BS EN 12678:2016

BSI Standards Publication

Chemical used for treatment of water intended for human consumption — Potassium peroxomonosulfate

National foreword

This British Standard is the UK implementation of EN 12678:2016. It supersedes BS EN 12678:2008 which is withdrawn.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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English Version

Chemical used for treatment of water intended for human consumption - Potassium peroxomonosulfate

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Peroxomonosulfate de potassium

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Kaliumperoxomonosulfat

This European Standard was approved by CEN on 18 March 2016.

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COMITÉ EUROPÉEN DE NORMALISATION
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Contents

Page

European foreword

This document (EN 12678:2016) 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of an identical text or by endorsement, at the latest by November 2016, and conflicting national standards shall be withdrawn at the latest by November 2016.

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.

This document supersedes EN 12678:2008.

Significant technical difference between this edition and EN 12678:2008 is as follows:

- 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 [3]).

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 1 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.

NOTE 2 This product is a biocide and needs to comply with the relevant legislation in force. In the European Union, at the time of publication, this legislation is REGULATION (EU) No 528/2012 [1]).

1 Scope

This European Standard is applicable to potassium peroxomonosulfate used for treatment of water intended for human consumption. It describes the characteristics of potassium peroxomonosulfate and specifies the requirements and the corresponding test methods for potassium peroxomonosulfate. 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 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

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

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, *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

Potassium peroxomonosulfate triple salt.

3.1.2 Synonym or common name

Potassium peroxomonosulfate, Potassium monopersulfate, Potassium hydrogenperoxomonosulfate, Pentapotassium-bis(peroxomonosulfate)bis(sulfate).

3.1.3 Relative molecular mass

Triple salt: 614,76.

(Active ingredient $KHSO_5$: 152,17).

3.1.4 Empirical formula of triple salt

$K_5H_3S_4O_{18}$ ($2\ KHSO_5.\ KHSO_4.\ K_2SO_4$).

Active ingredient $KHSO_5$.

3.1.5 CAS Registry Number[1)]

70693-62-8.

3.1.6 EINECS reference[2)]

274-778-7.

3.2 Commercial form

Potassium peroxomonosulfate as commercial product exists as a triple salt comprising potassium peroxomonosulfate ($2KHSO_5$) potassium hydrogen sulfate ($KHSO_4$) and potassium sulfate (K_2SO_4).

3.3 Physical properties of triple salt

3.3.1 Appearance and odour

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

3.3.2 Density

The bulk density of the product is approximately between 1 g/cm^3 and 1,2 g/cm$^{3.}$

3.3.3 Solubility in water

The solubility of the product is:

- approximately 250 g/l at 20 °C;
- approximately 300 g/l at 50 °C;
- approximately 330 g/l at 70 °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 60 °C.

3.3.7 Specific heat

Not applicable.

3.3.8 Viscosity (dynamic)

Not applicable.

3.3.9 Critical temperature

Not applicable.

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1) Chemical Abtracts Service Registry Number.

2) European Inventory of Existing Commercial Chemical Substances.

3) 100 kPa = 1 bar

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3.4 Chemical properties

Potassium peroxomonosulfate is a powerful oxidizing agent. Aqueous solutions of the product exhibit a strongly acid reaction; a mass fraction solution of 3 % has a pH value of 2 at 20 °C.

The standard reduction potential E_0 of potassium peroxomonosulfate for the reaction:

$$HSO_5^- + 2H^+ + 2^{e-} \leftrightarrows HSO_4^- + H_2O \quad (1)$$

is:

+ 1,82 V at 25°C

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for potassium peroxomonosulfate 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 the 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 $KHSO_5$ (potassium peroxomonosulfate) at a mass fraction greater than 45 percent or the manufacturer's declared values.

Typical composition in mass fraction should be approximately: 45 % potassium peroxsomonosulfate ($KHSO_5$), 25 % potassium hydrogen sulfate ($KHSO_4$), and 30 % potassium sulfate (K_2SO_4).

4.3 Impurities and main by-products

See 4.1.

4.4 Chemical parameters

NOTE For the purpose of this European Standard, "chemical parameters" are those defined in the EU Directive 98/83/EC of 3 November 1998 (see [2]).

