**BS EN 16037:2012**

BSI Standards Publication

# Chemicals used for treatment of water intended for human consumption — Sodium hydrogen sulfate

## National foreword

This British Standard is the UK implementation of EN 16037:2012.

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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# Chemicals used for treatment of water intended for human consumption - Sodium hydrogen sulfate

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

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Natriumhydrogensulfat

This European Standard was approved by CEN on 24 May 2012.

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COMITÉ EUROPÉEN DE NORMALISATION
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# Foreword

This document (EN 16037:2012) 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of an identical text or by endorsement, at the latest by January 2013, and conflicting national standards shall be withdrawn at the latest by January 2013.

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# 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 hydrogen sulfate used for treatment of water intended for human consumption. It describes the characteristics of sodium hydrogen sulfate and specifies the requirements and the corresponding test methods for sodium hydrogen sulfate. 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 1483, *Water quality — Determination of mercury — Method using atomic absorption spectrometry*

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

ISO 2479, *Sodium chloride for industrial use — Determination of matter insoluble in water or in acid and preparation of principal solutions for other determinations*

ISO 2483, *Sodium chloride for industrial use — Determination of the loss of mass at 110 degrees C*

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

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

ISO 6332, *Water quality — Determination of iron — Spectrometric method using 1,10-phenanthroline*

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

Sodium hydrogen sulfate.

### 3.1.2 Synonym or common name

Sodium bisulfate.

### 3.1.3 Relative molecular mass

120,06 g/mol.

### 3.1.4 Empirical formula

$NaHSO_4$ .

### 3.1.5 CAS-Registry-Number(1)

7681-38-1.

### 3.1.6 EINECS-Number(2)

231-665-7.

## 3.2 Commercial form

Powder or beads, free flowing.

## 3.3 Physical properties

### 3.3.1 Appearance and odour

White to slightly yellow, odourless.

### 3.3.2 Density

The bulk density of the product is approximately between 1 400 $kg/m^3$ and 1 450 $kg/m^3$.

### 3.3.3 Solubility in water

Approximately 1 080 g/l at 25 °C.

### 3.3.4 Vapour pressure

Not applicable.

### 3.3.5 Boiling point

Not applicable.

### 3.3.6 Melting point at 100 kPa(3)

Approximately 180 °C.

Note 1 to entry: The product decomposes at higher temperatures to sodium disulfate and water.

### 3.3.7 Specific heat

Not applicable.

### 3.3.8 Viscosity (dynamic)

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.

### 3.3.9 Critical temperature

Not applicable.

### 3.3.10 Critical pressure

Not applicable.

### 3.3.11 Physical hardness

Not applicable.

## 3.4 Chemical properties

Sodium hydrogen sulfate is hygroscopic.

Aqueous solutions of the product exhibit a acid reaction and are corrosive to metals:

- acid constant $pK_S = 1,99$
- a solution with a mass fraction of 20 % has a pH value between 1 and 1,2 at 25 °C.

# 4 Purity criteria

## 4.1 General

This European Standard specifies the minimum purity requirements for sodium hydrogen sulfate 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.

NOTE 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 a mass fraction of sodium hydrogen sulfate greater than 95,2 %.

## 4.3 Impurities and by-products

The content of impurities and by-products shall be in accordance with Table 1.

**Table 1 — Impurities and by-products**

| Parameter | | Limit in % (mass fraction) |
|---|---|---|
| Sodium sulfate | max. | 4,8 |
| Water | max. | 0,8 |
| Water insoluble substances | max. | 0,05 |
| Iron | max. | 0,01 |

### 4.4 Chemical Parameters

The product shall conform to the requirements specified in Table 2.

