BS EN 12671:2016

BSI Standards Publication

Chemicals used for treatment of water intended for human consumption — Chlorine dioxide generated in situ

National foreword

This British Standard is the UK implementation of EN 12671:2016. It supersedes BS EN 12671:2009 which is withdrawn.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.

Published by BSI Standards Limited 2016

ISBN 978 0 580 86572 5

ICS 13.060.20; 71.100.80

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 August 2016.

Amendments/corrigenda issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 12671

May 2016

ICS 71.100.80

Supersedes EN 12671:2009

English Version

Chemicals used for treatment of water intended for human consumption - Chlorine dioxide generated in situ

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Dioxyde de chlore généré in situ

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Vor Ort erzeugtes Chlordioxid

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

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of 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 United Kingdom.

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

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Contents

European foreword

This document (EN 12671:2016) 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 12671:2009.

Significant technical differences between this edition and EN 12671:2009 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 [3]);

b) Subclause 6.2 – updating of risk and safety labelling according to EU Regulation [3] and its latest Adaptations to Technical Progress).

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

Introduction

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

1) this document provides no information as to whether the product may be used without restriction in any of the Member States of the EU or EFTA;

2) it should be noted that, while awaiting the adoption of verifiable European criteria, existing national regulations concerning the use and/or the characteristics of this product remain in force.

NOTE 1 Conformity with this 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 document is subject to regulation or control by National Authorities.

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

1 Scope

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

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)*

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

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

3 Description

3.1 Identification

3.1.1 Chemical name

Chlorine dioxide.

3.1.2 Synonym or common name

None.

3.1.3 Relative molecular mass

67,46.

3.1.4 Empirical formula

ClO_2.

3.1.5 Chemical formula

$O\underset{\cdots}{-}Cl\underset{\cdots}{-}O$ (resonance structure).

3.1.6 CAS Registry Number [1]

10049-04-4.

3.1.7 EINECS reference [2]

233-162-8.

---

[1] Chemical Abstracts Service Registry Number.

[2] European Inventory of Existing Commercial Chemical Substances.

3.2 Presentation form

For water treatment, chlorine dioxide is generated *in situ* as an aqueous solution on or near the site of use and transferred to the site of use.

3.3 Physical properties

3.3.1 Appearance

The pure product is an orange gas or liquid, which forms a yellow solution in water.

NOTE If the solution becomes red-brown, it is a sign of decomposition.

3.3.2 Density

Gas: 3,09 g/l, (2,4 g/l relative, air = 1) at 273 K and 101,3 kPa [3].

Liquid: 1,64 g/ml at 20 °C.

3.3.3 Solubility in water

In Table 1 the solubility values (S) for chlorine dioxide are given in grams per cubic meter (g/m^3) water at a pressure of 101,3 kPa for different temperatures:

Table 1 — Solubility values

Temperature of water °C	**S** $\left(\frac{g/m^3 H_2O}{g/m^3 gas}\right)$
0	70 ± 0,7
5	(60,3)
10	(53,7)
15	45
20	(42,7)
25	(33)
30	(30,1)
35	26,5 ± 0,8

NOTE 1 S is a ratio, not an absolute value of concentration.

NOTE 2 The S values are directly measured values except those in brackets which are extrapolated data.

3.3.4 Vapour pressure

The vapour pressure of pure chlorine dioxide as a function of temperature is given in Table 2.

---

[3] 100 kPa = 1 bar.

Table 2 — Vapour pressure of pure chlorine dioxide

Temperature [C°]	**Vapour pressure** [kPa]
0	82,3
5	90,4
10	98,8
11	100,5
20	116,5 (extrapolated)
25	125,8 (extrapolated)
30	135,3 (extrapolated)
35	145,1 (extrapolated)
40	155,0 (extrapolated)

3.3.5 Boiling point at 101,3 kPa [4]

11 °C (for pure chlorine dioxide).

3.3.6 Crystallization point

- 59 °C (for pure chlorine dioxide).

3.3.7 Specific heat

The specific heat of solutions of chlorine dioxide is very similar to that of pure water.

3.3.8 Viscosity (dynamic)

The dynamic viscosity of solutions of chlorine dioxide is very similar to that of pure water.

3.3.9 Critical temperature

153 °C (for pure chlorine dioxide).

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3.3.12 Dissolution heat

The heat of the dissolution in water is – 26,8 kJ/mol (exothermic).

3.4 Chemical properties

Chlorine dioxide is a molecule containing an unpaired electron and has the characteristics of a “molecule-free-radical”. Relevant Redox potentials of chlorine dioxide and related molecules are (E_o values at 25 °C in volts):

---

[4] 100 kPa = 1 bar.

$$HCIO_2 + 3H^+ + 4e^- \Rightarrow CI^- + 2H_2O \qquad E_0 = 1{,}57\ V$$

$$CIO_2\ (\text{dissolved gas}) + 1e^- \Rightarrow CIO_2^- \qquad E_0 = 1{,}15\ V$$

$$CIO_3^- + 1e^- + 2H^+ \Rightarrow ClO_2 + H_2O \qquad E_0 = 1{,}15\ V$$

$$ClO_2\ (\text{dissolved liquid}) + 1e^- \Rightarrow CIO_2^- \qquad E_0 = 0{,}95\ V$$

$$CIO_2^- + 4e^- + 4\ H^+ \Rightarrow CI^- + 2H_2O \qquad E_0 = 0{,}78\ V$$

4 Purity criteria

4.1 General

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

Users of this product should check the national regulations in order to clarify whether it is of appropriate purity for treatment of water intended for human consumption, taking into account raw water quality, required dosage, contents of other impurities and additives used in the product not stated in 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 raw materials lead to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

4.2 Composition of *in situ* generated product

Chlorine dioxide (ClO_2) is produced as aqueous solution on or near the site of use. For safety reasons the aqueous ClO_2 solution without intermediate storage in a storage tank (i.e. without headspace) shall not exceed a concentration of 20 g/l.