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

Table 1 — Chemical parameters

Parameter		**Limit** (mg/kg of dry product)	
		Type 1	**Type 2**
Arsenic (As)	max.	2	10
Cadmium (Cd)	max.	1	10
Chromium (Cr)	max.	0,4	10
Mercury (Hg)	max.	4	8
Nickel (Ni)	max.	1	10
Lead (Pb)	max.	2	10
Antimony (Sb)	max.	10	10
Selenium (Se)	max.	10	10
NOTE Cyanide is usually not relevant in a strong oxidizing medium. Pesticides and polycyclic aromatic hydrocarbons are not by-products of the manufacturing process.			

5 Test methods

5.1 Sampling

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

5.2 Analysis

5.2.1 Determination of potassium peroxomonosulfate ($KHSO_5$) (active ingredient)

5.2.1.1 Principle

Iodometric titration with sodium thiosulfate standard volumetric solution in sulfuric acid medium. The method depends on the oxidizing action of the peroxomonosulfate ion (HSO_5^-) on iodide ions, Formula (2) and the subsequent determination of iodine formed, through the reducing agent sodium thiosulfate, Formula (3). The inflection point of the potentiometric titration is located around 250 mV (reference to Ag/AgCl-Electrode).

$$HSO_5^- + 3\ Kl + H_2SO_4 \rightarrow HSO_4^- + Kl_3 + K_2SO_4 + H_2O \qquad (2)$$

$$Kl_3 + 2\ Na_2S_2O_3 \rightarrow Kl + 2\ Nal + Na_2S_4O_6 \qquad (3)$$

5.2.1.2 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.

5.2.1.2.1 Sulfuric acid solution, mass fraction 25 %.

Place 750 ml of water in a heat resistant beaker (volume 2 000 ml). Measure 135 ml of sulfuric acid, mass fraction 98 % , and dilute in the water by small additions and under gentle stirring. Cover the beaker with a watch glass and keep it for several hours in a safe place to cool.

WARNING — During dilution the solution becomes very hot.

5.2.1.2.2 Hydrochloric acid solution, mass fraction 10 %.

5.2.1.2.3 Potassium iodide solution, mass fraction 30 %.

Weigh, to the nearest 0,1 g, 60 g of potassium iodide, iodate-free grade, and dissolve it in 140 ml of water. Keep the solution in a dark place.

5.2.1.2.4 Starch solution, mass fraction 1 %.

Weigh 1,00 g of soluble starch and make a slurry with 5 ml of water. Add 95 ml of water to the slurry and boil for several minutes to dissolve it. Cool the solution. This solution needs refrigeration to avoid decomposition of the starch which results in a vague end point. Keep the solution cool and use it within one week.

Commercial starch solutions as indicators for iodine titration exist and may be used in place of the specified starch solution provided that their efficiency has been previously tested.

5.2.1.2.5 Potassium iodate (KIO_3).

5.2.1.2.6 Sodium thiosulfate standard volumetric solution, $c(Na_2S_2O_3.5H_2O)$ = 0,1 mol/l.

Standard volumetric solutions of sodium thiosulfate are commercially available.

Alternatively a standard volumetric solution may be prepared by the following procedure:

Dissolve 24,8 g Na2S2O3 . Five H_2O in a 1 000 ml one-mark volumetric flask in about 0,75 l water. After the temperature has equalized make up to the mark with water and mix thoroughly.

To standardize: Weigh, to the nearest 0,1 mg, 3,600 g (*m*) of dry potassium iodate. Dissolve in water in a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix (standard reference solution *c*(1/6 KIO3) = 0,1 mol/l). Place 200 ml of water in a 500 ml stoppered conical flask, add (2 ± 0,5) g of potassium iodide and stir to dissolve. Then introduce, by means of a pipette, 10,0 ml of sodium thiosulfate solution for standardization, add (15 ± 1) ml of hydrochloric acid solution (diluted 1 + 1 by volume) and (5 ± 1) ml of starch solution (5.2.1.2.4). Titrate immediately with the potassium iodate standard reference solution until the appearance of a blue coloration persisting for at least 30 s occurs. Record the volume *(V1)* of iodate used.

