicting national standards shall be withdrawn at the latest by September 2015.

This document supersedes EN 12926:2008.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

Significant technical difference between this edition and EN 12926:2008 is as follows:

- a) deletion of reference to EU Directive 67/548/EEC of June 27, 1967 in order to take into account the latest Regulation in force (see [2]);
- b) 6.2 – updating of risk and safety labelling according to EU Regulation [2] and its latest Adaptations to Technical Progress).

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

In respect of potential adverse effects on the quality of water intended for human consumption, caused by the product covered by this European Standard:

- a) this European Standard provides no information as to whether the product may be used without restriction in any of the Member States of the EU or EFTA;
- b) it should be noted that, while awaiting the adoption of verifiable European criteria, existing national regulations concerning the use and/or the characteristics of this product remain in force.

NOTE Conformity with this European Standard does not confer or imply acceptance or approval of the product in any of the Member States of the EU or EFTA. The use of the product covered by this European Standard is subject to regulation or control by National Authorities.

1 Scope

This European Standard is applicable to sodium peroxodisulfate used for treatment of water intended for human consumption. It describes the characteristics of sodium peroxodisulfate and specifies the requirements and the corresponding test methods for sodium peroxodisulfate. It gives information on its use in water treatment.

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

EN 1233, *Water quality - Determination of chromium - Atomic absorption spectrometric methods*

EN ISO 12846, *Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846)*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling*

ISO 6206, *Chemical products for industrial use — Sampling — Vocabulary*

ISO 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*

ISO 8288:1986, *Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods*

3 Description

3.1 Identification

3.1.1 Chemical name

Sodium peroxodisulfate.

3.1.2 Synonym or common name

Sodium persulfate.

3.1.3 Relative molecular mass

238,11.

3.1.4 Empirical formula

$\text{Na}_2\text{S}_2\text{O}_8$.

3.1.5 Chemical formula

$\text{Na}_2\text{S}_2\text{O}_8$.

3.1.6 CAS Registry Number ¹⁾

7775-27-1.

3.1.7 EINECS reference ²⁾

231-892-1.

3.2 Commercial form

Sodium peroxodisulfate is available as a crystalline powder.

3.3 Physical properties

3.3.1 Appearance and odour

The product is white, odourless, crystalline free-flowing salt.

3.3.2 Density

The bulk density of the product is approximately 1,15 g/cm³.

3.3.3 Solubility in water

The solubility of the product in water is approximately:

- 515 g/l at 10 °C;
- 545 g/l at 20 °C;
- 605 g/l at 40 °C;
- 680 g/l at 60 °C.

3.3.4 Vapour pressure

Not applicable.

3.3.5 Boiling point at 100 kPa ³⁾

Not applicable.

3.3.6 Melting point

The product decomposes above 65 °C.

3.3.7 Specific heat

Not known.

¹⁾ Chemical Abstracts Service Registry Number

²⁾ European Inventory of Existing Commercial Chemical Substances

³⁾ 100 kPa = 1 bar.

3.3.8 Viscosity (dynamic)

Not applicable.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

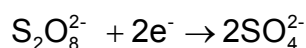
Not applicable.

3.4 Chemical properties

Sodium peroxodisulfate is a powerful oxidizing agent.

Sodium peroxodisulfate also serves as a source of radicals.

The standard reduction potential E_O is + 2,06 V at 25 °C for the following reaction:



4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for sodium peroxodisulfate used for the treatment of water intended for human consumption. Limits are given for impurities commonly present in the product. Depending on the raw material and the manufacturing process other impurities may be present and, if so, this shall be notified to the user and when necessary to relevant authorities.

Users of this product should check the national regulations in order to clarify whether it is of appropriate purity for treatment of water intended for human consumption, taking into account raw water quality, required dosage, contents of other impurities and additives used in the product not stated in the product standard.

Limits have been given for impurities and chemicals parameters where these are likely to be present in significant quantities from the current production process and raw materials. If the production process or raw materials leads to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

4.2 Composition of commercial product

The commercial product shall contain not less than 99 mass fraction percent of $\text{Na}_2\text{S}_2\text{O}_8$.

4.3 Impurities and main by-products

Sodium peroxodisulfate does not contain significant concentrations of impurities or by-products.