The concentration of the aqueous ClO_2 solution with intermediate storage in a storage tank (i.e. with headspace) should not exceed a concentration of 3 g/l, to ensure an adequate distance to the explosion limit (see B.1).

4.3 Impurities and main by-products

Impurities and main by-products of the starting products used for the generation (indicated in A.1.1) can be found in the *in situ* generated product in respective proportional concentrations.

Inadequate design, operation and maintenance of reactors can give rise to the formation of chlorine and traces of chlorate ion and, eventually, the presence of unreacted chlorite, chlorate and/or chlorine (see [6]); for analysis see 5.2 and A.4.

4.4 Chemical parameters

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

Limits of chemical parameters being potentially present in chlorine dioxide solution have been specified in the corresponding EN standards of the starting products (indicated in A.1.1).

5 Test methods

5.1 Sampling

Sampling of chlorine dioxide solutions shall avoid photochemical decompositions, losses by evaporation of the product and consumption by the glassware and dilution water. Samples shall be taken at the exit of the reactor or from the storage tank with a sampling tube and the analytical procedures started as fast as possible.

In order to achieve these objectives the following step by step procedure shall be adopted:

— sampling shall be made in accordance with the general requirements given in ISO 3165 and take ISO 6206 into account;

— all glassware shall be conditioned **immediately** before sampling, with the solution under investigation and this preliminary rinsing sample shall be discarded;

— liquid samples for analytical control shall be introduced **directly** into the analytical reagent solutions; the sampling device and procedure shall ensure that the sample is directly contacted with the analytical reagent without running along the walls of the analytical glassware;

— the sample vessels shall be stoppered, leaving minimal head-space, to store the sample with reagent mixture;

— at high concentration of chlorine dioxide (>10 g/l) the samples shall be collected in a vessel, containing water; the analytical result shall be corrected accordingly for the dilution factor;

— titration analysis shall preferably be carried out immediately after sampling and reaction;

— if immediate titration or measurement is not possible, prior to the analytical measurements the sample plus reagent shall be stored in the dark at low temperature about 5 °C and contact with ambient air shall be avoided;

— if immediate collection and analysis are not possible, sample the reactor effluent in a 250 ml conical flask stored on crushed ice and, by introducing the liquid at the bottom of the flask and fill the flask **completely** allowing overflow of chlorine dioxide solution.

The volume of the samples shall be adjusted in accordance with the analytical procedure described hereafter.

5.2 Determination of chlorine dioxide and chlorite concentrations

5.2.1 General

This standard method concerns the determination of chlorine dioxide and chlorite concentrations in stored solution.

NOTE Other oxidizing agents could interfere with the determination.

5.2.2 Principle

5.2.2.1 General

Phosphate-buffered iodide is first reacted with the chlorine dioxide sample and titrated at pH 7,2 and subsequently acidified to pH 2 and titration is continued.

5.2.2.2 With iodometry at pH 7,2

$$ClO_2 + l^- \Rightarrow ClO_2^- + 1/2\ l_2 \qquad (1)$$

and

$$Cl_2 + 2\ l^- \Rightarrow l_2 + 2Cl^- \qquad (2)$$

5.2.2.3 Subsequent iodometry at pH 2

$$ClO_2^- + 4\ I^- + 4\ H^+ \Rightarrow Cl^- + 2\ H_2O + 2\ I_2 \qquad (3)$$

The ratio of equivalents titrated at pH 7,2 and pH 2 shall be 1 to 4 within a deviation of less than 3 % and indicate at least 97 % of the expected yield. If not appropriate, adjustments and an additional control as given in 5.2.2.4 may be made, and more selective controls made occasionally according to the methods described in A.3 and A.4.

5.2.2.4 Chlorite determination

Determination of chlorite concentration after degassing of a separate sample followed by iodometry at pH 2 (reaction is as in 5.2.2.3 and measure only the chlorite concentration of the sample). The degassing procedure is given in A.4.1.

5.2.3 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.

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

5.2.3.2 Phosphate buffer of pH = 7,2.

Dissolve in 1 l of water, 28,2 g of sodium dihydrogen phosphate ($NaH_2PO_4 . 2H_2O$) and 100 g monohydrogen phosphate ($Na_2HPO_4 . 12H_2O$).

If necessary, precise adjustment of the pH value may be done with aliquots of sodium hydroxide (NaOH) or phosphoric acid (H_3PO_4).

