BS EN 938:2016

BSI Standards Publication

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

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National foreword

This British Standard is the UK implementation of EN 938:2016. It supersedes BS EN 938:2009 which is withdrawn.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

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

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

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Natriumchlorit

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 938:2016) 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of an identical text or by endorsement, at the latest by November 2016, and conflicting national standards shall be withdrawn at the latest by November 2016.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 938:2009.

Significant technical differences between this edition and EN 938:2009 are 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) use of the changed classification and labelling (see [2]).

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 the 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 chlorite used for treatment of water intended for human consumption. It describes the characteristics of sodium chlorite and specifies the requirements and the corresponding test methods for sodium chlorite. 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 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 8288, *Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods*

ISO 9174, *Water quality — Determination of chromium — Atomic absorption spectrometric methods*

3 Description

3.1 Identification

3.1.1 Chemical name

Sodium chlorite.

3.1.2 Synonym or common name

None.

3.1.3 Relative molecular mass

90,44.

3.1.4 Empirical formula

$NaClO_2$.

3.1.5 Chemical formula

Na-O-Cl = O.

3.1.6 CAS Registry Number [1)]

7758-19-2.

1) Chemical Abstracts Service Registry Number.

3.1.7 EINECS reference [2)]

231-836-6.

3.2 Commercial form

The product is supplied as a powder or as an aqueous solution of sodium chlorite.

3.3 Physical properties

3.3.1 Appearance

The products are either a white powder or a greenish-yellow aqueous solution.

3.3.2 Density

The density of sodium chlorite solutions is given in Table 1.

Table 1 — Density of sodium chlorite solutions

Aqueous solution concentration % (mass fraction)	**Density** g/ml at 20 °C
25	1,210
31	1,270

3.3.3 Solubility in water

The solubility of sodium chlorite depending on temperature is given in Table 2.

Table 2 — Solubility of sodium chlorite

Temperature °C	**Solubility** g/l
5	340
17	390
30	460
45	530
60	550

3.3.4 Vapour pressure

Not applicable.

3.3.5 Boiling point at 100 kPa [3)]

Not applicable.

3.3.6 Crystallization point

The crystallization point of sodium chlorite depending on concentration is given in Table 3.

2) European Inventory of Existing Commercial Chemical Substances.

3) 100 kPa = 1 bar.

Table 3 — Crystallization point of sodium chlorite

Aqueous solution concentration % (mass fraction)	**Crystallization point** °C
25	– 14,5
31	3

3.3.7 Specific heat

Not known.

3.3.8 Viscosity (dynamic)

The viscosity of sodium chlorite depending on concentration is given in Table 4.

Table 4 — Viscosity of sodium chlorite

Aqueous solution concentration % (mass fraction)	**Viscosity** mPa.s at 20 °C
25	2,33
31	3,26

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 chlorite is a strong oxidizing agent. It generates chlorine dioxide with acidic solutions or chlorine and reacts with organic compounds.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for sodium chlorite 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 sodium chlorite is available as a powder or as an aqueous solution with sodium chlorite content of 7,5 percent by mass fraction to 35 percent by mass fraction.

The content of sodium chlorite shall be equal to or greater than the manufacturer's declared value.

4.3 Impurities and main by-products

The product shall conform to the requirements specified in Table 5.

Table 5 — Impurities

Impurity	**Limit** **g/kg sodium chlorite** **100 % mass fraction**
Sodium chlorate ($NaClO_3$) max.	40
Sodium nitrate ($NaNO_3$) max.	1
NOTE Sodium chlorate can be a by-product of the manufacturing process.	

4.4 Chemical parameters

NOTE For the purposes of this standard, "chemical parameters" are those defined in the EU Directive 98/83/EC of November 13, 1998 (see [1]).

The content of chemical parameters shall conform to the requirements specified in Table 6.

