BS EN 901:2013

BSI Standards Publication

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

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National foreword

This British Standard is the UK implementation of EN 901:2013. It supersedes BS EN 901:2007 which is withdrawn.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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Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Hypochlorite de sodium

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Natriumhypochlorit

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Foreword

This document (EN 901:2013) 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of an identical text or by endorsement, at the latest by November 2013, and conflicting national standards shall be withdrawn at the latest by November 2013.

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 901:2007.

Significant technical differences between this edition and EN 901:2007 are as follows:

- replacement of warning and safety precautions notes by labelling according to Regulation (EC) No 1272/2008.

According to the CEN-CENELEC Internal Regulations, the national standards organisations 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 regarding 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. Use of the product covered by this European Standard is subject to regulation or control by National Authorities.

This product is a biocide and should comply with the relevant legislation in force. In the European Union, at the time of publication, this legislation is Directive 1998/8/EC [1].

1 Scope

This European Standard is applicable to sodium hypochlorite used for treatment of water intended for human consumption. It describes the characteristics of sodium hypochlorite and specifies the requirements and the corresponding test methods for sodium hypochlorite. It gives information on its use in water treatment. It also determines the rules relating to safe handling and use of sodium hypochlorite (see Annex B).

NOTE While this standard is not applicable to sodium hypochlorite generated in-situ (see bibliographic reference [7]), the limits for impurities and chemical parameters apply.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

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

3 Description

3.1 Identification

3.1.1 Chemical name

Sodium hypochlorite.

3.1.2 Synonym or common names

Liquid bleach, soda bleach, bleach lye.

3.1.3 Relative molecular mass

74,44.

3.1.4 Empirical formula

$NaClO$.

3.1.5 Chemical formula

$NaClO$.

3.1.6 CAS Registry Number [1]

7681-52-9.

3.1.7 EINECS reference [2]

231-668-3.

3.2 Commercial form

The product is supplied as an aqueous solution with an available (active) chlorine concentration up to a mass fraction of 18 %.

3.3 Physical properties

3.3.1 Appearance and odour

The product is a clear yellowish-green solution with a faint chlorinous odour.

3.3.2 Density

The density of the product varies between 1,13 g/ml and 1,30 g/ml at 20 °C.

3.3.3 Solubility in water

The product is capable of being mixed with water in any proportion.

3.3.4 Vapour pressure

Approximately 2,5 kPa at 20 °C.

3.3.5 Boiling point at 100 kPa [3]

Not applicable.

3.3.6 Crystallisation and freezing point

At about – 10 °C crystallisation of $NaOCl . 6 H_2O$ starts.

Freezing of the concentrated product takes place between - 20 °C and - 30 °C.

3.3.7 Specific heat

The specific heat is 3,48 kJ/(kg.K) for a solution with an available active chlorine concentration of mass fraction between 14 % and 15 %.

3.3.8 Viscosity (dynamic)

2,6 mPa.s at 20 °C.

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1) Chemical Abstracts 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

The product is an alkaline solution with a pH value greater than 11 at 20 °C.

It reacts with acids and acidic salts to form chlorine.

Vigorous reactions occur with reducing chemicals. It is a strong oxidant ($E°_{Red}$ for (ClO^-) = 0,89 V).

$$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$$

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for sodium hypochlorite used for treating 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, the user, and when necessary the relevant authorities, shall be notified.

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

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

4.2 Composition of commercial product

Sodium hypochlorite is available only in solutions with concentrations up to 18 % active chlorine at the time of delivery by the producer. Common concentrated products contain a minimum of 12 % active chlorine. Diluted solutions are also available.

The concentration of sodium hypochlorite shall be equal to or greater than the value specified by the manufacturer.

4.3 Impurities and main by-products

The product contains sodium chloride (NaCl) in equimolar amounts at minimum, and a small portion of sodium hydroxide (NaOH) which keeps the product alkaline. Thus a little amount of sodium carbonate (Na_2CO_3) can be present, too.

The sodium chlorate ($NaClO_3$) content shall not exceed a mass fraction of 5,4 % of available chlorine at the time of delivery by the producer. The product shall be visibly free from deposits or suspended matter.

NOTE Sodium chlorate is a by-product of the manufacturing process and can be formed during storage (see 6.5.1).

4.4 Chemical parameters

The product shall conform to the requirements specified in Table 1.

Table 1 — Chemical parameters

Parameter		**Limit in mg/kg of available chlorine**	
		Type 1	**Type 2**
Arsenic (As)	max.	1	5
Antimony (Sb)	max.	20	25
Cadmium (Cd)	max.	2,5	5
Chromium (Cr)	max.	2,5	5
Lead (Pb)	max.	15	15
Mercury (Hg)	max.	3,5	5
Nickel (Ni)	max.	2,5	10
Selenium (Se)	max.	20	25
		Limit in g/kg of available chlorine	
Sodium bromate[a]	max.	2,5	5,0

[a] Sodium bromate is a by-product of the manufacturing process.

NOTE Cyanide, which does not exist in a strong oxidising medium such as sodium hypochlorite, is not a relevant chemical parameter. Pesticides and polycyclic aromatic hydrocarbons are not by-products of the manufacturing process. For parametric values of sodium hypochlorite on trace metal content in drinking water, see bibliographic reference [1].

5 Test methods

5.1 Sampling

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

5.2 Analysis

5.2.1 Determination of available chlorine content (main product)

5.2.1.1 General

This method applies to all commercial products with available chlorine contents within the range of 70 g/l to 170 g/l.

NOTE It detects all oxidising agents being active in weak acidic solutions, i.e. hypochlorite/chlorine, iodate, and partially chloramines, Fe(III), etc. Bromate and chlorate are not covered under these conditions.