5.2.3.3 Sulfuric acid $c(H_2SO_4) = 6$ mol/l.

5.2.3.4 Potassium iodate (KlO_3) powdered.

5.2.3.5 Hydrochloric acid standard volumetric solution $c(HCl) = 0,1$ mol/l or sulfuric acid $c(H_2SO_4) = 0,5$ mol/l.

5.2.3.6 Potassium iodide, (Kl) crystalline.

5.2.3.7 Zinc iodide (ZnI_2)-starch indicator.

Disperse 4 g starch into a small quantity of water. Add the dispersion to a solution of 20 g zinc chloride ($ZnCl_2$) in 100 ml of water. The solution is boiled until the volume has been reduced to 100 ml and finally diluted to 1 l while adding 2 g of ZnI_2.

An alternative starch indicator is soluble starch 5 g + $ZnCl_2$ 4 g + salicylic acid 1,25 g; disperse the starch in a small volume of water. Dissolve $ZnCl_2$ and salicylic acid in 500 ml water, boil and, while boiling, add the starch dispersion. Continue boiling for 5 min and finally dilute to 1 l.

5.2.3.8 Standardization of sodium thiosulfate solution:

5.2.3.8.1 Reactions:

$5KI + 5H^+ \Rightarrow 5HI + 5K^+$ (4)

$KIO_3 + H^+ \Rightarrow HIO_3 + K^+$ (5)

$HIO_3 + 5HI \Rightarrow 3I_2 + 3H_2O$ (6)

$3I_2 + 6S_2O_3^{2-} \Rightarrow 6I^- + 3S_4O_6^{2-}$ (7)

5.2.3.8.2 Determination:

Add 0,05 g of potassium iodate (5.2.3.4), 0,5 g of potassium iodide (5.2.3.6) into 50 ml water and a further 50 ml water in a conical flask. After mixing, add 10 ml of hydrochloric acid standard volumetric solution (5.2.3.5). Titrate the liberated iodine immediately with the sodium thiosulfate standard volumetric solution (5.2.3.1) until the solution is pale yellow.

Add 0,5 ml of starch indicator (5.2.3.7) and titrate to the end point, i.e. the disappearance of the blue-black colour. Record the volume V_t of the sodium thiosulfate solution added.

5.2.3.8.3 Calculation:

The concentration, c_t, expressed in moles per litre, of the sodium thiosulfate solution is given by the following formula:

$$c_t = \frac{c_a \times V}{V_t} \tag{8}$$

where

c_a is the concentration, in moles per litre, of the hydrochloric acid (5.2.3.5);

V is the volume, in millilitres, of the hydrochloric acid (5.2.3.5);

V_t is the volume, in millilitres, of the sodium thiosulfate solution used.

5.2.4 Apparatus

Ordinary laboratory apparatus and glassware:

The glassware shall be dark brown (to protect against photodecomposition) washed with a dilute solution (approximately 1 g/l) of chlorine dioxide and rinse with water ; the glassware used for the determinations of chlorine dioxide and related oxidants shall be reserved for this specific use and kept maintained separately.

5.2.5 Procedure

Prepare sets of three conical flasks of 250 ml immediately before the sampling: take 80 ml of water, followed by 20 ml buffer solution (5.2.3.2) and approximately 1 g of potassium iodide (5.2.3.6). Use immediately or keep in the dark if immediate use is not possible.

Introduce a volume (V_s) of chlorine dioxide solution which (presumably) contains between 3 mg and 10 mg of ClO_2.

Titration of sample under conditions of 5.2.2.2 gives a volume V_1 of the sodium thiosulfate standard volumetric solution (5.2.3.1). After this first titration add 5 ml of the sulfuric acid (5.2.3.3) and after shaking the titration is continued to give an additional volume V_2 of the sodium thiosulfate standard volumetric solution (5.2.3.1).

5.2.6 Expression of results

5.2.6.1 Calculation

The concentration of chlorine dioxide (Cs) expressed in milligrams per litre is given by the following formula:

$$Cs = \frac{(V_1 + V_2) \times c \times 67{,}5 \times 1\,000}{5 \times V_s} \qquad (9)$$

where

V_1 is the volume in millilitres, of the sodium thiosulfate standard volumetric solution (5.2.3.1) used for the titration at pH 7,2;

V_2 is the volume in millilitres, of the sodium thiosulfate standard volumetric solution (5.2.3.1) used for the titration at pH 2;

V_s is the volume in millilitres, of the test portion of chlorine dioxide;

c is the actual concentration, expressed in moles per litre, of the sodium thiosulfate standard volumetric solution (5.2.3.1).

It is first to be verified that $4 \times V_1 = V_2$ with acceptable accuracy of 3 %. If not, the results are rejected and the whole procedure shall be repeated, and/or, action shall be taken as indicated in 5.2.2.

5.2.6.2 Precision

Repeatability: 20 mg/l.