Table 6 — Chemical parameters

Parameter		**Limit** **mg/kg sodium chlorite** **100 % mass fraction**	
		Type 1	**Type 2**
Arsenic (As)	max.	1,1	7,5
Cadmium (Cd)	max.	1,5	7,5
Chromium (Cr)	max.	1,1	7,5
Mercury (Hg)	max.	1,1	3,7
Nickel (Ni)	max.	1,1	7,5
Lead (Pb)	max.	1,1	7,5
Antimony (Sb)	max.	1,1	7,5
Selenium (Se)	max.	1,1	7,5
NOTE Cyanide which does not exist in a strong oxidizing medium such as sodium chlorite 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

5.1.1 General

Observe the general recommendations of ISO 3165 and take ISO 6206 into account.

5.1.2 Sampling from drums and bottles

5.1.2.1 General

5.1.2.1.1 Mix the contents of the container to be sampled by shaking the container, by rolling it or by rocking it from side to side, taking care not to damage the container or spill any of the liquid.

5.1.2.1.2 If the design of the container is such (for example, a narrow-necked bottle) that it is impracticable to use a sampling implement, take a sample by pouring after the contents have been thoroughly mixed. Otherwise, proceed as described in 5.1.2.3.

5.1.2.1.3 Examine the surface of the liquid. If there are signs of surface contamination, take samples from the surface as described in 5.1.2.2; otherwise, take samples as described in 5.1.2.3.

5.1.2.2 Surface sampling

Take a sample using a suitable ladle. Lower the ladle into the liquid until the rim is just below the surface, so that the surface layer runs into it. Withdraw the ladle just before it fills completely and allow any liquid adhering to the ladle to drain off. If necessary, repeat this operation so that, when the other selected containers have been sampled in a similar manner, the total volume of sample required for subsequent analysis is obtained.

5.1.2.3 Bottom sampling

Take a sample using an open sampling tube, or a bottom-valve sampling tube, suited to the size of container and the viscosity of the liquid.

When using an open sampling tube, close it at the top and then lower the bottom end to the bottom of the container. Open the tube and move it rapidly so that the bottom of the tube traverses the bottom of the container before the tube is filled. Close the tube, withdraw it from the container and allow any liquid adhering to the outside of the tube to drain off.

When using a bottom-valve sampling tube, close the valve before lowering the tube into the container and then proceed in a similar manner to that when using an open sampling tube.

5.1.3 Sampling from tanks and tankers

From each access point, take samples as follows:

a) from the surface of the liquid, using a ladle as described in 5.1.2.2;

b) from the bottom of the tank or tanker, using a sampling tube as described in 5.1.2.3 or using a specially designed bottom-sampling apparatus;

c) from one or more positions, depending on the overall depth, between the bottom and the surface using a weighted sampling can.

5.2 Analysis

5.2.1 Determination of sodium chlorite (main product)

5.2.1.1 General

This method applies to the measurements of sodium chlorite content in commercial sodium chlorite solutions and is specific for these species.

5.2.1.2 Principle

Automated iodometric titration with an excess of sulfuric acid. This method is based on the reducing action of the iodide ion on the chlorite species and on the subsequent determination of iodine formed, by redox titration against sodium thiosulfate; the potential step is located around 230 mV.

5.2.1.3 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.

5.2.1.3.1 Sulfuric acid solution, $c(H_2SO_4)$ = 0,5 mol/l.

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

Dissolve 24,8 g of $Na_2S_2O_3.5H_2O$ in water. Add 0,5 ml of chloroform as preservative, dilute to volume with water in a 1 000 ml one-mark volumetric flask and mix thoroughly.

To standardize: Weigh, to the nearest 0,1 mg, (160 ± 10) mg (*m*) of primary standard potassium dichromate into a tared glass beaker. Place the contents of the beaker in a 500 ml stoppered conical flask, add 100 ml of water and (2 ± 0,5) g of potassium iodide and stir to dissolve. Add (15 ± 1) ml of hydrochloric acid solution (diluted 1 + 1 by volume), swirl, and allow to stand for 5 min. Titrate with the sodium thiosulfate solution until the solution is pale yellow. Add (5 ± 1) ml of starch solution 1 % (*mass fraction*) and titrate to the end point, i.e. to the disappearance of the blue-black colour. Record the volume *(V)* used.

The 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:

$$c = \frac{m}{V \times 49{,}0317} \quad (1)$$

where

m is the mass, in milligrams, of potassium dichromate ($K_2Cr_2O_7$) weighed;

V is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution used.