4.4 Chemical parameters

NOTE For the purpose of this standard, "chemical parameters" are those defined in the EU Directive 98/83/EC of 3 November 1998 (see [1]).

The content of chemical parameters shall conform to the requirements specified in Table 1.

Table 1 — Chemical parameters

Parameter		Limit in mg/kg of Na ₂ S ₂ O ₈	
		Type 1	Type 2
Arsenic (As)	max.	0,05	5
Cadmium (Cd)	max.	0,05	2
Chromium (Cr)	max.	0,5	5
Mercury (Hg)	max.	2	2
Nickel (Ni)	max.	0,2	5
Lead (Pb)	max.	0,05	5
Antimony (Sb)	max.	5	10
Selenium (Se)	max.	5	10

NOTE Cyanide, which does not exist in a strong oxidizing medium such as sodium peroxodisulfate, is not a relevant chemical parameter. Pesticides and polycyclic aromatic hydrocarbons are not by-products of the manufacturing process.

5 Test methods

5.1 Sampling

Observe the recommendations of ISO 3165 and take account of ISO 6206. Prepare the laboratory sample(s) required by the relevant procedure described in ISO 8213.

5.2 Analysis

5.2.1 General

All measurements should be made with a tolerance of $\pm 10\%$ unless otherwise stated.

5.2.2 Determination of sodium peroxodisulfate (main product)

5.2.2.1 Principle

Determination of peroxodisulfate content by back-titrating a predetermined excess of iron(II) with potassium permanganate.

5.2.2.2 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 3 in accordance with EN ISO 3696.

5.2.2.2.1 Potassium permanganate standard volumetric solution ; $c(\text{KMnO}_4) = 0,02 \text{ mol/l}$.

5.2.2.2.2 Sulfuric acid (H_2SO_4), density $\rho = 1,84 \text{ g/ml}$.

5.2.2.2.3 Phosphoric acid (H_3PO_4), density $\rho = 1,68 \text{ g/ml}$.

5.2.2.2.4 Iron(II) sulfate solution; $c(\text{FeSO}_4) = 0,1 \text{ mol/l}$.

Dissolve 77 g of iron (II) ammonium sulfate in 500 ml water, add 150 ml of sulfuric acid (5.2.2.2.2) and 50 ml of phosphoric acid (5.2.2.2.3) and make up to 2 000 ml with water. Filter before use.

5.2.2.2.5 Potassium chloride (KCl).

5.2.2.2.6 Potassium chloride; $c(\text{KCl}) = 3 \text{ mol/l}$.

Dissolve 224 g potassium chloride (5.2.2.2.5) in water, add 2 ml of phosphoric acid (5.2.2.2.3) and make up to 1 000 ml with water.

5.2.2.3 Apparatus

Ordinary laboratory apparatus and glassware, together with automated potentiometric titration apparatus with program-control of the addition of the solution from the burette.

5.2.2.4 Procedure

5.2.2.4.1 Preparation of test solution

Weigh, to the nearest of 0,1 mg, 0,30 g of sodium peroxodisulfate (m), transfer to a 250 ml glass beaker and dissolve with a small amount of water.

5.2.2.4.2 Determination

Introduce the test solution (5.2.2.4.1) for the potentiometric titration in the apparatus (5.2.2.3). Add a predetermined excess of the iron(II) sulfate solution (5.2.2.2.4) and titrate against the potassium permanganate standard volumetric solution (5.2.2.2.1). Record the volume (V) used.

Carry out a blank determination, in duplicate, at the start of the determination and after 10 titrations of test solutions.

5.2.2.5 Expression of results

The sodium peroxodisulfate content, C_1 , expressed as a mass fraction percentage is given by the following formula:

$$C_1 = \frac{(V_0 - V) \times 0,1 \times c \times 100 \times 119,05}{1000 \times m} \quad (1)$$

where

m is the mass in grams of the test portion;

c is the actual concentration expressed in moles per litre of the permanganate standard volumetric solution;

V_0 is the volume in millilitres of the potassium permanganate standard volumetric solution used for the blank determination;

V is the volume in millilitres of the potassium permanganate standard volumetric solution used for the determination;

119,05 is the mass in grams of sodium peroxodisulfate, corresponding to 1,00 ml of potassium permanganate solution $c(\text{KMnO}_4) = 1,00 \text{ mol/l}$.