6 Labelling, distribution and storage

6.1 Labelling according to the EU legislation [5]

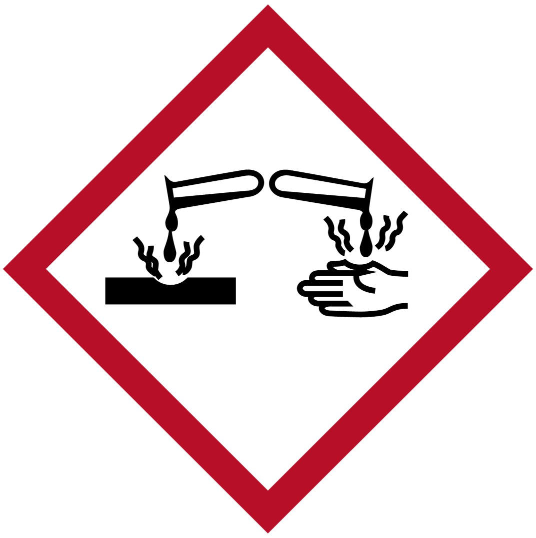
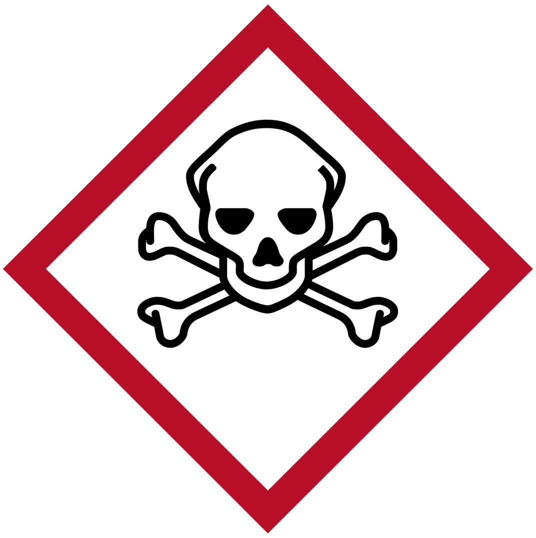
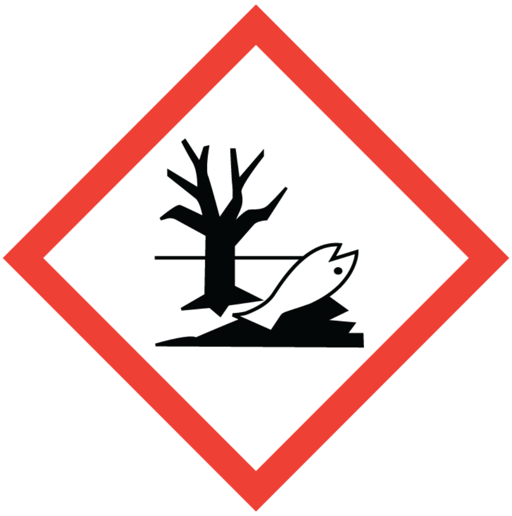
Labelling requirements in Table 3 shall apply to chlorine dioxide solution at the date of publication of this document.

Table 3 — Risk and safety labelling

Solutions of chlorine dioxide concentration	
C ≥ 5 %	H314
1 % ≤ C < 5 %	H315
3 % ≤ C < 5 %	H318
0,3 % ≤ C < 10 %	H319
C ≥ 3 %	H335

---

[5] See [3].

Hazard pictogram  **Figure 1 — GHS05**  **Figure 2 — GHS06**  **Figure 3 —GHS09**	— Signal word: **Danger** — Hazard statements: H301: Toxic if swallowed H314: Cause severe skin burns and eye damage H315: Causes skin irritation H318: Causes serious eye damage H319: Causes serious eye irritation H335: May cause respiratory irritation H400: Very toxic to aquatic life Precautionary statements ('P statements') should be provided by the company being responsible for the marketing of the substance. They should be indicated on the packaging label and in the extended safety data sheet (eSDS) of the substance.

The legislation [3], and its amendments for the purposes of its adaptation to technical and scientific progress contains a list of substances classified by the EU. Substances not listed in this regulation should be classified on the basis of their intrinsic properties according to the criteria in the regulation by the person responsible for the marketing of the substance.

6.2 Means of distribution

For local short time storage of diluted solutions (e.g. less than 3 g/l, for less than 30 min, at pH value in the range of 2,0 to 5,5 in operational conditions) and, also for generating equipment, appropriate materials are: dark brown glass and borosilicate glassware, polyvinylchlorid (PVC), cross-linked HD-polyethylene, polyfluorocarbons. “Chromium steels” and stainless steels are less suited for contact with chlorine dioxide. Rubber and general plastics materials shall be proven specifically for resistance to chlorine dioxide.

6.3 Storage, stability

In aqueous solution, at dilutions between 0,5 g/l and 2 g/l, when stored in the dark, chlorine dioxide is stable for several hours. Exposure to direct sunlight and heat shall be avoided. It is generally recommended to limit the local storage to less than 30 min.

WARNING — Even solutions of chlorine dioxide at concentrations < 0,3 % can cause harmful gas emissions. Therefore safety measures shall be followed accordingly (see Annex B).

Annex A
(informative)

General information on chlorine dioxide

A.1 Origin

A.1.1 Raw materials

Chlorine dioxide is produced from raw materials which fulfil the requirements as specified by the following standards:

- chlorine for water treatment: EN 937, see [15];
- sodium hypochlorite for water treatment: EN 901, see [13];
- hydrochloric acid for water treatment: EN 939, see [17];
- sulfuric acid for water treatment: EN 899, see [12];
- sodium chlorite for water treatment: EN 938, see [16];
- sodium peroxodisulfate for water treatment: EN 12926, see [19];
- potassium peroxomonosulfate for water treatment: EN 12678, see [18];
- sodium chlorate for water treatment: EN 15028, see [20];
- hydrogen peroxide for water treatment: EN 902, see [14].