5.2.1.2 Principle

Sodium hypochlorite reacts with potassium iodide to release iodine in the presence of acetic acid. The iodine is titrated with sodium thiosulfate standard volumetric solution in the presence of starch indicator solution.

The titration may also be carried out potentiometrically by the aid of titration automates, in which case the addition of soluble starch is unnecessary.

5.2.1.3 Reagents

All reagents shall be of a recognised analytical grade and the water used shall conform to grade 3, as specified in EN ISO 3696:1995 (de-ionised water for common laboratory purposes).

5.2.1.3.1 Potassium iodide solution, mass fraction 10 %

Weigh, to the nearest 0,1 mg, 100 g of potassium iodide, iodate-free, and dissolve in water and dilute to 1 l.

5.2.1.3.2 Acetic acid concentrated, of purity at least of mass fraction 99 %

5.2.1.3.3 Sodium thiosulfate standard volumetric solution, c(Na2S2O3.5H2O) = 0,1 mol/l

Standard volumetric solutions are commercially available, which might have to be diluted.

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

Dissolve 24,8 g $Na_2S_2O_3.5H_2O$ in a 1 000 ml one-mark volumetric flask in 0,75 l of water. After the temperature has equalised, make up to the mark with water and mix thoroughly.

To standardise: Weigh, to the nearest 0,1 mg, 3,600 g (m) of dry potassium iodate. Dissolve in water in a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix (standard reference solution $c(1/6\ KIO_3) = 0,1$ mol/l). Place 200 ml of water in a 500 ml stoppered conical flask, add (2 ± 0,5) g of potassium iodide and stir to dissolve. Then introduce, by means of a pipette, 10,0 ml of sodium thiosulfate solution for standardization, add (15 ± 1) ml of hydrochloric acid solution (diluted 1 + 1 by volume) and (5 ± 1) ml of starch solution (5.2.1.3.4). Titrate immediately with the potassium iodate standard reference solution until the appearance of a blue coloration that persists for 30 s. Record the volume (V_1) of iodate used.

The actual concentration, c, of the sodium thiosulfate standard volumetric solution ($Na_2S_2O_3.5H_2O$), expressed in moles per litre is given by Formula (1):

$$c = \frac{V_1 \times c_1}{V} \qquad (1)$$

where

c_1 is the concentration, expressed in moles per litre, of the potassium iodate standard reference solution [$c(1/6\ KIO_3) = 0,1$ mol/l];

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

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

5.2.1.3.4 Starch solution, mass fraction of 1 %

Make a slurry with (1 ± 0,1) g of starch and (5 ± 1) ml of water. Add (90 ± 5) ml of boiling water to the slurry. Stir to dissolve it and cool the solution. This solution needs to be refrigerated to avoid the decomposition of the starch which 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.

5.2.1.4 Apparatus

Ordinary laboratory apparatus and glassware.

5.2.1.5 Procedure

5.2.1.5.1 Test solution

Weigh to the nearest 0,1 mg 1 g of the laboratory sample (record mass m_1 in grams) into a 250 ml conical flask and dilute with water up to 100 ml.

5.2.1.5.2 Determination

Add 10 ml of the potassium iodide solution (5.2.1.3.1) and 5 ml of concentrated acetic acid (5.2.1.3.2).

Titrate at once with the sodium thiosulfate standard volumetric solution (5.2.1.3.3) until the iodine colour is nearly gone. Add 3 ml of the starch indicator solution (5.2.1.3.4) and complete the titration until the disappearance of the blue-black colour. Record the volume V_1, of the sodium thiosulfate standard volumetric solution added.

5.2.1.6 Expression of results

The available chlorine (Cl_2) content, C_2, expressed in mass fraction in %, is given by Formula (2):

$$C_2 = (V_1 \times c \times 3{,}545) / (m_1) \qquad (2)$$

where

V_1 is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution (5.2.1.3.3);

c is the concentration in moles per litre, of the sodium thiosulfate standard volumetric solution (see 5.2.1.3.3);

3,545 is the mass in milligrams of chlorine (Cl_2) corresponding to 1 ml of sodium thiosulfate solution of $c(Na_2S_2O_3.5H_2O)$ = 0,100 mol/l;

m_1 is the mass in grams of the laboratory sample used to prepare the test solution (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 hypochlorite solutions for commercial use; it is specific for these species.

5.2.2.1.2 Principle

Direct determination of chlorate ions in a diluted solution of sodium hypochlorite by ion chromatography with suppressed conductimetric detection.

5.2.2.1.3 Reagents

All reagents shall be of a recognised analytical grade and the water used shall have a conductivity of 0,056 µS/cm (conform to grade 1, as specified in EN ISO 3696:1995).

5.2.2.1.3.1 Sodium carbonate and sodium hydrogen carbonate, eluant solution.

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

5.2.2.1.3.2 Sulfuric acid solution c(H2SO4) = 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 Sodium chlorate stock solution 1 g/l.

Weigh, to the nearest 0,000 1 g, 0,255 1 g of $NaClO_3$. Dissolve in 200 ml of the water (grade 1, EN ISO 3696:1995).

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 pre-column

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 Generator of water (grade 1, EN ISO 3696:1995).

5.2.2.1.5 Chromatographic conditions

- Eluant flow rate: 2 ml/min;
- regenerant flow rate: 2,5 ml/min;
- full scale of conductivity: 30 mS;
- residual conductivity: < 18 mS.

5.2.2.1.6 Procedure

5.2.2.1.6.1 Preparation of calibration solutions

Prepare calibration solutions in volumetric flasks by diluting accurately measured volumes of the chlorate stock solution (5.2.2.1.3.4) with the eluant solution (5.2.2.1.3.1), in accordance with Table 2.