5.2.1.3.3 Potassium iodide.

5.2.1.4 Apparatus

Ordinary laboratory apparatus and glassware with together the following:

5.2.1.4.1 Automatic potentiometric titrimeter.

5.2.1.4.2 Automatic burette, 10 ml, equipped with an injection tip.

5.2.1.4.3 Electromechanical stirrer.

5.2.1.4.4 Glass titration beaker, 400 ml.

5.2.1.4.5 Platinum – Silver/Silver-chloride combination electrode with a porous plug electrolytic junction.

5.2.1.5 Procedure

5.2.1.5.1 Test solution

Weigh, to the nearest 0,1 mg, a test portion (m) between 0,11 g and 0,15 g the laboratory sample.

5.2.1.5.2 Determination

Transfer the test solution (5.2.1.5.1) to a 400 ml titration beaker with 300 ml of water and 4 g of potassium iodide (5.2.1.3.3) and add, with stirring, 20 ml of H_2SO_4 (5.2.1.3.1).

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

Introduce the electrode into the titration beaker and titrate with the sodium thiosulfate standard volumetric solution (5.2.1.3.2).

5.2.1.6 Expression of results

The sodium chlorite ($NaClO_2$) content, C_1, expressed as a percentage by mass (% of mass fraction) is given by the following formula; assume 90,44 g of sodium chlorite ($NaClO_2$) is equivalent to 1 000 ml of sodium thiosulfate $c(Na_2S_2O_3.5H_2O)$ = 0,1 mol/l:

$$C_1 = \frac{V_1 \times c \times 2{,}262}{m} \qquad (2)$$

where

V_1 is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution (5.2.1.3.2) used for the titration at the end point;

c is the concentration, moles per litre, of the sodium thiosulfate standard volumetric solution (5.2.1.3.2);

m is the mass in grams of the test portion (5.2.1.5.1).

5.2.2 Impurities

5.2.2.1 Determination of sodium chlorate content ($NaClO_3$)

5.2.2.1.1 General

This method is used to determine the chlorate content, in the range between 3,75 g/l and 15 g/l, in sodium chlorite solutions for commercial use; it is specific for these species.

5.2.2.1.2 Principle

Direct determination of chlorate ion in a diluted solution of sodium chlorite by separation and chemical suppressed conductimetric detection (ionic chromatography).

NOTE Calibration is linear for concentration of chlorate ion between 3,75 mg/l and 15 mg/l in the diluted solution.

5.2.2.1.3 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.

5.2.2.1.3.1 Sodium carbonate and sodium hydrogen carbonate, eluant solution.

Mix one volume of sodium carbonate $c(Na_2CO_3)$ = 2 mol/l with one volume of sodium hydrogen carbonate $c(NaHCO_3)$ = 0,75 mol/l.

5.2.2.1.3.2 Sulfuric acid solution $c(H_2SO_4)$ = 0,025 mol/l regenerant solution.

5.2.2.1.3.3 Helium gas, high purity, for degassing eluant and regenerant solutions.

5.2.2.1.3.4 Water, ultra pure, conductivity = 0,056 µS/cm.

5.2.2.1.3.5 Sodium chlorate stock solution at 1 g/l:

Weigh, to the nearest 0,000 1 g, 0,255 1 g of $NaClO_3$. Dissolve in 200 ml of the ultrapure water (5.2.2.1.3.4).

5.2.2.1.4 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

5.2.2.1.4.1 Ion chromatograph.

5.2.2.1.4.2 Chemical suppressed conductivity detector.

5.2.2.1.4.3 Anionic column and precolumn:

Resin composed of 15 µm polystyrene/divinylbenzene substrate agglomerated with anion exchange latex that has been aminated.

5.2.2.1.4.4 Data logger/plotter able to record and display the chromatographic peak heights.

5.2.2.1.4.5 Densimeter, temperature setting 20 °C.

5.2.2.1.5 Chromatographic conditions

a) Eluant flow rate: 2 ml/min;

b) regenerant flow rate: 2,5 ml/min;

c) full scale of conductivity: 30 mS;

d) residual conductivity: < 18 mS;

e) linearity range: ClO_3^-: 1 mg/l to 15 mg/l of injected solution.