A.1.2 Manufacturing process

Numerous reactions to produce chlorine dioxide have been described and operated. For the scale of production required for water treatment, for example:

$$NaClO_3 + \tfrac{1}{2}\,H_2SO_4 + \tfrac{1}{2}\,H_2O_2 \Rightarrow ClO_2 + \tfrac{1}{2}\,O_2 + \tfrac{1}{2}\,Na_2SO_4 + H_2O \qquad (A.1)$$

$$2\,NaClO_2 + Cl_2 \Rightarrow 2\,ClO_2 + 2\,NaCl \qquad (A.2)$$

NOTE Acidified hypochlorite can be used as an alternative source of chlorine.

and

$$5\,NaClO_2 + 4\,HCl \Rightarrow 4\,ClO_2 + 5\,NaCl + 2H_2O \qquad (A.3)$$

an alternative reaction is:

$$2\,NaClO_2 + Na_2S_2O_8 \Rightarrow 2ClO_2 + 2\,Na_2SO_4 \qquad (A.4)$$

All reactions are operated under controlled conditions and concentrations with process water in closed reactors.

Present available reactor designs according to the stoichiometry given above enable to produce chlorine dioxide solutions with a yield of 90 % and higher. Residual impurities are traces of chlorate for reaction (A.1) and chlorine and chlorite for reactions (A.2-A.4). The formation of chlorate for reactions (A.2)-(A.4) is avoided by adequate reactor design, operating and pH control. More details are given in [5] and [6].

A.2 Use

A.2.1 Function

Chlorine dioxide is widely used in water treatment for oxidation and disinfection purpose, particularly post-disinfection giving an active residual concentration (see [4], [5], [6], [9], [10] and [11]).

In water treatment the reactions of chlorine dioxide are most often initiated by a free radical addition mechanism on the electrophylic site of the target molecule followed by transpositions and complementary oxidation reactions. Most encountered reaction products are carboxylic acids and transiently aldehydes, ketones and quinones. Part of the chlorine dioxide that is consumed is transformed into chlorite, i.e. between 40 % and 80 %, depending on the quality of the water.

A.2.2 Form in which it is used

Chlorine dioxide is generated as an aqueous solution. Working solutions concentrations are typically in the range of 0, 5 g/l to 2 g/l ClO_2 preferably less than 1 g/l. The pH value of the working solutions should be in the range of 2-4 for reactions (A.1) and pH 5,5-8,0 for reactions (A.2)-(A.4). To ensure proper pH stability, the pH should be measured within 30 min. Irradiation by sunlight of the stock solutions should be avoided.

A.2.3 Treatment dose

Treatment dose with chlorine dioxide depends on the water quality, on the purpose of the treatment and on national regulations (permitted maximum concentration and/or minimum concentration). Usually it is not more than some tenth of a milligram per litre of water.

A.2.4 Means of application

Chlorine dioxide is directly applied as an aqueous working solution to the water to be treated. No specific contacting equipment should be used except protection against corrosion at the injection point. Hydraulic mixing by the water flow is sufficient for dispersion of the reagent.

A.2.5 Secondary effects

Chlorine dioxide can form oxidized and, to a less degree, chlorinated by-products with the organic matter being naturally present in the raw water. Secondary chlorinations are avoided if traces of ammonia are present. Chloride, chlorate and chlorite ions are the general end products. Depending on the starting materials used the concentration of the related inorganic salt is slightly increased, too (see A.1.2).

A.2.6 Removal of excess product

Chlorine dioxide as well as residual chlorite can be reduced into chloride by appropriate activated carbon or with sulfur dioxide at pH 5 and lower or ferrous salt at neutral pH.

A.3 Spectrometric method for specific determination of ClO_2

A.3.1 Principle

Spectrometric measurement of the decrease in absorbance at 548 nm of a dilute solution of 1,5-bis-(4-methylphenylamino-2-potassium sulfonate)-9,10-anthraquinone (Acid Chrome Violet K (ACVK)), when reacted with an appropriate amount of chlorine dioxide solution. The method is specific for chlorine dioxide in the reactor effluents.

A.3.2 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.3.2.1 ACVK-solution (see [7] and [8]).

The dye is identified by the Colour Index Number 61710 (see [7]) (which was Nr 6170 in older editions). It is available under various commercial purities and names. It is recommended to use the analytical grade known as Alizarin Violet 3R with molecular mass 622,25. A stock solution is prepared at a concentration of about 0,2 mmol/l by dispersing 124,45 mg of the dye in about 200 ml of water placed in a volumetric flask of 1 l. After mixing during 30 min, add 20 mg of sodium hexametaphosphate and continue mixing during10 min; add 200 ml of water and 48,5 g of ammonium chloride and continue mixing until the solution has warmed up to room temperature and then 1,6 g of ammonia (expressed as NH_3), and complete the solution to 1 l. The volumetric flask is stoppered and stored overnight. When stored in a glass-stoppered vessel in the laboratory, the stock reagent solution is appropriate for use during at least one month.