**Table 2 — Chemical parameters**

| Parameter | | Limit in mg/kg $NaHSO_4$ |
|---|---|---|
| Arsenic (As) | max. | 0,1 |
| Cadmium (Cd) | max. | 0,1 |
| Chromium (Cr) | max. | 1 |
| Mercury (Hg) | max. | 0,1 |
| Nickel (Ni) | max. | 1 |
| Lead (Pb) | max. | 1 |
| Antimony (Sb) | max. | 1 |
| Selenium (Se) | max. | 1 |
| NOTE Pesticides, polycyclic aromatic hydrocarbons and halogenated organic substances are not by-products of the manufacturing process. For parametric values on chemical parameters content in drinking water, see [1]. | | |

## 5 Test methods

### 5.1 Sampling

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

### 5.2 Analysis

#### 5.2.1 Determination of sodium hydrogen sulfate

#### 5.2.1.1 Principle

Alkalimetric titration with sodium hydroxide solution.

#### 5.2.1.2 Reagents

**5.2.1.2.1** All reagents shall be of a recognized analytical grade. De-ionized water (conforming to grade 3 of EN ISO 3696) is sufficient.

**5.2.1.2.2** Sodium hydoxide solution, $c(NaOH) = 0,1$ mol/l

#### 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.

##### 5.2.1.3.3 Electromechanical stirrer

**5.2.1.3.4 Glass beaker**, capacity 250 ml

#### 5.2.1.4 Procedure

##### 5.2.1.4.1 Test solution

Weigh, to the nearest 0,1 mg, a test portion of approximately 0,2 g into a dry, clean beaker (5.2.1.3.4).

##### 5.2.1.4.2 Determination

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

Place the pH electrode in the titration beaker and titrate with the sodium hydroxide solution (5.2.1.2.2).

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 sodium hydrogen sulfate content, $C_1$, expressed as a percentage by mass, is given by the following formula (1):

$$C_1 = \frac{V \times c \times 120}{m} \tag{1}$$

where

$V$ is the volume, expressed in millilitres, of the sodium hydroxide solution (5.2.1.2.2) used for the titration;

$c$ is the concentration, in moles per litre, of the sodium hydroxide solution (5.2.1.2.2);

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

120 is the mass equivalent of sodium hydrogen sulfate in grams corresponding to 1 000 ml of sodium hydroxide solution with $c$(NaOH) = 0,1 mol/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 $z$

where

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

NOTE Repeatibility conditions are conditions where mutually independent 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 By-products

#### 5.2.2.1 Determination of water

The content of water is determined according to ISO 2483.

#### 5.2.2.2 Determination of water insoluble substances

The content of insoluble substances is determined according to ISO 2479.

#### 5.2.2.3 Determination of sodium sulfate

The content of sodium sulfate, $C_S$, expressed in mass fraction %, is calculated by the following formula (2):

$$C_s = 100 - C_1 - C_W - C_i - C_2 \quad (2)$$

where

$C_1$ is the content of sodium hydrogen sulfate (see 5.2.1);

$C_W$ is the content of water (see 5.2.2.1);

$C_i$ is the content of insoluble substances (see 5.2.2.2);

$C_2$ is the content of iron (see 5.2.2.4).

#### 5.2.2.4 Determination of iron (Fe)

##### 5.2.2.4.1 Principle

Iron is determined by visible absorption spectrometry of its 1,10-phenanthroline complex.

##### 5.2.2.4.2 Reagents

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

**5.2.2.4.2.1 Nitric acid, solution**, $c(HNO_3) = 2{,}5$ mol/l.

##### 5.2.2.4.3 Procedure

###### 5.2.2.4.3.1 Test solution

Weigh, to the nearest 0,1 mg, 1 g ($m$) of a test portion into a 100 ml one-mark volumetric flask. Add 0,5 ml of nitric acid (5.2.2.4.2.1), dilute with a few millilitres of water and mix. Dilute to volume with water and homogenize.

###### 5.2.2.4.3.2 Determination

The concentration of iron in the test solution (5.2.2.4.3.1) is determined according to ISO 6332.