Calibration conditions:

Four levels of calibration and a blank level. Each level is measured three times.

5.2.2.1.6 Procedure

5.2.2.1.6.1 Preparation of calibration solutions

Prepare chlorate standard solutions by diluting the sodium chlorate stock solution (5.2.2.1.3.5) with the eluant solution (5.2.2.1.3.1), prepare calibration solutions in accordance with Table 7.

Table 7 — Calibration solution for determination of chlorate content

Solution	ClO_3^- in mg/l
1	3,75
2	7,5
3	11,25
4	15

5.2.2.1.6.2 Preparation of test solution

Heat the sodium chlorite laboratory sample to 20 °C and check the density in grams per millilitre with a densimeter (5.2.2.1.4.5) set for 20 °C.

Prepare dilutions with the eluant solution (5.2.2.1.3.1) in order to be within the range of calibration.

5.2.2.1.6.3 Measurement of calibration and test solutions

Measure each calibration solution three times; for each solution the relative standard deviation shall be lower than 0,5 %.

Dilute each test solution in order to obtain two levels of concentration located respectively in the lower part of the calibration curve and in the upper part of the calibration curve. Repeat the measurements twice more in order to keep the relative standard deviation at not more than 0,5 %.

5.2.2.1.7 Expression of results

The chlorate content, of the test solution is obtained from the regression line obtained with the five levels of calibration results in the sodium chlorite solution.

The chlorate (ClO_3^-) content of the laboratory sample, C_2, expressed in milligrams per litre is given by the following general formula:

$$C_2 = y \times \frac{V_2}{m_1} \quad (3)$$

where

y is the concentration obtained from calibration curve;

V_2 is the volume, in millilitres, of the dilution;

m_1 is the mass, in grams, of the test solution.

The sodium chlorate ($NaClO_3$) content, C_3, expressed in grams per kilogram of sodium chlorite of a mass fraction of 100 % is given by the following formula:

$$C_3 = C_2 \times \frac{C_1}{100 \times \rho} \quad (4)$$

where

C_1 is the sodium chlorite content in percentage by mass (5.2.1.6);

p is the density, in grams per millilitre of the sodium chlorite solution.

5.2.2.1.8 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:

$$r = 0{,}05\ z \quad (5)$$

where

z is the mean of the two results, expressed in grams per kilogram.

NOTE Repeatability 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.

5.2.3 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

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

5.2.3.1.2.1 Nitric acid, concentrated, density ρ = 1,42 g/ml.

5.2.3.1.3 Procedure

5.2.3.1.3.1 Test portion

Weigh, to the nearest 0,001 g, 20 g (m_3) from the laboratory sample into a glass beaker.

5.2.3.1.3.2 Test solution

Evaporate until a wet residue is obtained, cool, add 1 ml of nitric acid (5.2.3.1.2.1), dilute with a few millilitres of water, transfer quantitatively to a 100 ml volumetric flask and dilute to volume with water and mix.

Carry out the evaporation carefully and not to dryness in order to avoid possible losses of arsenic and selenium.

5.2.3.1.3.3 Determination

Determine the content of toxic substances 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;

— **Cr**: in accordance with ISO 9174;

— **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 5.2.3.1.4.

5.2.3.1.4 Expression of results

From the interim results (y) determined (see 5.2.3.1.3.3), the content, C_4, of each chemical parameter in the laboratory sample, expressed in milligrams per kilogram of sodium chlorite of a mass fraction of 100 % is calculated from the following general formula:

$$C_4 = y \times \frac{V_4}{m_3} \times \frac{100}{C_1} \quad (6)$$

where

y is the interim result (5.2.3.1.3.3);

V_4 is the volume, in millilitres, of the test solution (5.2.3.1.3.2) (= 100 ml);

m_3 is the mass, expressed in grams, of the test portion;

C_1 is the sodium chlorite ($NaClO_2$) content in percentage by mass (5.2.1.6).

5.2.3.2 Determination of mercury (Hg)

5.2.3.2.1 Principle

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

5.2.3.2.2 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.