Test: a 10-fold dilution of a sample of the stock solution as prepared with water has an absorbance of 0,155 cm^{-1} at 548 nm.

A.3.2.2 Chlorine dioxide stock solution.

Chlorine dioxide is generated by reacting a dilute aqueous solution of sodium chlorite with acetic anhydride, $(CH_3CO)_2O$, according to following stoichiometric formula:

$$4NaClO_2 + 2(CH_3CO)_2O + H_2O \Rightarrow 2ClO_2 + NaClO_3 + NaCl + 2CH_3COOH + 2CH_3COONa \qquad (A.5)$$

The reaction is completed with a solution containing about 1 g/l of $NaClO_2$ (10 mmol/l to 12 mmol/l) to which 1,3 ml to 1,5 ml acetic anhydride is added. The solution, when stored in the dark and refrigerated, is stable during several weeks. Calibration by iodometric titration is necessary before use as a standard for comparisons.

A.3.2.3 Other reagents:

A.3.2.3.1 Buffered potassium iodide (KI) which is prepared by mixing in 1 l of water and the following: KI, 20 g; $Na_2HPO_4 . 2H_2O$, 7,3 g and KH_2PO_4, 3,5 g.

A.3.2.3.2 Potassium iodide, (KI), crystalline.

A.3.2.3.3 Sulfuric acid $c(H_2SO_4)$ = 6 mol/l.

A.3.2.3.4 Sodium thiosulfate standard volumetric solution $c(Na_2S_2O_3)$ = 0,1 mol/l in water, calibrated as given in 5.2.3.8.

A.3.2.3.5 Zinc iodide (ZnI_2)-starch indicator.

Disperse 4 g starch into a small quantity of water. Add the dispersion to a solution of 20 g zinc chloride ($ZnCl_2$) in 100 ml of water. The solution is boiled until the volume has been reduced to 100 ml and finally diluted to 1 l while adding 2 g of ZnI_2.

A.3.3 Apparatus

A.3.3.1 Standard volumetric apparatus.

The glassware should be dark brown preliminary washed with a dilute solution (about 1 g/l) of chlorine dioxide. The glassware used for the determinations of chlorine dioxide should be reserved for this specific use and kept maintained separately.

A.3.3.2 Double-beam spectrophotometer operating at 548 nm and equipped with cells of optical pathway 5 cm or longer.

A.3.4 Procedure

A.3.4.1 Calibration

Introduce 80 ml of water in a 250 ml conical flask and add 20 ml phosphate buffer solution (A.3.2.3.1) of pH 7,2 and approximately 1 g KI (A.3.2.3.2). Add, by maintaining the transfer pipette dipped into the reagent solution, a volume V_0 of chlorine dioxide stock solution (A.3.2.2) containing a quantity of chlorine dioxide between 3 mg and 10 mg. Titrate with the sodium thiosulfate standard volumetric solution while adding 4 drops to 6 drops of the starch indicator at the end of the titration. Record the volume of titrant used as V_1. Add immediately 5 ml of sulfuric acid solution (A.3.2.3.3) and, after shaking, continue to titrate to end with an additional volume of sodium thiosulfate (V_2). Check first that $4 \times V_1 = V_2$; within a range of difference of $0{,}03 \times V_2$. Then calculate the concentration $\rho(\text{ClO}_2)$ in milligrams per litre of the stock solution of chlorine dioxide by the formula:

$$\rho(ClO_2)=\frac{(V_1+V_2) \times c(\text{Na}_2\text{S}_2\text{O}_3) \times 67{,}46 \times 1\ 000}{5V_0} \qquad \text{(A.6)}$$

where

V_0 is the volume in millilitres, of the chlorine dioxide stock solution (A.3.2.2);

V_1 is the volume, in millilitres, of the sodium thiosulfate standard volumetric solution used at pH 7,2;

V_2 is the volume in millilitres, of the sodium thiosulfate standard volumetric solution used at pH 2;

$c(\text{Na}_2\text{S}_2\text{O}_3)$ is the actual concentration, expressed in moles per litre, of the sodium thiosulfate solution (A.3.2.3.4).

Place 20 ml of ACVK stock solution (A.3.2.1) in a 200 ml volumetric flask and complete to volume by water free of chlorine dioxide, (this is the blank sample dilution). At the same time, in other 20 ml ACVK samples, introduce probes of standard chlorine dioxide solution to obtain concentrations in the range 0 mg/l to 2,5 mg/l. After completing to volume at 200 ml, absorbances are measured within 10 min at 548 nm versus the blank sample dilution using optical cells of 5 cm pathway or longer. Record the difference in absorbances (blank-chlorine dioxide sample) in function of the concentration of chlorine dioxide. (The molar absorption coefficient ranges between 2 600 $\text{mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{l}$ and 2 800 $\text{mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{l}$ depending on the manufacturing series of the dyestuff. These variations are of no importance for the differential method. A new calibration needs to be made for each new preparation of ACVK-stock solution).