The content of active oxygen, (C_2), expressed in mass fraction percent is given by the following formula:

$$C_2 = C_1 \times 0,0672 \quad (2)$$

5.2.3 Impurities

Not applicable.

5.2.4 Chemical parameters

5.2.4.1 Determination of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni) and selenium (Se).

5.2.4.1.1 Principle

The elements arsenic, antimony, cadmium, chromium, lead, nickel and selenium are determined by atomic absorption spectrometry.

5.2.4.1.2 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to the appropriate grade specified in EN ISO 3696.

5.2.4.1.2.1 Nitric acid, concentrated, density $\rho = 1,42$ g/ml.

5.2.4.1.2.2 Nitric acid, solution $c(\text{HNO}_3) = 2,5$ mol/l.

5.2.4.1.2.3 Barium nitrate, $\text{Ba}(\text{NO}_3)_2$.

5.2.4.1.3 Procedure

5.2.4.1.3.1 Test portion

Weigh, to the nearest 0,01 g:

- for Cd, Ni, Pb, As and Sb: 1 g (m_1) of the laboratory sample into a 100 ml one-mark volumetric flask;
- for Cr: 2 g (m_1) of the laboratory sample into a 100 ml one-mark volumetric flask;
- for Se: 0,5 g (m_1) of the laboratory sample into a 100 ml one-mark volumetric flask.

5.2.4.1.3.2 Test solution

For Cd: dissolve the test portion with 40 ml of water and after adding 20 ml of barium nitrate (5.2.4.1.2.3), bring solution briefly to boiling point and after cooling make up to the mark with water. The determination is made with the clear supernatant solution after the barium sulfate has settled out.

For Cr and Ni: add 0,5 ml of nitric acid (5.2.4.1.2.2) to the test portion, dilute with a few millilitres of water and mix. Make up to the mark with water and homogenize.

For Pb and As: dissolve the test portion with a few millilitres of water and mix. Make up to the mark with water and homogenize.

For Se and Sb: add 2 ml of nitric acid (5.2.4.1.2.1) to the test portion, dilute with few millilitres of water and mix. Make up to the mark with water and homogenize.

5.2.4.1.3.3 Determination

Determine the content of chemical parameters in the test solution (5.2.4.1.3.2) in accordance with the following methods:

- **Cd, Ni and Pb:** In accordance with ISO 8288:1986, Method A;
- **Cr:** In accordance with EN 1233;
- **As, Se and Sb:** In accordance with the method given in Annex C.

These methods will give an interim result (y) expressed in milligrams per litre which needs to be corrected to give the final concentration according to the formula in 5.2.4.1.4.

5.2.4.1.4 Expression of results

From the interim results (y) determined (see 5.2.4.1.3.3), the content, C_3 , of each chemical parameter in the laboratory sample, expressed in milligrams per kilogram of sodium peroxodisulfate is given by the following formula:

$$C_3 = y \times \frac{V_1}{m_1} \times \frac{100}{C_1} \quad (3)$$

where

- y is the interim result (5.2.4.1.3.3);
- V_1 is the volume, expressed in millilitres, of the test solution (5.2.4.1.3.2) (= 100 ml);
- m_1 is the mass, expressed in grams, of the test portion;
- C_1 is the sodium peroxodisulfate content in mass fraction percent of product (5.2.2.5).

5.2.4.2 Determination of the mercury content (Hg)

5.2.4.2.1 Principle

The element mercury is determined by flameless atomic absorption spectrometry in accordance with EN ISO 12846.

5.2.4.2.2 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to the appropriate grade specified in EN ISO 3696.

5.2.4.2.2.1 Potassium permanganate solution, $c(\text{KmnO}_4) = 50 \text{ g/l}$.

5.2.4.2.2.2 Sulfuric acid, concentrated, density $\rho = 1,84 \text{ g/ml}$.

5.2.4.2.2.3 Hydroxylammonium chloride solution, $c(\text{NH}_2\text{OH}\cdot\text{HCl}) = 100 \text{ g/l}$.

5.2.4.2.2.4 Potassium dichromate solution, $c(\text{K}_2\text{Cr}_2\text{O}_7) = 4 \text{ g/l}$ in 50 % by volume nitric acid solution.

5.2.4.2.3 Procedure

5.2.4.2.3.1 Test portion

Weigh, to the nearest 0,01 g, 10 g (m_2) of the laboratory sample, into a glass beaker.