5.2.3.2.2.1 Potassium permanganate solution, $\rho(KMnO_4)$ = 50 g/l.

5.2.3.2.2.2 Sulfuric acid, concentrated, density P = 1,84 g/ml.

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

5.2.3.2.2.4 Potassium dichromate solution, $\rho(K_2Cr_2O_7)$ = 4 g/l in a volume fraction of 50 % of nitric acid solution.

5.2.3.2.3 Procedure

5.2.3.2.3.1 Test portion

Pipette 10 g (m_4) of the laboratory sample and transfer to approximately 70 ml of water taking care to avoid sputtering.

5.2.3.2.3.2 Test solution

Quantitatively transfer the test portion to a washing flask (e.g. Durand bottle), capacity 250 ml, the gas inlet of which is made of a porous frit. Dilute the contents of the washing flask with water to obtain a total volume of 100 ml. Transfer to a volumetric flask (solution A).

Pipette, accurately 10 ml of the solution A. Transfer to a 250 ml conical flask 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_T) volumetric flask. Dilute to the mark with water and mix.

5.2.3.2.3.3 Determination

Proceed as described in EN ISO 12846.

5.2.3.2.4 Expression of results

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

$$y = y_A \times \frac{V_T}{10} \tag{7}$$

where

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

V_T is the volume in millilitres of the test solution.

The content of mercury, C_5, in milligrams per kilogram of sodium chlorite, mass fraction of 100 % is given by the following formula:

$$C5 = y \times \frac{10}{m_4} \times \frac{100}{C_1} \tag{8}$$

where

m_4 is the mass, expressed in grams, of the test portion;

C_1 is the sodium chlorite content in percentage by mass (5.2.1.6).

6 Labelling - Transportation - Storage

6.1 Means of delivery

Sodium chlorite shall be delivered in polyethylene drums containers or tankers of up to 25 t capacity.

In order that the purity of the products 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 chlorite is not listed within Annex VI of Regulation (EC) No 1272/2008 [2]

Annex VI of Regulation (EC) No 1272/2008 [2] and its amendments and adaptations to technical progress contain a list of substances classified by the EU. Substances which are 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 chlorite solid is listed as UN Number [5)] 1496.

4) See [2].

RID [6] ADR [7]: Class 5.1, code O_2, packing group II.

IMDG [8]: Class 5.1, Packing group II.

IATA [9]: Class 5.1, Packing group II.

Sodium chlorite solution is listed as UN Number [5] 1908.

RID [6] ADR [7]: Class 8, code C9, packing group II.

IMDG [8]: Class 8, Packing group II.

IATA [9]: Class 8, Packing group II.

6.4 Marking

The marking shall include the following:

a) name “Sodium chlorite”, trade name and grade;

b) net mass ;

c) name and address of supplier and/or manufacturer;

d) statement “this product conforms to EN 938, type,…”.

6.5 Storage

6.5.1 General

The product shall be stored in containers used exclusively for sodium chlorite. It shall be stored away from direct sunlight, in a cool, well-ventilated area, but at a temperature not lower than the crystallization point (see 3.3.6). Large quantities shall be stored outdoors or in a room equipped with an automatic fire-extinguishing system. Refer to local authorities regulations.

6.5.2 Long term stability

The product is stable for at least one year.

6.5.3 Storage incompatibilities

The product shall not be allowed to come into contact with acids, acidic salts, reducing agents or organic compounds (wood, paper, grease,…).

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.

Annex A
(informative)

General information on sodium chlorite

A.1 Origin

A.1.1 Raw materials

Sodium chlorite is manufactured from sodium chlorate ($NaClO_3$), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4).