The actual concentration, *c*, of the sodium thiosulfate standard volumetric solution ($Na_2S_2O_3.5H_2O$), expressed in moles per litre, is given by the following formula:

$$c = \frac{V_1 \times c_1}{V} \tag{4}$$

where

c_1 is the concentration, expressed in moles per litre, of the potassium iodate standard reference solution [*c*(1/6 KIO3) = 0,1 mol/l];

V is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution used for the standardization (V = 10 ml);

V_1 is the volume, in millilitres, of potassium iodate standard reference solution used in the titration.

5.2.1.3 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

5.2.1.3.1 Potentiometric titrimeter.

5.2.1.3.2 Automatic burette, volume 50 ml, equipped with an injection tip (made of brown glass).

5.2.1.3.3 Electromechanical stirrer.

5.2.1.3.4 Glass titration beaker, capacity 250 ml (made of brown glass).

5.2.1.3.5 Platinum-Ag/AgCl combination electrode with electrolytic junction with built-in diaphragm.

5.2.1.4 Procedure

5.2.1.4.1 Test solution

Weigh, to the nearest 0,1 mg, a test portion of approximately 0,7 g (m) into a dry, clean beaker (5.2.1.3.4).

Add 20 ml of potassium iodide solution (5.2.1.2.3) and 10 ml of sulfuric acid (5.2.1.2.1). After dissolution under gentle stirring cover the beaker with a watch glass and keep the solution in the dark for 30 min. Then add 100 ml of water.

5.2.1.4.2 Determination

Input the calculation data in the titration microprocessor in accordance with the instruction manual.

Place the electrodes in the titration beaker and titrate with the sodium thiosulfate solution (5.2.1.2.6).

Record the titration curve and determine the inflection point as the equivalent point of the potentiometric titration.

5.2.1.5 Expression of results

The potassium peroxomonosulfate ($KHSO_5$) content, C_1, expressed as a percentage by mass, is given by the following formula:

$$C_1 = \frac{V \times c \times 76{,}1}{m} \quad (5)$$

where

V is the volume, expressed in millilitres, of the sodium thiosulfate standard volumetric solution (5.2.1.2.6) used for the titration;

c is the concentration, in moles per litre, of the sodium thiosulfate solution (5.2.1.2.6) ;

m is the mass of the test portion, expressed in grams.

76,1 is the mass in grams of $KHSO_5$ corresponding to 1 000 ml of sodium thiosulfate $c(Na_2S_2O_3.5H_2O)$ = 0,1mol/l.

5.2.1.6 Repeatability limit

The absolute difference between two single test results, obtained under repeatability conditions, shall not be greater than the repeatability value, r, as calculated from the following formula:

$$r = 0{,}001\ z \qquad (6)$$

where

z is the mean of the two results, expressed in mass fraction %.

NOTE Repeatability conditions are conditions where mutually independant test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

5.2.2 Chemical parameters

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

5.2.2.1.1 Principle

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

5.2.2.1.2 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.

5.2.2.1.2.1 Nitric acid, concentrated, density $\rho = 1{,}42$ g/ml.

5.2.2.1.2.2 Nitric acid, solution, c (HNO_3) = 2,5 mol/l.

5.2.2.1.2.3 Barium nitrate, Ba $(NO_3)_2$.

5.2.2.1.3 Procedure

5.2.2.1.3.1 Test portion

Weigh, to the nearest 0,01 g:

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

5.2.2.1.3.2 Test solution

For Cd: dissolve the test portion with 40 ml of water and after adding 20 ml of barium nitrate (5.2.2.1.2.3), bring solution briefly to boiling point and after cooling dilute to volume with water and homogenize. 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 (5.2.2.1.2.2) to the test portion, dilute with a few millilitres of water and mix. Dilute to volume with water and homogenize.

For Pb and As: dissolve the test portion with a few millilitres of water and mix. Dilute to volume with water and homogenize.

For Se and Sb: add 2 ml of nitric acid (5.2.2.1.2.1) to the test portion, dilute with a few millilitres of water and mix. Dilute to volume with water and homogenize.

5.2.2.1.3.3 Determination

Determine the content of chemical parameters in the test solution (5.2.2.1.3.2) in accordance with the following methods:

— **Cd, Ni and Pb**: in accordance with ISO 8288, 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 that needs to be corrected to give the final concentration according to Formula (7) in 5.2.2.1.4.