5.2.4.2.3.2 Test solution

Quantitatively transfer the test portion to a 100 ml (V_2) volumetric flask. Dilute with water to the mark and mix (solution A).

Pipette, accurately 10 ml of the solution A. Transfer to a 250 ml conical flask and add 60 ml of water, 20 ml of a potassium permanganate solution (5.2.4.2.2.1) and five 1 ml portions of sulfuric acid (5.2.4.2.2.2). Bring to the boil and maintain boiling for 10 min. Allow to cool. Dissolve the precipitate (MnO_2) with hydroxylammonium chloride (5.2.4.2.2.3), add 5 ml of the potassium dichromate solution (5.2.4.2.2.4) and transfer to a 100 ml (V_3) volumetric flask. Dilute to the mark with water and mix.

5.2.4.2.3.3 Determination

Proceed as described in EN ISO 12846.

5.2.4.2.4 Expression of results

The interim result for mercury content (y) expressed in milligrams per litre is given by the following formula:

$$y = y_A \times \frac{V_3}{10} \quad (4)$$

where

y_A is the result obtained in 5.2.4.2.3.3, for the concentration of mercury in the test solution, expressed in milligrams per litre;

V_3 is the volume in millilitres of the test solution.

The mercury content, C_4 , in milligrams per kilogram of sodium peroxodisulfate is given by the following formula:

$$C_4 = y \times \frac{V_2}{m_2} \times \frac{100}{C_1} \quad (5)$$

where

y is the previously determined interim result for mercury content;

V_2 is the volume in millilitres, of the solution A (see 5.2.4.2.3.2);

m_2 is the mass, expressed in grams, of the test portion (5.2.4.2.3.1);

C_1 is the sodium peroxodisulfate content in mass fraction percent (5.2.2.5).

6 Labelling – Transportation – Storage

6.1 Means of delivery

Sodium peroxodisulfate shall be delivered in polyethylene bags or fibre drums with polyethylene linings.

In order that the purity of the product is not affected, the means of delivery shall not have been used previously for any different product or it shall have been specially cleaned and prepared before use.

6.2 Labelling according to the EU Legislation ⁴⁾

At the date of publication of this document, sodium peroxodisulfate is not listed within Annex VI of [2]

Annex VI of [2] and its amendments and adaptations to technical progress contain a list of substances classified by the EU. Substances not in this Annex VI should be classified on the basis of their intrinsic properties according to the criteria in the Regulation by the person responsible for the marketing of the substance.

6.3 Transportation regulations and labelling

Sodium peroxodisulfate is listed as UN Number ⁵⁾ 1505.

RID ⁶⁾: class 5.1, item 18c.

ADR ⁷⁾: class 5.1, item 18c.

IMDG ⁸⁾: class 5.1 page 5185.

IATA ⁹⁾: class 5.1.

6.4 Marking

The marking shall include the following:

- the name “Sodium peroxodisulfate”, trade name, and type;
- the net mass;
- the name and address of supplier and/or manufacturer;
- the statement “this product conforms to EN 12926, type...”.

6.5 Storage

6.5.1 General

The product shall be stored in original packages in a cool and dry place, away from any sources of heat or incompatible materials.

6.5.2 Long term stability

The product is stable with no decrease in active substance for one year, when the product is stored at below 30 °C.

⁴⁾ See [2].

⁵⁾ United Nations Number.

⁶⁾ Regulations concerning International carriage of Dangerous goods by rail.

⁷⁾ European Agreement concerning the international carriage of Dangerous goods by Road.

⁸⁾ International Maritime transport of Dangerous Goods.

⁹⁾ International Air Transport Association.

6.5.3 Storage incompatibilities

Avoid heat and moisture (decomposes above 65 °C).

Avoid contact with alkaline or reducing substances.

Avoid contact with oxidizable organic substances and combustible materials.

Keep away from metals and metal compounds (e.g. copper, cobalt, nickel, manganese, iron etc.).

Annex A (informative)

General information on sodium peroxodisulfate

A.1 Origin

A.1.1 Raw materials

Sodium peroxodisulfate is manufactured from sodium hydrogen sulfate (NaHSO_4) and sulfuric acid.