Table 2 — Calibration solutions for determination of chlorate content

Solution	ClO_3^- in mg/l	$NaClO_3$ in mg/l
1	3,75	4,78
2	7,5	9,57
3	11,25	14,35
4	15	19,13

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

5.2.2.1.6.2 Preparation of test solution

Weigh to the nearest 0,1 mg 250 mg of the laboratory sample (record mass m_2 in milligrams) into a 100,0 ml measuring flask, fill up with eluant solution (5.2.2.1.3.1) and homogenise the test solution by shaking the sealed flask carefully.

5.2.2.1.6.3 Measurement of calibration and test solutions

Measure each calibration and test solution three times using a constant injection volume according to the requirements of the respective ion chromatograph. For each solution, the relative repeatability standard deviation shall be lower than 0,5 %.

5.2.2.1.7 Expression of results

The sodium chlorate content of the test solution (y in mg/l) is calculated from the calibration line which is obtained by linear regression with the five levels (four chlorate solutions and one blank solution) in the calibration procedure.

The sodium chlorate ($NaClO_3$) content of the laboratory sample, C_2, expressed in grams per kilograms is given by Formula (3):

$$C_2 = (y \times V_2)/m_2 \tag{3}$$

where

y is the concentration of the test solution in milligrams per litre obtained via the regression line of the calibration;

V_2 is the volume, in millilitres, of the test solution (5.2.2.1.6.2);

m_2 is the mass of the laboratory sample, in milligrams (5.2.2.1.6.2).

The sodium chlorate ($NaClO_3$) content of the laboratory sample, C_3 expressed in mass fraction in % of available chlorine is given by Formula (4):

$$C_3 = \frac{(C_2 \times 10)}{C_1} \tag{4}$$

where

C_2 is the sodium chlorate ($NaClO_3$) content in g/kg of the laboratory sample;

C_1 is the available chlorine (Cl_2) content in mass fraction in % (5.2.1.6).

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 Formula (5):

$$r = 0{,}001\, z \tag{5}$$

where

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

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.

5.2.2.2 Determination of sodium bromate content ($NaBrO_3$)

5.2.2.2.1 General

This method is used to determine the bromate content, in the range between 2 mg/l and 1 000 mg/l, in sodium hypochlorite solutions for commercial use.

5.2.2.2.2 Principle

Direct determination of bromate ions in a diluted solution of sodium hypochlorite by ion chromatography with suppressed conductimetric detection.

The range of measurement can be limited by analytical column capacity. A dilution of the sample in the measurement range can be necessary. A convenient pre-treatment of the sample might be required (for example to remove any chloride, sulfate, carbonate or metals).

Direct determination of bromate by separation and indirect UV detection may also be carried out. The complete analytical procedure is described in Annex D.

5.2.2.2.3 Reagents

All reagents shall be of a recognised analytical grade and the water used shall have a conductivity of 0,056 µS/cm (conform to grade 1 as specified in EN ISO 3696:1995).

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

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

5.2.2.2.3.3 Stock sodium carbonate solution, $c(Na_2CO_3)$ = 0,5 mol/l.

Dissolve 53,0 g of anhydrous sodium carbonate in 800 ml of water (grade 1, EN ISO 3696:1995) in a 1 000 ml volumetric flask and make up to the volume with water (grade 1, EN ISO 3696:1995).

Store the solution at 2 °C to 6 °C in a polyethylene or glass bottle and renew it every 6 months.

5.2.2.2.3.4 Eluent carbonate solution, $c(Na_2CO_3)$ = 0,009 mol/l.

Introduce 36 ml of the stock sodium carbonate solution 0,5 mol/l (5.2.2.2.3.3) into a 2 000 ml volumetric flask and make up to the volume with water (grade 1, EN ISO 3696:1995).

Store the solution at 2 °C to 6 °C in polyethylene or glass bottle and renew it every week.

Degas the solution with helium (5.2.2.2.3.2) before use according to the instructions given by the manufacturer.

Eluent should be maintained under an inert helium atmosphere to avoid carbonate contamination.

5.2.2.2.3.5 Stock standard bromate solution, $w(BrO_3)$ = 1 000 mg/l

Dry 1,5 g of potassium bromate for at least 1 h at 105 °C. Store the dried product in a desiccator. Weigh, to the nearest 0,0 001 g,1,3 057 g of the dry potassium bromate. Introduce into a 1 000 ml volumetric flask. Dissolve in 800 ml of water (grade 1, EN ISO 3696:1995) and make up to the volume with water (grade 1, EN ISO 3696:1995). Store the solution at 2 °C to 6 °C in polyethylene or glass bottle and renew it every 12 months.

A commercial standard stock solution at required concentration may be also used.

5.2.2.2.3.6 Bromate standard solution, $w(BrO_3)$ = 10 mg/l

Introduce 1 ml of stock standard bromate solution (5.2.2.2.3.5) into a 100 ml volumetric flask. Make up to the volume with water (grade 1, EN ISO 3696:1995).

Store the solution at 2 °C to 6 °C in polyethylene or glass bottle and renew it every 3 months.

5.2.2.2.4 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

5.2.2.2.4.1 Ion chromatograph

5.2.2.2.4.2 Chemical or electrochemical suppressed conductivity detector

5.2.2.2.4.3 Anionic column and pre-column

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

5.2.2.2.4.4 Pre-treatment cartridges

- Cationic exchangers as Ag-form (Silver) (cartridge);
- cationic exchangers as H-form (Hydrogen) (cartridge).

If necessary, cationic exchangers as Ba-form (Barium) (cartridge) may be used to suppress sulfate interferences.

5.2.2.2.4.5 Generator, **of water** (grade 1, EN ISO 3696:1995).

5.2.2.2.5 Chromatographic conditions

- eluant flow rate: 1 ml/min;
- regenerant flow rate: 2,5 ml/min or electrochemical regeneration;
- recommended sampling loop size: 50 µl to 100 µl.