A.1.2 Manufacturing process

It is usually produced by reduction of sodium chlorate to chlorine dioxide and neutralization by sodium hydroxide and hydrogen peroxide according to the following formula:

$$2\ NaClO_3 + 2H_2SO_4 + H_2O_2 \dashrightarrow 2\ ClO_2 + 2\ NaHSO_4 + 2H_2O + O_2$$

$$2\ ClO_2 + 2\ NaOH + H_2O_2 \dashrightarrow 2\ NaClO_2 + 2H_2O + O_2$$

A.2 Use

A.2.1 Function

Its function in water treatment is the generation of chlorine dioxide by reaction with chlorine or hydrochloric acid or sodium peroxodisulfate process.

$$2\ NaClO_2 + Cl_2 \dashrightarrow 2ClO_2 + 2\ NaCl$$

$$5\ NaClO_2 + 4HCl \dashrightarrow 4ClO_2 + 5\ NaCl + 2\ H_2O$$

$$2\ NaClO_2 + Na_2S_2O_8 \dashrightarrow 2\ ClO_2 + 2\ Na_2\ SO_4$$

A.2.2 Form in which it is used

It is used as an aqueous solution.

A.2.3 Treatment dose

The treatment dose depends of the raw water composition. Care should be taken not to exceed a maximum concentration of chlorine dioxide in the water supply, usually a few tenths of 1 mg/l and to refer to the local regulation.

A.2.4 Means of application

It is applied by means of a chlorine dioxide generator.

A.2.5 Secondary effects

The secondary effects include the following:

a) oxidation of iron, manganese;

b) odour and colour removal;

c) oxidation of organic compounds.

A.2.6 Removal of excess product

The most practical method is the use of sodium hydrogen sulfite, sodium disulfite at pH value 5 to 6 or sodium sulfite. Granular activated carbon may also be used, as well as ferrous salts at neutral pH.

A.3 Routine analyses

A.3.1 Determination of sodium chlorite (NaClO2)

A.3.1.1 General

This method is used to determine the content of sodium chlorite in commercial sodium chlorite solutions and it is specific for these species.

A.3.1.2 Principle

Manual iodometric titration with an excess of sulfuric acid. This method is based on the reducing action of the iodide ion on the chlorite species and on the subsequent determination of iodine formed, by redox titration against sodium thiosulfate.

A.3.1.3 Reagents

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

A.3.1.3.1 Potassium iodide (Kl) solution, 100 g/l.

A.3.1.3.2 Sulfuric acid solution, 50 g/l.

A.3.1.3.3 Starch solution, indicator 1 % mass fraction.

Make a slurry with (1 ± 0,1) g starch and (5 ± 1) ml water. Add (90 ± 5) ml boiling water. Stir to dissolve it and cool the solution. This solution needs refrigeration to avoid the decomposition of the starch with results in a vague end point. Keep the solution cool and use it within one week.

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

A.3.1.3.4 Sodium thiosulfate standard volumetric solution, $c(Na_2S_2O_3.5H_2O)$ = 0,1 mol/l.

Dissolve 24,8 g of $Na_2S_2O_3.5H_2O$ in water. Add 0,5 ml of chloroform as preservative, dilute to volume with water in a 1 000 ml one-mark volumetric flask and mix thoroughly.

To standardize: Weigh, to the nearest 0,1 mg, (160 ± 10) mg (m) of primary standard potassium dichromate into a tared glass beaker. Place the contents of the beaker in a 500 ml stoppered conical flask, add 100 ml of water and (2 ± 0,5) g of potassium iodide and stir to dissolve. Add (15 ± 1) ml of sulfuric acid solution (A.3.1.3.2), swirl, and allow to stand for 5 min. Titrate with the sodium thiosulfate solution until the solution is pale yellow. Add (5 ± 1) ml of starch solution (A.3.1.3.3) and titrate to the end point, i.e. to the disappearance of the blue-black colour. Record the volume *(V)* used.

The 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:

$$c = \frac{m}{V \times 49{,}0317} \qquad \text{(A.1)}$$

where

m is the mass, in milligrams, of potassium dichromate ($K_2Cr_2O_7$) weighed;

V is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution used.

A.3.1.4 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

A.3.1.4.1 Densimeter, temperature setting 20 °C.

A.3.1.4.2 Automatic pipette, range between 0,1 ml and 1 ml.

A.3.1.5 Procedure

A.3.1.5.1 Test solution

Heat the sodium chlorite laboratory sample to 20 °C and check the density in grams per millilitre with a densimeter (A.3.1.4.1) set for 20 °C.