5.2.2.1.4 Expression of results

From the interim results (*y*) determined (see 5.2.2.1.3.3), the content, C_2, of each chemical parameter in the laboratory sample, expressed in milligrams per kilogram of potassium peroxomonosulfate is given by the following formula:

$$C_2 = y \times \frac{V}{m} \times \frac{100}{C_1} \quad (7)$$

where

y is the interim result (5.2.2.1.3.3);

V is the volume, expressed in millilitres, of the test solution (5.2.2.1.3.2) (= 100 ml);

m is the mass, expressed in grams, of the test portion;

C_1 is the potassium peroxomonosulfate content in percentage by mass of product (see 5.2.1.5).

5.2.2.2 Determination of the mercury content (Hg)

5.2.2.2.1 Principle

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

5.2.2.2.2 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.

5.2.2.2.2.1 **Potassium permanganate solution**, $c(KMnO_4)$ = 50 g/l.

5.2.2.2.2.2 **Sulfuric acid, concentrated**, density ρ = 1,84 g/ml.

5.2.2.2.2.3 **Hydroxylammonium chloride solution**, $c(NH_2OH.HCl)$ = 100 g/l.

5.2.2.2.2.4 **Potassium dichromate solution**, $c(K_2Cr_2O_7)$ = 4 g/l in 50 % volumic fraction nitric acid solution.

5.2.2.2.3 Procedure

5.2.2.2.3.1 Test portion

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

5.2.2.2.3.2 Test solution

Quantitatively transfer the test portion to a 100 ml (V_1) 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 (5.2.2.2.2.1) and five 1 ml portions of sulfuric acid (5.2.2.2.2.2). Heat and keep boiling for 10 min. Allow to cool. Just dissolve the precipitate (MnO_2) with hydroxylammonium chloride (5.2.2.2.2.3), add 5 ml of the potassium dichromate solution (5.2.2.2.2.4) and transfer to a 100 ml (V_2) volumetric flask. Dilute to the mark with water and mix.

5.2.2.2.3.3 Determination

Proceed as described in EN ISO 12846.

5.2.2.2.4 Expression of result

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

$$y = y_A \times \frac{V2}{10} \tag{8}$$

where

y_A is the result obtained in 5.2.2.2.3.3, for the concentration of mercury in the test solution, expressed in milligrams per litre ;

V_2 is the volume in millilitres of the test solution.

The mercury content, C_3, in milligrams per kilogram of potassium peroxomonosulfate is given by the following formula:

$$C_3 = y \times \frac{V1}{m_2} \times \frac{100}{C_1} \tag{9}$$

where

y is the previously determined interim result for mercury content;

V_1 is the volume, in millilitres, of the solution A (see 5.2.2.2.3.2);

m_2 is the mass, expressed in grams, of the test portion (5.2.2.2.3.1);

C_1 is the potassium peroxomonosulfate content in percent by mass (see 5.2.1.5).

6 Labelling - Transportation - Storage

6.1 Means of delivery

Potassium peroxomonosulfate shall be delivered in polyethylene bags, with net contents of 25 kg to 50 kg or fibre drums with polyethylene linings, with net contents of 50 kg to 100 kg.

Never use paper bags.

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, potassium peroxomonosulfate is not listed within Annex VI of [3]

Annex VI of [3] 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

Potassium peroxomonosulfate is listed as UN Number [5] 3260

- RID [6]: Class 8, Classification Code C2, Packaging Group III.;
- ADR [7]: Class 8, Classification Code C2, Packaging Group II ;
- IMDG [8]: Class 8, Packaging Group III, EmS: F-A, S-Q;
- IATA [9]: Class 8, Packaging Group III.

6.4 Marking

The marking shall include the following:

- the name: “potassium peroxomonosulfate triple salt”, trade name and type;
- the net mass;
- the name and address of supplier and/or manufacturer;
- the statement “This product conforms to EN 12678, type”.

6.5 Storage

6.5.1 Generals

Store the product in original packages in a cool and dry place, away from any sources of heat or incompatible materials.

6.5.2 Long term stability

Stable for a long period of time when stored below 25 °C and under dry conditions. The active oxygen loss per month is less than mass fraction 0,5 % relative.

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[4] See [3].

[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 60 °C).

Avoid contact with alkaline or reducing substances.

Avoid contact with oxidizable organic substances and combustible materials.