5.2.2.2.6 Procedure

5.2.2.2.6.1 Preparation of calibration solutions

Prepare calibration solutions in volumetric flasks by diluting accurately measured volumes of the bromate stock solution (5.2.2.2.3.5) with the eluant carbonate solution (5.2.2.2.3.4) in accordance with Table 3.

Table 3 — Calibration solutions for determination of bromate content

Solution	BrO_3^- in mg/l	$NaBrO_3$ in mg/l
1	0,2	0,236
2	0,5	0,59
3	1	1,18
4	2	2,36

NOTE 1 Calibration is linear for concentration of bromate ion between 0,2 mg/l and 2 mg/l in the diluted solution.

NOTE 2 The calibration solutions will be prepared freshly on the day of use.

5.2.2.2.6.2 Sample pre-treatment (if required)

If sample pre-treatment is necessary (presence of chloride and/or carbonate in large amount in the sample that can interfere with the bromate determination), calibration solutions and diluted test solutions shall be treated as follows:

- connect the cationic exchangers (cartridges) in series in order of Ag-H;
- using a 10 ml syringe, flush the cartridges with 10 ml of water;
- fill a 10 ml syringe with sample and attach it to the cartridge set;
- flush it with 5 ml of sample;
- continue to inject sample through the cartridges and collect the next 5 ml of treated sample for analysis;
- purge the treated sample with helium gas for 5 min to remove the remaining carbonate.

If necessary, a Ba-form cartridge may be added to remove sulfate; the three pre-treatment cartridges should then be attached in the following order: Ba-form, Ag-form, and H-form.

5.2.2.2.6.3 Preparation of test solutions

Weigh to the nearest 0,1 mg, 250 mg of the laboratory sample (record mass m_3 in milligrams) into a 100,0 ml measuring flask, fill up with eluant solution (5.2.2.2.3.4) and homogenise the test solution by shaking the sealed flask carefully.

5.2.2.2.6.4 Measurement of calibration and test solutions

Measure each calibration solution and test solution three times using a constant injection volume according to the requirements of the respective ion chromatograph. For each solution, the relative repeatability standard deviation shall be lower than 0,5 %.

5.2.2.2.7 Expression of results

The sodium bromate content of the test (y_1 in mg/l) is calculated from the calibration line which is obtained by linear regression with the five levels (four bromate solutions and one blank solution) in the calibration procedure. The sodium bromate ($NaBrO_3$) content of the laboratory sample, C_4, expressed in milligrams per kilogram is given by Formula (6):

$$C_4 = (y_1 \times V_3 \times 10) / m_3 \qquad (6)$$

where

y_1 is the concentration of the test solution in mg/l obtained via the regression line of the calibration;

V_3 is the volume in millilitres of the test solution (5.2.2.2.6.3);

m_3 is the mass of the laboratory sample in milligrams (5.2.2.2.6.3).

The sodium bromate ($NaBrO_3$) content of the laboratory sample, C_5, expressed in mass fraction of available chlorine is given by Formula (7):

$$C_5 = (C_4 \times 10)/C_1 \qquad (7)$$

where

C_4 is the sodium bromate ($NaBrO_3$) content in mg/kg of the laboratory sample;

C_1 is the available chlorine (Cl_2) content in mass fraction in % (5.2.1.6).

5.2.2.2.8 Repeatibility 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 Formula (8):

$$r = 0{,}005\ z \qquad (8)$$

where

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

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 recognised analytical grade and the water used shall conform to grade 2 as specified in EN ISO 3696:1995.

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_4) 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, make up to the 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 elements in the test solution (5.2.3.1.3.2) in accordance with the following methods:

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

These methods will give an interim result (y) expressed in milligrams per litre which needs to be converted to give the final concentration according to the formula in 5.2.3.1.3.4.

5.2.3.1.3.4 Expression of results

From the interim result (y) determined (see 5.2.3.1.3.3), the content, C_6, of each element in the laboratory sample, expressed in milligrams per kilogram of available chlorine is given by Formula (9):

$$C_6 = y \times \frac{V_4}{m_4} \times \frac{100}{C_1} \tag{9}$$

where

y is the interim result (5.2.3.1.3.3);

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

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

C_1 is the available chlorine (Cl_2) content in mass fraction in % (5.2.1.6).

5.2.3.2 Determination of mercury content (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 recognised analytical grade and the water used shall conform to the grade 3 as specified in EN ISO 3696:1995.

5.2.3.2.2.1 Nitric acid, mass fraction 65 %.

5.2.3.2.2.2 Sulfuric acid, mass fraction 30 %.

5.2.3.2.2.3 Hydroxylammonium chloride solution ($NH_2OH.HCl$) , mass fraction 10 %.

5.2.3.2.2.4 Tin(II) chloride solution, mass fraction 10 %.

5.2.3.2.3 Procedure

5.2.3.2.3.1 Test portion

Pipette 10 g (m_5) 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 gas washing flask, capacity 250 ml, with the gas inlet equipped with a porous glass frit. Dilute the contents of the gas washing flask with water to obtain a total volume of 100 ml. Transfer to a volumetric flask (solution A).

Pipette accurately 5 ml of the sodium hypochlorite (solution A) and dilute in a 250 ml graduated gas washing flask. During gentle shaking, add 30 ml of hydroxylammonium chloride solution (5.2.3.2.2.3), 5 ml of nitric acid (5.2.3.2.2.1) and 2 ml of tin(II) chloride solution (5.2.3.2.2.4) successively. Close immediately the gas washing flask with the gas inlet equipped with a porous glass frit.

5.2.3.2.3.3 Determination

Proceed as described in EN ISO 12846.