A.1.2 Manufacturing process

It is produced by electrolytic oxidation of NaHSO_4 in sulfuric acid, following by precipitation.

A.2 Use

A.2.1 Function

The product is used to oxidize oxidizable impurities (organic and inorganic) in water. Can be used as an oxidant for the generation of ClO_2 from NaClO_2 .

A.2.2 Form in which it is used

The product is used as an aqueous solution in demineralized water, containing 100 g/l to 200 g/l of sodium peroxodisulfate.

A.2.3 Treatment dose

A typical dose is 50 mg of sodium peroxodisulfate per litre of raw water.

A.2.4 Means of application

The product is usually applied using a metering pump.

A.2.5 Secondary effects

Increase of sodium and sulfate content of the treated water. Lowering of the pH value of the water by formation of NaHSO_4 .

A.2.6 Removal of excess product

Addition of reducing agents (e.g. SO_2 , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$).

Annex B (normative)

General rules relating to safety

B.1 Rules for safe handling and use

The supplier shall provide current safety instructions.

B.2 Emergency procedures

B.2.1 First aid

Wash affected skin area with plenty of water and soap.

In case of contact with eyes, rinse immediately and thoroughly with plenty of water for at least 15 min and seek medical advice.

If swallowed, give plenty of water to drink. Seek medical advice.

If inhaled, remove to fresh air. Seek medical advice.

B.2.2 Spillage

Sweep up into dry plastics containers. Rinse residues away with water. Observe locally valid waste disposal regulations.

B.2.3 Fire

Extinguish with water or water mist.

Annex C (normative)

Determination of arsenic, antimony and selenium (atomic absorption spectrometry hydride technique)

SAFETY PRECAUTIONS: Arsenic, antimony and selenium and their hydrides are toxic. Handle with care.

C.1 General principle

Arsenious acid, antimonous acid and selenious acid, the As(III), Sb(III) and Se(IV) oxidation states of arsenic, antimony and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic, antimony and selenium.

The sample is digested to solubilize particulate As, Sb and Se. The digested solutions are treated separately for determination of As, Sb and Se to convert them to As(III), Sb(III) and Se(IV) oxidation states respectively.

C.2 Interferences

Interferences are minimized because the As, Sb and Se hydrides are removed from the solution containing most potential interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (approximately 100 µg/l of Ag, Au, Pt, Pd, etc.) concentrations of Cu, Ni and Pb at or greater than 1 mg/l, and concentrations between 0,1 mg/l and 1 mg/l of hydride-forming elements (Bi, Sn and Te) can suppress the response of As, Sb and Se hydrides due to the formation of mixed metal – As-Sb or –Se compounds. The presence of As, Sb and Se in each other's matrices can cause similar suppression. Reduced nitrogen oxides resulting from HNO₃ digestion and nitrite also can suppress instrumental response for all elements. Large concentrations of iodide interfere with the Se determination by reducing Se to its elemental form. Do not use any glassware for determining Se that has been used with iodide reduction of As(V).

C.3 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 3 in accordance with EN ISO 3696.

C.3.1 Sodium tetrahydroborate (sodium borohydride).

Dissolve 8 g NaBH₄ in 200 ml of NaOH, c(NaOH) = 0,1 mol/l. Prepare fresh daily.

C.3.2 Sodium iodide, preductant solution.

Dissolve 50 g NaI in 500 ml water. Prepare fresh daily.

C.3.3 Sulfuric acid, solution c(H₂SO₄) = 9 mol/l.

C.3.4 Sulfuric acid, solution c(H₂SO₄) = 1,25 mol/l.

Cautiously add 35 ml sulfuric acid, density (ρ) = 1,84 g/ml to about 400 ml water, allow to cool, and adjust volume to 500 ml.

C.3.5 Nitric acid, density (ρ) = 1,42 g/ml.

C.3.6 Perchloric acid, density (ρ) = 1,66 g/ml.

C.3.7 Hydrochloric acid, density (ρ) = 1,16 g/ml.

C.3.8 Argon (or nitrogen), commercial grade.

C.3.9 Hydrogen, commercial grade.