A.3.4.2 Determination

For the analysis, place 20 ml probes of ACVK stock solution in 200 ml volumetric flasks. Make **the blank dilution at the same time as the probe dilutions.** Make probe dilutions by introducing with a pipette, appropriate samples of chlorine dioxide reactor effluents into the 20 ml dyestuff. For this transfer first flush the pipette with the ClO_2 sample and during the transfer the pipette is dipped into the dye solution. After the transfer of the sample dilute the whole with blank water to 200 ml. Record the difference in absorbance at 548 nm within 10 min and the chlorine dioxide concentration is obtained by interpolation on the calibration curve. For the best applicability of the method, the sample or a dilution of it is adjusted to obtain a concentration of chlorine dioxide in the final dilution to 200 ml between 1mg/l and 2,5 mg/l. The final result is obtained by multiplying the concentration as measured by the dilution factor applied.

A.3.5 Precision

Based on the solutions as measured (200 ml): the detection limit is 0,02 mg/l ; the repeatability is 0,01 mg/l. These values shall be multiplied by the dilution factors as applied.

A.3.6 Specificity

The method is free of interferences with aqueous chlorine, chloramines, chlorite, chlorate, aqueous bromine and hydrogen peroxide (see [5]).

A.4 Determination of chlorite and chlorate ions contents in aqueous chlorine dioxide as produced by the reactors

A.4.1 General

If ionic chromatography is not locally available, it is recommended to proceed to degassing the sample according to the procedure described in A.4.2 and storing the degassed sample in the cold and protected from direct light for later analysis. If ionic chromatography is not possible, indicative values of chlorate concentrations can be obtained by iodometric methods described in literature (see [4] and [5]). These titrimetric methods are subject to potential interferences and their results need to be considered as indicative only.

A.4.2 Sample collection and preparation

Use the following procedure described for degassing:

Collect a sample of at least 100 ml in a conical flask according to the prescriptions indicated in 5.1 and 5.2.4. Start degassing immediately with nitrogen gas at a flow rate of 2 l/min or more blown through a capillary tube of 0,1 mm inside diameter while keeping the sample in the dark at a temperature not higher than 12 °C. After 8 min of degassing bring the sample to pH 5 with sulfuric acid (5.2.3.3), and continue degassing until probe testing of the sample indicates absence of reaction on addition of potassium iodide (5.2.3.6) and zinc iodide indicator (5.2.3.7). Then filter the remaining sample volume on 0,45 µm porosity membranes as used for bacteriological analysis of drinking water.

If no nitrogen is available on the site, the degassing may be done with air provided the latter is sufficiently pure.

A.4.3 Principle

A sample of the reactor effluent is degassed using the procedure described in A.4.2. After degassing, direct determination of chlorite and chlorate ions by separation and suppressed conductometric detection, i.e. ionic chromatography. The calibration is linear between 0,25 mg/l and 10 mg/l for both ions and dilutions of the sample are eventually made accordingly.

A.4.4 Reagents

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

A.4.4.1 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.

A.4.4.2 Sulfuric acid $c(H_2SO_4) = 0{,}025$ mol/l, regenerant solution.

A.4.4.3 Helium, gas, high purity for degassing eluant and regenerant solutions.

A.4.4.4 Deionized water.

A.4.4.5 Stock solutions:

- chlorate solution, 1 g/l, prepared by 200 ml volumes in accurate by weight of 0,000 1 g;
- chlorite solution, 1 g/l, prepared by 200 ml volumes in accurate by weight of 0,000 1 g.

A.4.5 Apparatus

Ordinary laboratory apparatus and glassware with the following:

A.4.5.1 Ion chromatograph.

A.4.5.2 Chemical suppressed conductivity detector.

A.4.5.3 Anionic column and precolumn: resin composed of 15 μm polystyrene-divinylbenzene substrate agglomerated with anion exchange latex that has been aminated.

A.4.5.4 Appropriate data logger-plotter.

A.4.6 Procedure

A.4.6.1 Chromatographic conditions:

- eluant flow rate: 2 ml/min.
- regenerant flow-rate: 2,5 ml/min.
- full scale conductivity: 30 mS.
- residual conductivity: less than 18 mS.
- linearity range: 0,25 mg/l to 10 mg/l either ClO_2^- and/or ClO_3^- in the injected solution.

A.4.6.2 Calibration:

Prepare four calibration solutions and a blank solution. Each solution is measured in triplicate. The calibration solutions are made-up from the stock solution (A.4.4.5), using diluant water (A.4.4.4) and preparing the following solutions:

- for ClO_3^-: 1,25 mg/l ; 2,50 mg/l ; 3,75 mg/l ; 5,00 mg/l;
- for ClO_2^-: 0,25 mg/l ; 0,50 mg/l ; 0,75 mg/l ; 1,00 mg/l.

A.4.6.3 Preparation of the test solutions:

Dilute to be in the range of the calibration solutions.

A.4.6.4 Determination:

Measure each calibration solution three times. For each solution the repeatability coefficient of variation should be lower than 5 %. Dilute each test solution in order to obtain two levels of concentration located respectively in the lower and in the upper part of the calibration curve. Repeat the measurements twice or more in order to keep the repeatability coefficient of variation at no more than 5 %.

A.4.7 Expression of results

The chlorite and chlorate ions contents, in milligrams per litre of the test solutions, are calculated by interpolation on the regression line obtained with the five levels of the calibration results.