5.2.3.2.3.4 Expression of results

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

$$y = y_\mathrm{A} \times \frac{V_\mathrm{T}}{10} \tag{10}$$

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_7, in milligrams per kilogram of available chlorine is given by Formula (11):

$$C_7 = y \times \frac{10}{m_5} \times \frac{100}{C_1} \qquad (11)$$

where

m_5 is the mass expressed in grams, of the test portion;

C_1 is the available chlorine content in mass fraction in % (5.2.1.6).

6 Labelling - transportation - storage

6.1 Means of delivery

Sodium hypochlorite shall be delivered:

a) in containers of polyethylene or polyvinyl chloride (PVC) with external glass fibre reinforcement (GFR);

b) in steel tank wagons lined with rubber or coated with a suitable plastic.

The containers shall be closed so that no pressure can build up inside and no liquid can escape. The closure shall be protected from unintentional opening.

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

6.2 Labelling according to the EU legislation [4)]

The following labelling requirements shall apply to sodium hypochlorite at the date of publication of this European Standard.

Figure 1 — GHS 05

— Signal word:

Danger

— Hazard statements:

H314: Causes severe skin burns and eye damage.

H400: Very toxic to aquatic life.

EUH031: Contact with acids liberates toxic gas (chlorine)

[4)] See [3].

Figure 2 — GHS 09

The regulation [3] contains a list of substances classified by the EU. It contains only a single entry for classification and labelling of the substance which is however not appropriate for the various solutions placed on the market, since the hazards vary at different concentrations depending on the individual content of free chlorine and free alkali; therefore no classification for diluted solutions can be given here. Diluted solutions and 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

Sodium hypochlorite solution is listed as UN Number [5] 1791.

- RID [6] ADR [7]: class 8, classification code C9, packing group II or packing group III.
- IMDG [8]: class 8.
- IATA [9]: class 8.

6.4 Marking

The marking shall include the following:

- name "sodium hypochlorite solution", trade name, grade and type;
- net mass;

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[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.

- name and address of supplier and/or manufacturer;
- statement "this product conforms to EN 901".

6.5 Storage

6.5.1 General

Sodium hypochlorite shall be protected against light, and particularly direct sunlight. It shall be stored in cool rooms in containers made from metal with internal coating or suitable plastics materials. To protect metal containers from corrosion, they shall be either rubber-lined or plastics-coated.

Pressure build-up in the containers should be prevented by suitable venting.

6.5.2 Long term stability

The stability is greatly affected by heat, light, pH, and the presence of heavy metal ions. The solution gradually decomposes resulting in the reduction of the concentration of the active chlorine and in the liberation of oxygen gas. The concentration of chlorate increases.

6.5.3 Storage incompatibilities

In the presence of acids or acidic salts: formation of chlorine.

In the presence of high concentrations of ammonia, ammonium salts and derivatives, and isocyanurate derivatives: vigorous reaction with the formation of highly explosive nitrogen trichloride.

Annex A
(informative)

General information on sodium hypochlorite

A.1 Origin

A.1.1 Raw materials

Sodium hypochlorite is manufactured from chlorine (Cl_2) and sodium hydroxide (NaOH).

A.1.2 Manufacturing process

It is produced by reacting gaseous chlorine with a solution of sodium hydroxide.

A.2 Use

A.2.1 Function

Sodium hypochlorite functions in water treatment are, removing ammonium compounds, oxidising sulfides and oxidising iron(II) to iron(III) and as a disinfectant.

A.2.2 Form in which it is used

It is used as delivered or diluted if necessary, depending on the required dose.

A.2.3 Treatment dose

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

A.2.4 Means of application

It is applied using a metering-pump, an injection feeder or a constant head gravity feeder.

A.2.5 Secondary effects

The secondary effects include the following:

- slight increase in pH value;
- slight increase in the chloride content;
- oxidation of organic compounds; formation of halogenated organic substances, especially trihalomethanes, is possible;
- local precipitation of carbonate at the injection point.

A.2.6 Removal of excess product

The most practical method is using a reducing agent such as sulfur dioxide gas or an aqueous solution of a sulfite compound. Other methods can use activated carbon or hydrogen peroxide.

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

In case of contact with the skin rinse with copious amounts of water and remove any contaminated clothing.

In case of contact with the eyes, rinse immediately with copious amounts of water for at least 15 min and consult a doctor.

B.2.2 Spillage

Do not drain into waste water piping. Collect any leaking liquid in plastic containers. Contain spilled liquid and absorb with absorbing material such as kieselguhr, universal absorbent, etc. - do not use sawdust. Collect contaminated residues in plastic containers. Clean contaminated tools by rinsing with plenty of water.

Dilute with water and reduce the solution with either sodium sulfite, sodium hydrogen sulfite, hydrogen peroxide or sodium thiosulfate. Disposal shall be carried out in accordance with the local regulations.

B.2.3 Fire

Non-combustible, but poses an extra hazard with fires.

Cool fire-endangered containers with water.

Use appropriate means to extinguish fires.

Annex C
(normative)

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

C.1 General principle

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

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

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

C.2 Interferences

Interferences are minimised because the As, Sb and Se hydrides are removed from the solution containing the 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 3696:1995.

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 of water. Prepare fresh daily.

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

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

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

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

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

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

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

C.3.9 Hydrogen, commercial grade.

C.3.10 Arsenic(III) solutions:

- stock As(III) solution: Dissolve 1,320 g of arsenic trioxide, As_2O_3, in water containing 4 g of NaOH. Transfer quantitatively to 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg As(III);

- intermediate As(III) solution: Dilute into a 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 contains 10,0 µg As(III);

- standard As(III) solution: Dilute into a 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 contains 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 a 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg As(V);

- intermediate As(V) solution: Prepare as for As(III) above; 1,00 ml contains 10,0 µg As(V);

- standard As(V) solution: Prepare as for As(III) above; 1,00 ml contains 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 a 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg Se(IV);

- intermediate Se(IV) solution: Dilute into a 1 000 ml one-mark volumetric flask 10 ml of stock Se(IV) solution to the mark with water containing 10 ml of hydrochloric acid (C.3.7) and mix; 1,00 ml contains 10,0 µg Se(IV);

- standard Se(IV) solution: Dilute into a 1 000 ml one-mark volumetric flask 10 ml of 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 the solution daily when checking the equivalent of instrument response for Se(IV) and Se(VI); 1,00 ml contains 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 of nitric acid (C.3.5). Transfer quantitatively to a 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg Se(VI);

- intermediate Se(VI) solution: Prepare as for Se(IV) above; 1,00 ml contains 10,0 μg Se(VI);
- standard Se(VI) solution: Prepare as for Se(IV) above; 1,00 ml contains 0,100 μg Se(VI).