C.3.10 Arsenic(III) solutions:

- stock As(III) solution: Dissolve 1,320 g of arsenic trioxide, As_2O_3 , in water containing 4 g NaOH. Transfer quantitatively to 1000 ml one-mark volumetric flask and dilute to the mark with water and mix; 1,00 ml = 1,00 mg As(III);
- intermediate As(III) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml stock As(III) solution to the mark with water containing 5 ml hydrochloric acid (C.3.7) and mix; 1,00 ml = 10,0 μg As(III);
- standard As(III) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml intermediate As(III) solution to the mark with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (C.3.5)) and mix; 1,00 ml = 0,100 μg As(III). Prepare diluted solutions daily.

C.3.11 Arsenic(V) solutions:

- stock As(V) solution; Dissolve 1,534 g arsenic pentoxide, As_2O_5 , in water containing 4 g NaOH. Transfer quantitatively to 1 000 ml one-mark volumetric flask and dilute to the mark with water and mix; 1,00 ml = 1,00 mg As(V);
- intermediate As(V) solution: Prepare as for As(III) above; 1,00 ml = 10,0 μg As(V);
- standard As(V) solution: Prepare as for As(III) above; 1,00 ml = 0,100 μg As(V).

C.3.12 Selenium(IV) solutions:

- stock Se(IV) solution: Dissolve 2,190 g sodium selenite, Na_2SeO_3 in water containing 10 ml hydrochloric acid (C.3.7) and transfer quantitatively to 1 000 ml one-mark volumetric flask and dilute to the mark with water and mix; 1,00 ml = 1,00 mg Se(IV);
- intermediate Se(IV) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml stock Se(IV) solution to the mark with water containing 10 ml hydrochloric acid (C.3.7) and mix; 1,00 ml = 10,0 μg Se(IV);
- standard Se(IV) solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml intermediate Se(IV) solution to the mark with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (C.3.5)) and mix. Prepare solution daily when checking the equivalent of instrument response for Se(IV) and Se(VI); 1,00 ml = 0,100 μg Se(IV)

C.3.13 Selenium(VI) solutions:

- stock Se(VI) solution: Dissolve 2,393 g sodium selenate Na_2SeO_4 in water containing 10 ml nitric acid (C.3.5). Transfer quantitatively to 1000 ml one-mark volumetric flask and dilute to the mark with water and mix; 1,00 ml = 1,00 mg Se(VI);
- intermediate Se(VI) solution: Prepare as for Se(IV) above; 1,00 ml = 10,0 μg Se(VI);

- standard Se(VI) solution: Prepare as for Se(IV) above; 1,00 ml = 0,100 µg Se(VI).

C.3.14 Antimony solutions:

- stock Sb solution: Dry 2 g of potassium antimonyl tartrate hemihydrate (antimony potassium tartrate) ($C_4H_4O_7SbK_0,5H_2O$) at 100 °C for 1h. Dissolve 1,669 g in water transfer quantitatively to 1000 ml one-mark volumetric flask and dilute to the mark with water and mix; 1,00 ml = 1,00 mg Sb;
- intermediate Sb solution: Dilute into 1 000 ml one-mark volumetric flask 10 ml stock Sb solution to the mark with water containing 10 ml hydrochloric acid (C.3.7) and mix; 1,00 ml = 10,0 µg Sb;
- standard Sb solution: Dilute into 1000 ml one-mark volumetric flask 10 ml intermediate Sb solution to the mark with water containing the same concentration of acid used for sample preservation (2 ml to 5 ml nitric acid (C.3.5)) and mix; 1,00 ml = 0,100 µg Sb. Prepare diluted solutions daily.

C.4 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

C.4.1 Atomic absorption spectrometer, equipped with gas flow meters for argon (or nitrogen) and hydrogen, As, Sb and Se electrodeless discharge lamps with background correction at measurement wavelengths and appropriate strip-chart recorder.

NOTE Certain atomic absorption atomizers and hydride reaction cells are available commercially for use with the sodium borohydride reagent.

C.4.2 Atomizer

Use one of the following:

- boling-type burner ¹⁰⁾ head for argon (or nitrogen)-air entrained-hydrogen flame;
- cylindrical quartz cell, 10 cm to 20 cm long, electrically heated by external Ni-Cr wire from 800 °C to 900 °C;
- cylindrical quartz cell with internal fuel rich hydrogen-oxygen (air) flame.

The transparency of quartz cells deteriorates over several months of use. The transparency can be restored by treatment with 40 % hydrofluoric acid (HF).