The determination gives an interim result ($y$) expressed in milligrams per litre that needs to be corrected to give the final concentration according to the formula in 5.2.2.4.4.

#### 5.2.2.4.4 Expression of results

From the interim results ($y$) determined (see 5.2.2.4.3.2), the content $C_2$ of iron in the test portion, expressed in milligrams per kilogram is given by the following formula (3):

$$C_2 = y \times \frac{V}{m} \qquad (3)$$

where

$Y$ is the interim result (see 5.2.2.4.3.2);

$V$ is the volume, expressed in millilitres, of the test solution (5.2.2.4.3.1) (= 100 ml);

$m$ is the mass, expressed in grams, of the test sample.

### 5.2.3 Chemical parameters

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

##### 5.2.3.1.1 Principle

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

##### 5.2.3.1.2 Reagents

###### 5.2.3.1.2.1 General

All reagents shall be of a recognised analytical grade and the water used shall conform to grade 2 specified in EN ISO 3696.

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

**5.2.3.1.2.3 Nitric acid, solution**, $c(HNO_3) = 2{,}5$ mol/l.

**5.2.3.1.2.4 Barium nitrate solution,** $c(Ba(NO_3)_2) = 75$ g/l.

##### 5.2.3.1.3 Procedure

###### 5.2.3.1.3.1 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.

#### 5.2.3.1.3.2 Test solution

For Cd: dissolve the test portion with 40 ml of water and after adding 30 ml of barium nitrate solution (5.2.3.1.2.4), 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 (5.2.3.1.2.3) 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 (5.2.2.1.2.2) to the test portion, dilute with a few millilitres of water and mix. Dilute to volume with water and homogenize.

#### 5.2.3.1.3.3 Determination

Determine the content of chemical parameters in the test solution (5.2.3.1.3.2) in accordance with the following methods:

- **Cd, Ni and Pb**: in accordance with ISO 8288, Method A for direct determination by flame atomic absorption spectrometry;
- **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 the formula in 5.2.3.1.4.

#### 5.2.3.1.4 Expression of results

From the interim results ($y$) determined (see 5.2.3.1.3.3), the content, $C_2$, of each chemical parameter in the

laboratory sample, expressed in milligrams per kilogram of sodium hydrogen sulfate is given by the following formula (4):

$$C_2 = y \times \frac{V}{m} \times \frac{100}{C_1} \tag{4}$$

where

$Y$ is the interim result (5.2.3.1.3.3);

$V$ is the volume, expressed in millilitres, of the test solution (5.2.3.1.3.2) (= 100 ml);

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

$C_1$ is the sodium hydrogen sulfate content in percentage by mass of product (see 5.2.1.5).

### 5.2.3.2 Determination of the mercury (Hg)

#### 5.2.3.2.1 Principle

The element mercury is determined by flameless atomic absorption spectrometry in accordance with EN 1483.

#### 5.2.3.2.2 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 2 specified in EN ISO 3696.

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

**5.2.3.2.2.2 Sulfuric acid, concentrated**, density $\rho$ = 1,84 g/ml.

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

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

#### 5.2.3.2.3 Procedure

**5.2.3.2.3.1 Test portion**

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

**5.2.3.2.3.2 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 (5.2.3.2.2.1) and five 1 ml portions of sulfuric acid (5.2.3.2.2.2). Heat and keep boiling for 10 min. Allow to cool. Just dissolve the precipitate ($MnO_2$) with hydroxylammonium chloride (5.2.3.2.2.3), add 5 ml of the potassium dichromate solution (5.2.3.2.2.4) and transfer to a 100 ml ($V_2$) volumetric flask. Dilute to the mark with water and mix.

**5.2.3.2.3.3 Determination**

Proceed as described in EN 1483.

#### 5.2.3.2.4 Expression of result

The interim result for mercury content ($y$) expressed in milligrams per litre is given by the following formula (5):

$$y = y_A \times \frac{V_2}{10} \qquad (5)$$

where

$y_A$ is the result obtained in 5.2.3.2.3.3, 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 sodium hydrogen sulfate is given by the following formula (6):

$$C_3 = y \times \frac{V}{m_2} \times \frac{100}{C_1} \qquad (6)$$

where

$y$ is the previously determined interim result for mercury content;

$V_1$ is the volume, in millilitres, of the solution A (see 5.2.3.2.3.2);

$m_2$ is the mass, expressed in grams, of the test portion (see 5.2.3.2.3.1);

$C_1$ is the sodium hydrogen sulfate content in percent by mass (see 5.2.1.5).

## 6 Labelling – Transportation – Storage

### 6.1 Means of delivery

Sodium hydrogen sulfate shall be delivered in polyethylene bags, with net contents of 25 kg, or in flexible bulk containers, with net contents of maximum 1 000 kg.

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 standard, the following labelling requirements shall apply to sodium hydrogen sulfate:

| | |
|---|---|
| Hazard pictogram<br><br>**Figure 1**<br>GHS 05 | – Signal word:<br>**Danger**<br>– hazard statement :<br>H318: Causes serious eye damage<br>NOTE Precautionary statements ("P statements") should be be provided by the company being responsible for the marketing of the substance. They should be indicated on the packaging label and in the extended safety data sheet (eSDS) of the substance. |

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[4] See [2].

NOTE The regulation [2] , and its amendments for the purposes of its adaptation to technical and scientific progress, contains a list of substances classified by the EU. Substances not listed in this regulation 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

At the date of publication of the standard, Sodium hydrogen sulfate is not listed as UN Number5) and not classified by the manufacturers as a dangerous good according to the transport regulations RID6), ADR7), IMDG8) and IATA9).

## 6.4 Marking

The marking shall include the following:

- the name: “sodium hydrogen sulfate” and trade name;
- the net mass;
- the name and address of supplier and/or manufacturer;
- the statement “This product conforms to EN 16037”.

## 6.5 Storage

### 6.5.1 General

Store the product in original packages or in tightly closed plastic containers in a cool and dry place. Do not use containers made of common construction metals (mild steel, stainless steel, zinc coated steel, etc.). Keep away from any sources of heat (avoid heat of > 60 °C to prevent agglomeration) or incompatible materials.

### 6.5.2 Long term stability

Stable when stored under conditions described in 6.5.1.

### 6.5.3 Storage incompatibilities

Avoid contact with alkaline substances (intense reaction). Avoid contact with common construction metals (corrosion, release of highly flammable hydrogen gas).

Avoid mixtures with hypochlorites and other compounds containing active chlorine (intense reaction, release of toxic chlorine gas).

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5) United Nations Number.

6) Regulations concerning the 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 Code.

9) International Air Transport Association. Dangerous Goods Regulations.

# Annex A
(informative)

# General information on sodium hydrogen sulfate

## A.1 Origin

### A.1.1 Raw materials

Sodium hydrogen sulfate is usually manufactured from sulfuric acid and sodium chloride. It can be made from sulfuric acid and sodium sulfate, or from sulfuric acid and sodium hydroxide or from sulfuric acid and sodium carbonate.

### A.1.2 Manufacturing process

The usual manufacturing process is the reaction of solid sodium chloride (salt) or sodium sulfate with equivalent amounts of concentrated sulfuric acid under heating according to the reaction formulae:

$$H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl \qquad (A.1)$$

$$H_2SO_4 + Na_2SO_4 \rightarrow 2\ NaHSO_4 \qquad (A.2)$$

## A.2 Use

### A.2.1 Function

It is most commonly used for adjustment of pH value. Other uses include generation of chlorine dioxide by acidification of sodium chlorite, regeneration of adsorbents and ion exchange resins.

### A.2.2 Form in which it is used

The product is used as aqueous solution containing 20 g/l to 200 g/l of $NaHSO_4$.

### A.2.3 Treatment dose

The dose depends of the application and water quality objectives.