C.3.14 Antimony solutions:

- stock Sb solution: Dry 2 g of potassium antimonyl tartrate hemihydrate (antimony potassium tartrate) ($C_4H_4O_7SbK.0,5\ H_2O$) at 100 °C for 1 h. Dissolve 1,669 g in water, transfer quantitatively to a 1 000 ml one-mark volumetric flask and make up to the mark with water and mix; 1,00 ml contains 1,00 mg Sb;
- intermediate Sb solution: Dilute into a 1 000 ml one-mark volumetric flask 10 ml of stock Sb solution to the mark with water containing 10 ml of hydrochloric acid (C.3.7) and mix; 1,00 ml contains 10,0 μg Sb;
- standard Sb solution: Dilute into a 1 000 ml one-mark volumetric flask 10 ml of 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 contains 0,100 μg Sb. Prepare the 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 an appropriate strip-chart recorder.

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

C.4.2 Atomiser

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 while 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 a reaction cell is given in Figure C.1.

A commercially available system is acceptable if it utilises 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-atomiser system selected, it shall meet the following quality-control considerations:

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

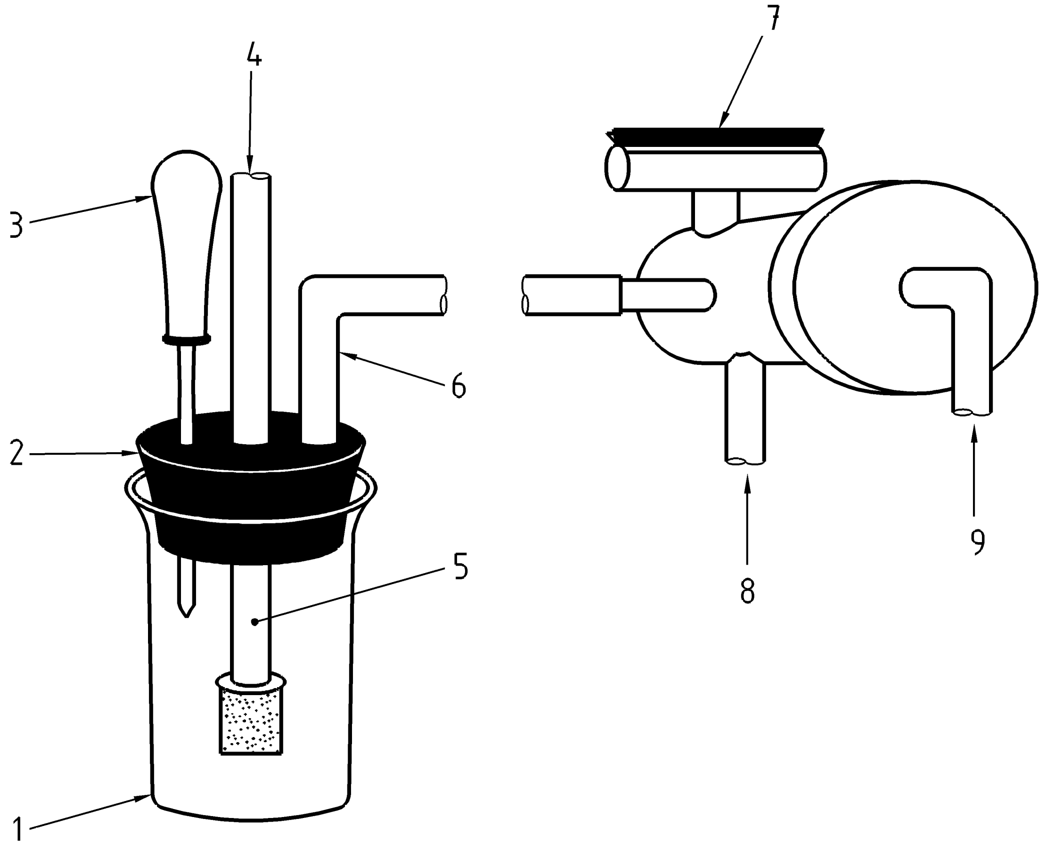
a) It shall provide a precise and reproducible calibration curve between 0 µg/l and 20 µg/l As, Sb or Se and a detection limit between 0,1 µg/l and 0,5 µg/l As, Sb or Se.

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

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 the production of hydrogen gas does not vary significantly between determinations.



Key

1	beaker 250 ml	6	outlet tube
2	rubber stopper	7	burner
3	dropper	8	hydrogen
4	auxiliary nitrogen	9	nitrogen
5	gas dispersion tube		

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

C.5 Procedure

C.5.1 Preparation of the apparatus

Connect the inlet of the reaction cell with the auxiliary purging gas controlled by a flow meter. If a drying cell between the reaction cell and atomiser is necessary, use only anhydrous $CaCl_2$ and not $CaSO_4$ as it can retain SeH_2. Before using the hydride generation/analysis system, optimise operating parameters. Aspirate the aqueous solutions of As, Sb and Se directly into the flame to facilitate atomiser alignment. Align quartz atomisers for maximum absorbance. Establish a 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 atomiser is used, optimise the 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.