SAFETY PRECAUTIONS: Be careful in handling HF which is toxic and corrosive and avoid prolonged contact of quartz with HF.

C.4.3 Reaction cell for producing As, Sb or Se hydrides

An example of reaction cell is given in Figure C.1.

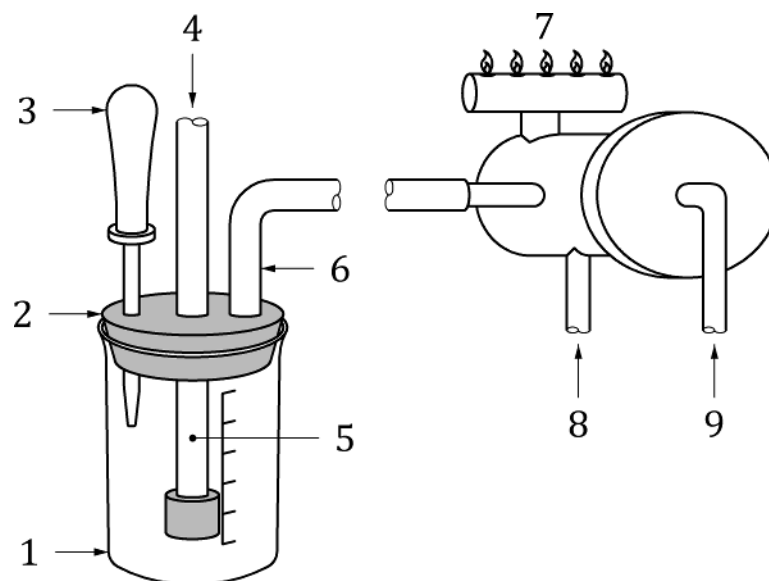
NOTE A commercially available system is acceptable if it utilizes liquid sodium borohydride reagents; accepts samples digested in accordance with C.5.3, accepts between 4 mol/l to 6 mol/l (HCl); and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

Irrespective of the hydride reaction cell-atomizer system selected, it shall meet the following quality-control considerations:

¹⁰⁾ Boling is the name of the inventor of this type of burner for rapid combustion of the hydrides.

- it shall provide a precise and reproducible calibration curve between 0 $\mu\text{g/l}$ and 20 $\mu\text{g/l}$ As, Sb or Se and a detection limit between 0,1 $\mu\text{g/l}$ and 0,5 $\mu\text{g/l}$ As, Sb or Se;
- when carried through the entire procedure, oxidation state couples (As(III) - As(V) or Se(IV) - Se(VI)) shall cause equal instrument response; and
- sample digestion shall yield 90 % or greater recovery of added As(III), As(V), Se(VI), Se(IV) or Sb.

C.4.4 Dropper and syringe capable of delivering 0,5 ml to 3,0 ml sodium borohydride reagent. Exact and reproducible addition is required so that production of hydrogen gas does not vary significantly between determinations.



Key

- Beaker 250 ml
- Rubber stopper
- Dropper
- Auxiliary nitrogen
- Gas dispersion tube
- Outlet tube
- Burner
- Hydrogen
- Nitrogen

Figure C.1 — Reaction cell for producing As, Sb or Se hydrides

C.5 Procedure

C.5.1 Preparation of the apparatus

Connect inlet of reaction cell with auxiliary purging gas controlled by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous CaCl_2 but not CaSO_4 because it can retain SeH_2 . Before using the hydride generation/analysis system, optimize operating parameters. Aspirate aqueous solutions of As, Sb and Se directly into the flame to facilitate atomizer alignment. Align quartz atomizers for maximum absorbance. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analysed. If a quartz atomizer is used, optimize cell temperature. If sodium borohydride reagent is added too

quickly, rapid evolution of hydrogen will unbalance the system. If the volume of solution being purged is too large, the absorption signal will be decreased. Recommended wavelengths are 193,7 nm, 196,0 nm and 217,6 nm for As, Se and Sb, respectively.

C.5.2 Preparation of calibration solutions

Transfer 0,00 ml ; 1,00 ml ; 2,00 ml ; 5,00 ml ; 10,00 ml ; 15,00 ml and 20,00 ml standard solutions of As(III), Se(IV) or Sb to 100 ml volumetric flasks and make up to volume with water containing the same acid concentration used for sample preservation (commonly 2 ml to 5 ml nitric acid (C.3.5)). This yields calibration solutions of 0 µg/l, 1 µg/l, 2 µg/l, 5 µg/l, 10 µg/l, 15 µg/l and 20 µg/l As, Se or Sb. Prepare fresh daily.