Using the automatic pipette, (A.3.1.4.2) transfer 0,2 ml to 0,3 ml of the test sample (volume = V_o) to a 250 ml conical flask with tight fitting stopper. Add, in the following order:

a) 50 ml of water;

b) 20 ml of Kl solution (A.3.1.3.1);

c) 10 ml of H_2SO_4, (A.3.1.3.2).

Put the stopper on the flask and leave in the dark for at least 5 min.

A.3.1.5.2 Determination

Titrate the test solution (A.3.1.5.1) with the sodium thiosulfate standard volumetric solution (A.3.1.3.4) in presence of the starch solution (A.3.1.3.3); the end point is obtained when the solution turns from blue-black to colourless. Record the volume V_1.

A.3.1.6 Expression of results

The sodium chlorite ($NaClO_2$) content, C_6, expressed as a percentage by mass, is given by the following formula:

$$C6 = \frac{V_1 \times c \times 2{,}262}{V_o \times \rho} \qquad \text{(A.2)}$$

where

V_1 is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution (A.3.1.3.4) required for the titration;

c is the concentration, in moles per litre, of the sodium thiosulfate standard volumetric solution (A.3.1.3.4);

V_o is the volume, in millilitres, of the test sample;

ρ is the density, in grams per millilitre, of the sodium chlorite solution.

A.3.2 Determination of chlorate ion (ClO_3^-)

A.3.2.1 General

This method is used to determine the chlorate content in commercial sodium chlorite solutions.

A.3.2.2 Principle

The method is based on the indirect titration of the chlorite and chlorate species that are present in solution, by excess addition of Mohr's salt followed by titration of the surplus with potassium dichromate. Using a simultaneous iodometric titration of chlorite it is possible to assess the concentration of chlorate in solution.

A.3.2.3 Reagents

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

A.3.2.3.1 Barium diphenylaminosulfonate solution, mass fraction of 0,5 %.

A.3.2.3.2 Sulfuric acid (H_2SO_4) solution (diluted 1 + 1 by volume).

A.3.2.3.3 Phosphoric acid (H_3PO_4) solution (diluted 1 + 1 by volume).

A.3.2.3.4 Ammonium iron (II) sulfate, hexahydrate (Mohr's salts) solution $c[(NH_4)_2\,F_e(SO_4)_2 \,.\, 6H_2O] = 0{,}2$ mol/l.

A.3.2.3.5 Potassium dichromate solution, $c(K_2Cr_2O_7) = 0{,}03$ mol/l.

A.3.2.4 Apparatus

Ordinary laboratory apparatus and glassware together with an automatic pipette, range 0,1 ml to 1 ml.

A.3.2.5 Procedure

A.3.2.5.1 General

From the iodometric titration of sodium chlorite (see A.3.1), note the following parameters:

- V_1 is the volume, in millilitres of sodium thiosulfate standard volumetric solution (A.3.1.3.4) used for the titration;
- c is the concentration, in moles per litre, of the sodium thiosulfate standard volumetric solution (A.3.1.3.4).

A.3.2.5.2 Determination

Transfer with the automatic pipette 0,2 ml to 0,3 ml of the test sample (volume = V_2) to a 250 ml conical flask containing 50 ml of water. Bring to boil and heat for 3 min so as to facilitate decomposition of any hydrogen peroxide that can be present. Cool, add 50 ml of Mohr's salt (A.3.2.3.4) and 25 ml of sulfuric acid (A.3.2.3.2) and bring again to boil.

Cool, add 10 ml of phosphoric acid (A.3.2.3.3) 0,5 ml of barium diphenylaminosulfonate (A.3.2.3.1) and titrate with potassium dichromate (A.3.2.3.5) until the solution turns violet, note the volume used (V_3).

A.3.2.5.3 Blank test determination

Carry out a blank test following exactly the same protocol as in A.3.2.5.1, note the volume used (V_4).