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 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.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 a 250 ml beaker. Alternatively, prepare standard solutions by adding aliquots of solutions containing 5 µg of As, Se or Sb directly to the beaker and dilute to 50 ml in this beaker, achieving a concentration of 100 µg/l of the respective solutions. Add 7 ml of sulfuric acid $c(H_2SO_4) = 9$ mol/l (C.3.3) and 5 ml of nitric acid (C.3.5). Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidising 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 of 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 of the 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

Add 5 ml of hydrochloric acid (C.3.7) to 50 ml of the digested standard solution or test solution in a 250 ml beaker (see Figure C.1) and mix. Add 5 ml sodium iodide prereductant solution (C.3.2), mix and wait 30 min.

NOTE 1 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 strictly controlled. This can require an automated delivery system.

Attach one beaker at a first time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the atomiser. Turn on a 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 of sodium borohydride reagent (C.3.1). After the instrument absorbance has reached a maximum and returned to the base line, remove the beaker, rinse the dispersion tube with water, and proceed to the next test solution or standard solution. Periodically compare the standard As(III) and As(V) curves for response consistency.

Check for the 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 no less than 90 %.

NOTE 2 See also bibliographic reference [4].

C.5.5 Determination of selenium with sodium borohydride

Add 15 ml of hydrochloric acid (C.3.7) to 30 ml of the digested standard solution or test solution, or to 30 ml of the undigested standard, or the sample in a 250 ml beaker, and mix. Heat for a predetermined period at a 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 the 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 %.

NOTE See also bibliographic reference [5].

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 of 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 a 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.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.

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:

$$r = 0{,}001\, z \tag{C.1}$$

where

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

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.

Annex D
(normative)

Determination of bromate ion content in sodium hypochlorite by liquid chromatography of ions and UV detection

D.1 General

This method specifies a method for determining dissolved bromate (BrO_3^-) in sodium hypochlorite in the measurement range of 2 mg/l to 1 000 mg/l.

This method does not require any sample pre-treatment.

The rate of sample dilution avoids all problems of saturation of the column ion capacity as well as an excessive depletion of the reduction capacity of the post-column reactant.

D.2 Interferences

The presence of chlorite concentration found in sodium hypochlorite does not interfere with the bromate determination.

No anion normally found in sodium hypochlorite hinders the bromate determination.

D.3 Principle

A sample of sodium hypochlorite is diluted 10 000 times.

The sample is eluted through an analytical column using a sodium carbonate solution.

The eluted bromate ion is converted into tribromide ion (Br_3^-) by a post-column reaction with bromide and nitrite under acidic condition at a temperature of 60 °C.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$Br_2 + Br^- \rightarrow Br_3^-$$

Determination of the tribromide ion is carried out using a UV spectrometric detection at 267 nm.

This device is added in series to a classic ion chromatography system.

D.4 Reagents

All reagents shall be of a recognised analytical grade and the water used shall conform to grade 1 in accordance with EN ISO 3696:1995.

D.4.1 Potassium bromate KBrO3

D.4.2 Sulfuric acid, H2SO4, 18 mol /l

D.4.3 Sodium carbonate, Na2CO3

D.4.4 Sodium bromide, NaBr

D.4.5 Sodium nitrite, NaNO2

D.4.6 Helium 99,999 %

D.4.7 Standard stock solution 1 000 mg/l bromate

Dry 1,5 g of potassium bromate for 1 h at 105 °C. Store in a desiccator.

Dissolve (1,3 057 ± 0,01) g of the dried potassium bromate in 800 ml of water in a 1 000 ml volumetric flask and make up the volume with water.

Store the solution at 2 °C to 6 °C in polyethylene or glass bottles and renew it every 12 months.

D.4.8 Bromate standard solution, 10 mg/l bromate

Pipette 1,00 ml of standard stock solution (D.4.7) into a 100 ml volumetric flask.

Make up to the mark with water.

Store the solution at 2 °C to 6 °C in polyethylene or glass bottles and renew it every 3 months.

D.4.9 Regenerant solution for the suppressor, c(H2SO4) = 0,025mol/l

Mix 7,0 ml sulfuric acid with 5 l water.

D.4.10 Post-reaction chemical acid solution, c(H2SO4) = 0,750 mol/l

Carefully mix 210 ml of sulfuric acid with water in a 5 l volumetric flask.

Make up to the mark with water.

D.4.11 Nitrite solution at 10,0 g/l

Dissolve 1,5 g of sodium nitrite in 80 ml of water in a 100 ml volumetric flask and make up the volume with water.

Prepare on the day of use.

D.4.12 Post-reaction solution c(Br-)= 0,5 mol/l, c(NO2-) = 0,0 0043 mol/l

Dissolve 102,9 g of sodium bromide into 500 ml of water in a 2 l volumetric flask.

Pipette 4 ml of the nitrite solution into the same volumetric flask.

Mix and make up the volume with water.

Prepare on the day of use.

D.4.13 Eluent solution carbonate c(CO32-)= 0,5 mol/l

Dissolve 53,0 g of anhydrous sodium carbonate in 800 ml of water in a 1 000 ml volumetric flask and make up to volume with water.

Store the solution at 2 °C to 6 °C in polyethylene or glass bottles and renew it every 6 months.

D.4.14 Eluent solution carbonate c(CO32-)= 0,009 mol/l

Pipette 36 ml of the sodium carbonate solution 0,5 mol/l into a 2 000 ml volumetric flask and make up to volume with water.

Store the solution at 2 °C to 6 °C in polyethylene or glass bottles and renew it every week.

Filter the eluent on a sintered glass filter with a pore size of 0,45 µm.

Purge with helium before use for 5 min at a flow rate of 3 l/min.