Avoid contact with metals and metal ions (e.g. Fe, Mn, Co, Ni).

Annex A
(informative)

General information on potassium peroxomonosulfate

A.1 Origin

A.1.1 Raw materials

Potassium peroxomonosulfate is manufactured from oleum (sulfuric acid + SO_3), hydrogen peroxide (H_2O_2) and potassium hydroxide (KOH).

A.1.2 Manufacturing process

Commercial product is formed from oleum and hydrogen peroxide, with subsequent partial neutralization by potassium hydroxide.

$$SO_3 + H_2SO_4 + 2\ H_2O_2 \rightarrow 2\ H_2SO_5 + H_2O \quad (A.1)$$

$$2\ H_2SO_5 + 2\ H_2SO_4 + 5\ KOH \rightarrow 2\ KHSO_5.KHSO_4.K_2SO_4 + 5\ H_2O \quad (A.2)$$

$$SO_3 + 3\ H_2SO_4 + 2\ H_2O_2 + 5\ KOH \rightarrow 2\ KHSO_5.KHSO_4.K_2SO_4 + 6\ H_2O \quad (A.3)$$

A.2 Use

A.2.1 Function

Oxidation of oxidizable matter (organic and inorganic) in water treatment.

A.2.2 Form in which it is used

As an aqueous solution in demineralized water, containing 20 g/l to 200 g/l of $KHSO_5$.

A.2.3 Treatment dose

Typical dose of $KHSO_5$ is 10 mg/l (g/m^3).

The treatment dose should be such that limits for potassium and sulfate ions in the drinking water are not exceeded.

A.2.4 Means of application

The product is usually applied using a metering pump.

A.2.5 Secondary effects

Increase of the salt content of the treated water, especially potassium ions and sulfate ions.

10 mg $KHSO_5$ (which corresponds to approximately to 22 mg of commercial product) corresponds to approximately 2,6 mg of K^+ and 6,3 mg of $SO_4{}^{2-}$ totally.

Lowering of the pH value of the water by formation of $KHSO_4$.

A.2.6 Removal of excess product

Addition of reducing agents (for example sulfur dioxide (SO_2), sodium sulfite (Na_2SO_3)).

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

Skin: wash thoroughly with plenty of water and soap.

Eyes: rinse immediately and thoroughly with plenty of water for at least 15 min and seek medical advice.

Inhalation: remove person to fresh air, if breathing is difficult seek medical help immediately.

Ingestion: give plenty of water to drink. Do not induce vomiting. Seek medical advice.

B.2.2 Spillage

Sweep up and collect into dry, clean, vented plastics containers. Residues are rinsed 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)

C.1 Safety precautions

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

C.2 General principle

Arsenious acid, antimonic 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.3 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 HNO_3 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.4 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.4.1 Sodium tetrahydroborate (sodium borohydride).

Dissolve 8 g $NaBH_4$ in 200 ml of NaOH, c(NaOH) = 0,1 mol/l. Prepare fresh daily.

C.4.2 Sodium iodide, prereductant solution.

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

C.4.3 Sulfuric acid, solution $c(H_2SO_4)$ = 9 mol/l.

C.4.4 Sulfuric acid, solution $c(H_2SO_4)$ = 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.4.5 Nitric acid, density (ρ) = 1,42 g/ml.

C.4.6 Perchloric acid, density (ρ) = 1,66 g/ml.

C.4.7 Hydrochloric acid, density (ρ) = 1,16 g/ml.

C.4.8 Argon (or nitrogen), commercial grade.

C.4.9 Hydrogen, commercial grade.

C.4.10 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 1 000 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.4.7) 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.4.5)) and mix; 1,00 ml = 0,100 µg As(III). Prepare diluted solutions daily.

C.4.11 Arsenic(V) solutions:

— stock As(V) solution; Dissolve 1,534 g of 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.4.12 Selenium(IV) solutions:

— stock Se(IV) solution: Dissolve 2,190 g of sodium selenite, Na_2SeO_3 in water containing 10 ml hydrochloric acid (C.4.7) 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.4.7) 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.4.5)) 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.4.13 Selenium(VI) solutions:

- stock Se(VI) solution: Dissolve 2,393 g of sodium selenate Na_2SeO_4 in water containing 10 ml nitric acid (C.4.5). 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.4.14 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 1 000 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.4.7) and mix; 1,00 ml = 10,0 µg Sb;
- standard Sb solution: Dilute into 1 000 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.4.5)) and mix; 1,00 ml = 0,100 µg Sb. Prepare diluted solutions daily.