A.3.2.6 Expression of results

The sodium chlorate ($NaClO_3$) content, C_9, expressed in grams per kilogram of sodium chlorite of a mass fraction of 100 %, is given by the following formula:

$$C_7 = \frac{\left[C_1\,(V_4 - V_3) - V_1 \times c\right]}{V_2} \times 17{,}74 \times \frac{100}{C_6} \qquad \text{(A.3)}$$

where

V_4 is the volume, in millilitres, of potassium dichromate (A.3.2.3.5) used in the blank test;

V_3 is the volume, in millilitres, of potassium dichromate (A.3.2.3.5) used for the test sample;

C_1 is the concentration, in moles per litre, of potassium dichromate (A.3.2.3.5);

V_1 is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution (A.3.1.3.4) (determination of chlorite);

c is the concentration, in moles per litre, of the sodium thiosulfate standard volumetric solution (determination of sodium chlorite);

V_2 is the volume, in millilitres, of test sample used for the blank test determination and for sodium chlorite determination;

C_6 is the sodium chlorite content in percentage by mass (A.3.1.6).

A.3.3 Determination of chemical parameters

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

— As: in accordance with ISO 17378-2 (see [3]).

— Se: in accordance with ISO/TS 17379-2 (see [4]).

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

Keep clothing contaminated with sodium chlorite wet, remove as quickly as possible and wash or immerse in water before it dries.

Obtain medical assistance promptly in the event of swallowing, eye contact, or all but minor skin burns.

Eye contact: Rinse immediately with gently flowing water for at least 15 min, holding the eyelids open.

Ingestion: Rinse mouth, give plenty of water or milk.

Never give anything by mouth or attempt to cause the vomiting of an unconscious person.

B.2.2 Spillage

Rinse with plenty of water.

Sodium chlorite is flammable in dried conditions.

B.2.3 Fire

Extinguish with water. Speed in extinguishing clothing fires and immersing burned areas in water is essential.

Do not use halon extinguisher.

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 Nal 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 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 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.4.12 Selenium(IV) solutions:

— stock Se(IV) solution: Dissolve 2,190 g sodium selenite, Na_2SeO_3 in water containing 10 ml hydrochloric acid (C.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 sodium selenate Na_2SeO_4 in water containing 10 ml nitric acid (C.4.5). 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(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 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.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.

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

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.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:

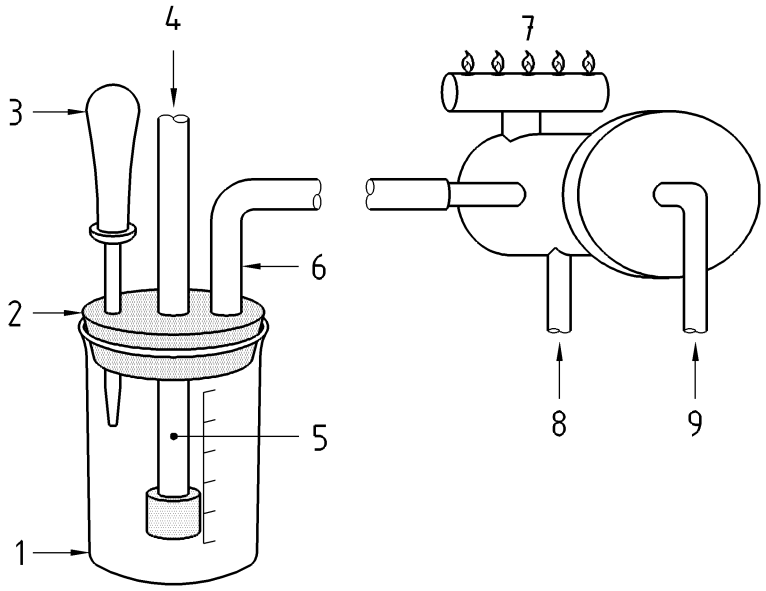
a) it shall provide a precise and reproducible calibration curve between 0 µg/l and 20 µg/l As, Sb or Se and a detection limit between 0,1 µg/l and 0,5 µg/l As, Sb or Se;

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
2 rubber stopper
3 dropper
4 auxiliary nitrogen
5 gas dispersion tube
6 outlet tube
7 burner
8 hydrogen
9 nitrogen

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 $CaCl_2$ and 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 of 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 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 $c(H_2SO_4)$ = 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 usually is 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 pre-reduction 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 interferences 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.

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)

[3] ISO 17378-2, *Water quality — Determination of arsenic and antimony — Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

[4] ISO/TS 17379-2, *Water quality — Determination of selenium — Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

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