D.5 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

D.5.1 Ion chromatography system

- Eluent reservoir;
- pump for isocratic technique;
- sample delivery device, including a sample injection system incorporating a sample loop of appropriate volume (e.g. 750 µl);
- column switching valves including a device for timing and controlling the valves and pump;
- separator column high capacity, specially designed for determining oxyhalides;
- pre-column to protect the separator column;
- conductivity detector with an anion suppressor device assembly (detector not in use for determining bromate), UV detector.

D.5.2 Post column device

- Reagent mix reservoir and pump to feed the reactor through a chemical suppressor;
- post column reactor;
- UV detector (267 nm).

D.6 Procedure

D.6.1 Preparation of calibration solutions

The calibration range is dependent on the expected bromate concentration in the sample. In most cases the concentration in sodium hypochlorite is less than 1 000 mg/l.

Prepare the calibration solutions, for example according to Table D.1:

Table D.1 — Calibration solutions for determination of bromate content

Solution	BrO_3^- in µg/l	$NaBrO_3$ in µg/l
1	10	11,8
2	20	23,6
3	40	47,19
4	60	70,78
5	80	94,37
6	100	118

Prepare the calibration solutions on the day of use.

D.6.2 Preparation of test solutions

Due to the extreme sensitivity of the method, the sample shall be diluted 10 000 times.

If the concentration of the sodium hypochlorite exceeds 150 g/l chlorine, use an extra two times dilution to avoid an excessive consumption of the bromide nitrite reagent.

D.6.3 Measurement of calibration and test solutions

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

Measure each test solution twice in order to keep the relative repeatability standard deviation at no more than 0,5 %.

D.6.4 Expression of results

The bromate content of the test solution is obtained from the regression line obtained with the calibration results in the sodium hypochlorite solution.

The sodium bromate ($NaBrO_3$) content of the laboratory sample, C_8, expressed in mg/l is given by Formula (D.1):

$$C_8 = yd \tag{D.1}$$

where

y is the concentration (in mg/l $NaBrO_3$) obtained from the calibration curve;

d is the dilution factor of the sample to be analysed.

The sodium bromate ($NaBrO_3$) content, C_9 expressed in mass fraction in % of available chlorine is given by Formula (D.2):

$$C_9 = \frac{C_8}{C_1 \times 10} \tag{D.2}$$

where

C_1 is the available chlorine (Cl_2) content expressed in g/l (5.2.1.6).

D.6.5 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 Formula (D.3):

$$r = 0{,}005\ z \tag{D.3}$$

where

z is the mean of the two results, expressed in % (m/m).

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.

Annex E
(informative)

Results of inter-laboratory tests on sodium bromate determination in sodium hypochlorite commercial solutions

An inter-laboratory test was carried out in 2002 with laboratories from France, Belgium, Norway and Netherlands. The sodium bromate content has been determined by ion chromatographic techniques (with conductimetric or UV detection).

Sample matrix is described in Table E.1 (see also bibliographic reference [6]).

The statistical treatment of results, according to ISO 5725-2, is described in Table E.2.

Table E.1 — Description of samples matrix

Sample #	**1**	**2**	**3**
Active chlorine (g/l)	≈ 160	≈ 160	≈ 160
Sodium chloride (g/l)	130 to 140	130 to 140	130 to 140
Sodium bromate (mg/l)	blank	590 (spike)	1 180 (spike)

Table E.2 — Statistical treatment for sodium bromate determination

Sample	n	l	KA_1 %	X_{ref} mg/L	X mg/L	RR %	S_R mg/L	VC_R %	S_r mg/L	VC_r %
1	27	10	3,6	blank	38,9	-	9,4	24	3,1	7,9
2	42	15	8,7	590	620	98,4	26	4,4	11,8	2
3	42	15	8,7	1 180	1 217	99,8	63,7	5,4	20	1,7

n: number of analytical values (without outliers)

l: number of participating laboratories

KA_1: percentage of outliers

X_{ref}: theoretical bromate content of the sample

X: mean of inter-laboratory test

RR: recovery

S_R: reproducibility standard deviation

VC_R: reproducibility relative standard deviation

S_r: repeatability standard deviation

VC_r: repeatability relative standard deviation

Annex F
(informative)

Environmental, health and safety precautions within chemical laboratories

When preparing the analytical methods for application of this document, consideration was given to minimising environmental impacts caused by using these methods of analysis.

It is the users' responsibility to use safe and suitable techniques when handling materials in the methods of analysis specified in this document.

The following list is not exhaustive but users of the analytical methods referred in this document may use it as a guide to the use of safe and proper techniques. They should:

- investigate if European Directives, transposed European legislation and national laws, regulations and administrative provisions apply;
- consult manufacturers/suppliers for specific details such as material safety data sheets and other recommendations;
- use safety equipment and wear protective clothing (usually goggles and coats), appropriate for the test product and the test chemicals, in all laboratory areas, to ensure the safety of the operator;
- be careful about flammable materials and substances that are toxic and/or human carcinogens and generally take care during transportation, decanting, diluting and dealing with spillages;
- use a fume cupboard during preparation of organic solvent solutions;
- store, handle and dispose of chemicals in a safe and environmentally satisfactory manner: including chemicals for laboratory test, test specimens, unused solvents and reagents that have to be disposed of.

Bibliography

[1] Directive 98/8/EC of the European Parliament and of the Council on the placing on the market of biocidal products

[2] 98/83/EC, Council Directive of 3rd November 1998 relating to the Quality of Water intended for Human Consumption

[3] 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)

[4] EN ISO 11969, *Water quality — Determination of arsenic — Atomic absorption spectrometric method (hydride technique) (ISO 11969)*

[5] ISO 9965, *Water quality — Determination of selenium — Atomic absorption spectrometric method (hydride technique)*

[6] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[7] EN 14805, *Chemicals used for treatment of water intended for human consumption — Sodium chloride for on site electrochlorination using non-membrane technology*

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