C.5 Apparatus

Ordinary laboratory apparatus (such as spectrometers computer with updated software) **and glassware,** together with the following:

C.5.1 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.5.2 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).

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

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

C.5.3 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.6.3, 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:

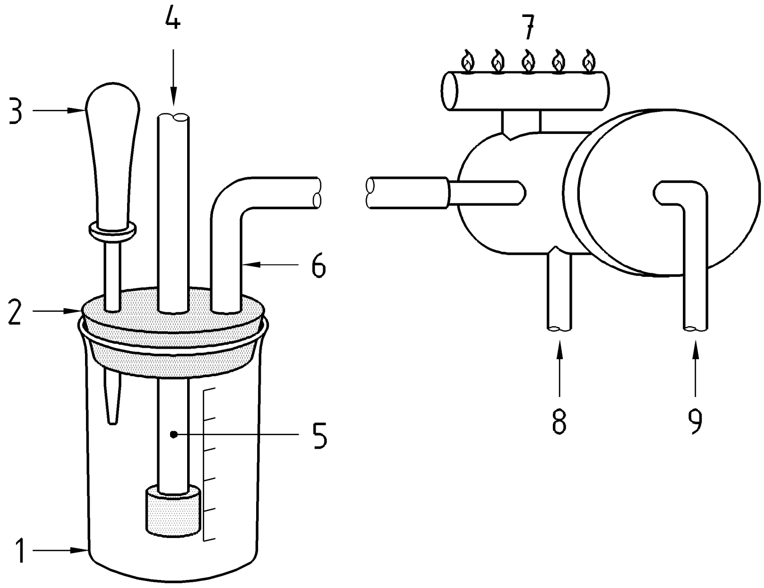
a) it shall provide a precise and reproducible calibration curve between 0 µg/l and 20 µg/l As, Sb or Se and a detection limit between 0,1 µg/l and 0,5 µg/l As, Sb or Se;

b) when carried through the entire procedure, oxidation state couples (As(III) - As(V) or Se(IV) - Se(VI)) shall cause equal instrument response; and

c) sample digestion shall yield 90 % or greater recovery of added As(III), As(V), Se(VI), Se(IV) or Sb.

C.5.4 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

1	Beaker 250 ml	6	Outlet tube
2	Rubber stopper	7	Burner
3	Dropper	8	Hydrogen
4	Auxiliary nitrogen	9	Nitrogen
5	Gas dispersion tube		

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

C.6 Procedure

C.6.1 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 analyzed. 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.6.2 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.4.5)).This yields calibrations 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.6.3 Preparation of test solutions and standard solutions

Add 50 ml of the sample or As(III), Se(VI) or Sb standard solution to 250 ml beakers. 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 $c(H_2SO_4)$ = 9 mol/l (C.4.3) and 5 ml nitric acid (C.4.5). 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 is usually indicated by a light-coloured solution. Cool slightly, add 25 ml water and 1 ml of perchloric acid (C.4.6) 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.6.4 Determination of arsenic with sodium borohydride

To 50 ml of the digested standard solution or the test solution in a 250 ml beaker (see Figure C.1) add 5 ml hydrochloric acid (C.4.7) and mix. Add 5 ml sodium iodide prereductant solution (C.4.2), 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.4.1). 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.6.5 Determination of selenium with sodium borohydride

To 30 ml of the digested standard solution or the test solution, or to 30 ml of the undigested standard, or the sample in a 250 ml beaker, add 15 ml hydrochloric acid (C.4.7) 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(Vl) 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.4.1). 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 µg/l Se(IV). Average recoveries shall be not less than 90 %.

C.6.6 Determination of antimony with sodium borohydride

To 30 ml of the digested standard solution or the test solution, or to 30 ml of the undigested standard solution, or the test solution in a 250 ml beaker, add 15 ml hydrochloric acid (C.4.7) 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.4.1). 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 interference's that suppress antimony hydride instrument response by treating a digested sample with 10 µg/l Sb. Average recoveries shall be not less than 90 %.

C.7 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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