C.5.3 Preparation of test solutions and standard solutions

Add 50 ml sample or As(III), Se(VI) or Sb standard solution to 250 ml beaker. Alternatively, prepare standard solutions by adding 100 µg/l standard As, Se or Sb solutions directly to the beaker and dilute to 50 ml in this beaker. Add 7 ml sulfuric acid $c(\text{H}_2\text{SO}_4) = 9 \text{ mol/l}$ (C.3.3) and 5 ml nitric acid (C.3.5). Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of nitric acid, to prevent solution from darkening.

Maintain an excess of nitric acid until all organic matter is destroyed. Complete digestion usually is indicated by a light-coloured solution. Cool slightly, add 25 ml water and 1 ml of perchloric acid (C.3.6) and again evaporate to SO_3 fumes to expel oxides of nitrogen.

Monitor effectiveness of digestion procedure used by adding 5 ml of a standard arsenic solution, 5 ml of a standard selenium solution or 5 ml of a standard antimony solution to 50 ml sample and measuring recovery. Average recoveries shall be greater than 90 %. Alternatively, use 100 ml micro-Kjeldahl flasks for the digestion of total recoverable arsenic, selenium or antimony, thereby improving digestion effectiveness. After final evaporation of SO_3 fumes, dilute to 50 ml for arsenic measurements or 30 ml for selenium and antimony measurements.

C.5.4 Determination of arsenic with sodium borohydride

To 50 ml of the digested standard solution or test solution in a 250 ml beaker (see Figure C.1) add 5 ml hydrochloric acid (C.3.7) and mix. Add 5 ml sodium iodide pre-reductant solution (C.3.2), mix and wait at least 30 min.

NOTE The sodium iodide has not been found necessary for certain hydride reaction cell designs if a 20 % to 30 % loss in instrument sensitivity is not important and variables of solution acid conditions, temperatures, and volumes for production of As(V) and arsine can be controlled strictly. This can require an automated delivery system.

Attach one beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the atomizer. Turn on strip-chart recorder and wait until the base line is established by the purging gas and all air is expelled from the reaction cell. Add 0,5 ml sodium borohydride reagent (C.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next test solution or standard solution. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 µg/l As(III) or As(V) as appropriate. Average recoveries shall be not less than 90 %.

C.5.5 Determination of selenium with sodium borohydride

To 30 ml of the digested standard solution or test solution, or to 30 ml of the undigested standard, or sample in a 250 ml beaker, add 15 ml hydrochloric acid (C.3.7) and mix. Heat for a predetermined period at temperature between 90 °C to 100 °C. Alternatively autoclave at 121 °C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 °C to 100 °C hot water bath or an aluminium block digester. Check effectiveness of the selected heating by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for

converting Se(VI) to Se(IV), with no loss of Se(IV), ranges between 5 min to 60 min when open beakers or test tubes are used. Do not digest standard Se(IV) and Se(VI) solutions used for this check of equivalency. After prereduction of Se(VI) and Se(IV) attach beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0,50 ml sodium borohydride reagent (C.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to the next test solution or standard solution. Check for presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 $\mu\text{g/l}$ Se(IV). Average recoveries shall be not less than 90 %.

C.5.6 Determination of antimony with sodium borohydride

To 30 ml of the digested standard solution or test solution, or to 30 ml of the undigested standard solution, or test solution in a 250 ml beaker, add 15 ml hydrochloric acid (C.3.7) and mix. Heat for a predetermined period (between 5 min and 60 min) at a temperature between 90 °C to 100 °C. After prereduction of Sb attach beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0,50 ml sodium borohydride reagent (C.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water and proceed to the next test solution or standard solution. Check for presence of chemical interferences that suppress antimony hydride instrument response by treating a digested sample with 10 $\mu\text{g/l}$ Sb. Average recoveries shall be not less than 90 %.

C.6 Calculation

Determine the calibration curve by plotting peak heights of standard solutions versus concentration. Measure peak heights of samples and read concentrations from the calibration curve. If sample was diluted (or concentrated) before sample digestion, apply an appropriate factor.

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