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

### A.2.4 Means of application

The aqueous solution of the product is usually applied using a metering pump.

### A.2.5 Secondary effects

Lowering of the pH value of the treated water, increasing the concentration of sodium and sulfate ions.

### A.2.6 Removal of excess product

Addition of alkaline agents (e.g. sodium hydrogen carbonate) is used to neutralize the excess acidity.

# 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 in plastics containers (no metallic containers). Observe local waste disposal regulations. Rinse residues away with plenty of water. Clean contaminated tools with plenty of water.

### B.2.3 Fire

Product itself does not burn. Cool endangered containers with water spray jet. Adapt extinguishing measure to the surrounding fire as foam, carbon dioxide, dry powder. Do not use water.

# 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, 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.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 $HNO_3$ 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.3 Reagents

All reagents shall be of a recognised 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 $NaBH_4$ in 200 ml of NaOH, $c(NaOH) = 0,1$ mol/l. Prepare fresh daily.

**C.3.2 Sodium iodide**, prereductant solution.

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

**C.3.3 Sulfuric acid**, solution $c(H_2SO_4) = 9$ mol/l.

**C.3.4 Sulfuric acid**, solution $c(H_2SO_4)$ = 1,25 mol/l.

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

**C.3.5 Nitric acid**, density ($\rho$) = 1,42 g/ml.

**C.3.6 Perchloric acid**, density ($\rho$) = 1,66 g/ml.

**C.3.7 Hydrochloric acid**, density ($\rho$) = 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 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.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 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 : Pepare 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 of 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 of 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) ($C_4H_4O_7SbK \cdot 0,5\ H_2O$) at 100 °C for 1 h. 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.3.7) 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.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 to 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.

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

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.

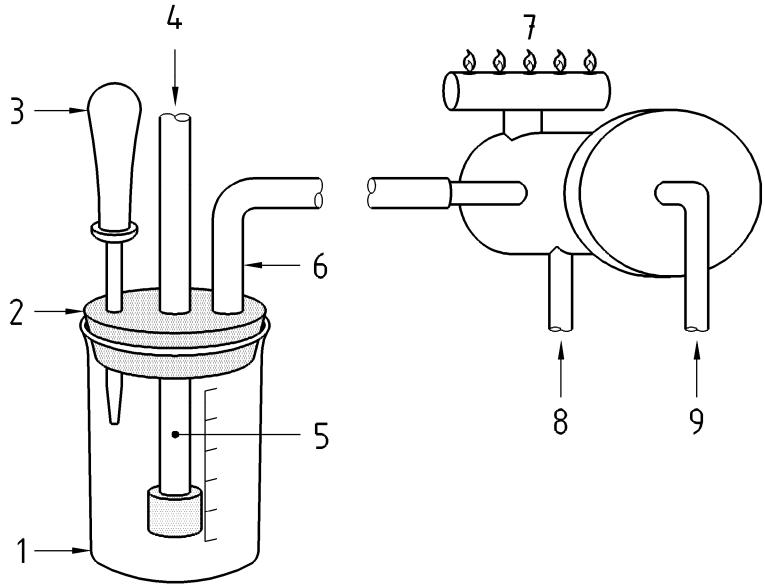
Irrespective of the hydride reaction cell-atomizer system selected, it shall meet the following quality-control considerations:

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.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**

| | | | | | |
|---|---|---|---|---|---|
| 1 | beaker 250 ml | 4 | auxiliary nitrogen | 7 | burner |
| 2 | rubber stopper | 5 | gas dispersion | 8 | hydrogen |
| 3 | dropper | 6 | outlet tube | 9 | 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 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.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 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.5.3 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.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 is usually 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 the 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 prereductant 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 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.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 µg/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 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.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 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.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.

# Bibliography

[1] 98/83/EC, Council Directive of 3 November 1998 on the quality of water intended for human consumption

[2] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (REACH)

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