A.4.8 Detection limit

0,02 mg/l expressed as ClO_2^- or ClO_3^- respectively.

Annex B
(normative)

General rules relating to safety

B.1 Rules for safe handling and use

Chlorine dioxide is very toxic on inhalation and irritating to eyes, respiratory system and skin (see 6.1). Similar precautions as for the use of chlorine shall be applied, i.e. venting of the premises, availability of personal protection equipment (goggles, resistant gloves, facial respiratory mask and/or self-contained breathing apparatus). Explosion and fire hazards occur at concentrations of volume fraction of 10 % and higher in air (this corresponds to the equilibrium vs. an aqueous solution of 10 g/l of ClO_2 at 13 °C). Gaseous chlorine dioxide can corrode and damage electronic circuits.

The dissolution in water is exothermic.

B.2 Emergency procedures

B.2.1 First aid

In case of contact with eyes rinse immediately with plenty of water for at least 15 min. Seek medical advice.

In case of contact with skin wash immediately with plenty of water; all contaminated clothes shall be removed.

In case of inhalation of gas allow the victim to rest in fresh air. Avoid deep respiration. Seek medical advice. Acceleration of blood pulse rate will be observed and vasodilator treatment can be required.

B.2.2 Spillage

In case of contact with clothes, remove the latter and rinse with plenty of water. Spilled products in the premises shall be sluiced with water.

B.2.3 Fire

Aqueous solutions of chlorine dioxide are not directly flammable. Extinguish surrounding fire with water, preferably using a weak spray system to dissolve the ambient gas. For electrical risks, apply the standards and codes of practice.

Inform the fire fighters about the production capacity installed and the hazardous precursor chemicals stored, to take protection measures against possible risks.

Bibliography

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

[2] REGULATION (EU) No 528/2012 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 22 May 2012 concerning the making available on the market and use of biocidal products

[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] MASSCHELEIN W.J. In: *Chlorine Dioxide*. (SCIENCE A.A., ed.). Ann Arbor, Michigan, 1979

[5] DORÉ M. *Chimie des oxydants et traitement des eaux*. Ed. Technique et Documentation-Lavoisier, Paris, 1989

[6] DEKKER M., ed. *W.J. Masschelein, Unit Processes in Drinking Water Treatment*. New-York, 1992; Processus Unitaires de Traitement des Eaux – Ed. CEBEDOC (1996)

[7] INDEX C. *The society of dyers and colorists*, Vol. 4, Second Edition, 1956

[8] MASSCHELEIN W.J., FRANSOLET G., LAFORGE P., SAVOIR R. *Ozone Sci. Eng.* 1989, **11** pp. 209–215

[9] KASCHKE W., SCHULE P. Verfahren zur Desinfektion von Trinkwasser mit Chloridioxid. *Wasser und Boden*. 1990, **4** pp. 231–244

[10] Verfahren zur Desinfektion mit Chlordioxid (2010)”

[11] Hauptverband der gewerblichen Berufsgenossenschaften: BGV D 5 *Chlorung von Wasser* (2003)

[12] EN 899, *Chemicals used for treatment of water intended for human consumption — Sulphuric acid*

[13] EN 901, *Chemicals used for treatment of water intended for human consumption — Sodium hypochlorite*

[14] EN 902, *Chemicals used for treatment of water intended for human consumption — Hydrogen peroxide*

[15] EN 937, *Chemicals used for treatment of water intended for human consumption — Chlorine*

[16] EN 938, *Chemicals used for treatment of water intended for human consumption — Sodium chlorite*

[17] EN 939, *Chemicals used for treatment of water intended for human consumption — Hydrochloric acid*

[18] EN 12678, *Chemicals used for treatment of water intended for human consumption — Potassium peroxomonosulfate*

[19] EN 12926, *Chemicals used for treatment of water intended for human consumption — Sodium peroxodisulfate*

[20] EN 15028, *Chemicals used for treatment of water intended for human consumption — Sodium chlorate*

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Copyright in BSI publications

All the content in BSI publications, including British Standards, is the property of and copyrighted by BSI or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use.

Save for the provisions below, you may not transfer, share or disseminate any portion of the standard to any other person. You may not adapt, distribute, commercially exploit, or publicly display the standard or any portion thereof in any manner whatsoever without BSI's prior written consent.

Storing and using standards

Standards purchased in soft copy format:

- A British Standard purchased in soft copy format is licensed to a sole named user for personal or internal company use only.
- The standard may be stored on more than 1 device provided that it is accessible by the sole named user only and that only 1 copy is accessed at any one time.
- A single paper copy may be printed for personal or internal company use only.

Standards purchased in hard copy format:

- A British Standard purchased in hard copy format is for personal or internal company use only.
- It may not be further reproduced – in any format – to create an additional copy. This includes scanning of the document.

If you need more than 1 copy of the document, or if you wish to share the document on an internal network, you can save money by choosing a subscription product (see 'Subscriptions').

Reproducing extracts

For permission to reproduce content from BSI publications contact the BSI Copyright & Licensing team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email subscriptions@bsigroup.com.

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Useful Contacts

Customer Services
Tel: +44 345 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 345 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK