SLOVENSKI STANDARD
SIST EN 12671:2009

01-maj-2009

Nadomešča:
SIST EN 12671:2000

Kemikalije, ki se uporabljajo za pripravo pitne vode - Klorov dioksid, proizveden na kraju samem

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

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

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Dioxyde de chlore obtenu sur site

Ta slovenski standard je istoveten z: **EN 12671:2009**

ICS:

13.060.20	Pitna voda	Drinking water
71.100.80	Kemikalije za čiščenje vode	Chemicals for purification of water

SIST EN 12671:2009 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 12671

January 2009

ICS 71.100.80

Supersedes EN 12671:2000

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 produit sur site

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

This European Standard was approved by CEN on 29 November 2008.

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 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 Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 12671:2009: E

Contents

Page

Foreword

This document (EN 12671:2009) 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 July 2009, and conflicting national standards shall be withdrawn at the latest by July 2009.

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.

Significant technical differences between this edition and EN 12671:2000 are as follows:

a) deletion of the reference to EU Directive 80/778/EEC of July 15,1980 in order to take into account the latest Directive in force (see [1]);

This document supersedes EN 12671:2000.

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, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland 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 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.

1 Scope

This document 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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references the latest edition of the referenced document (including any amendments) applies.

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

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

$O\overset{\cdot\cdot}{-}Cl\overset{\cdot\cdot}{-}O$ (resonance structure)

3.1.6 CAS Registry Number [1)]

10 049 - 04-4

1) Chemical Abstracts Service Registry Number.

3.1.7 EINECS reference [2)]

233 – 162 - 8

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 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 m³ water at a pressure of 101,3 kPa for different temperatures 1:

Table 1 –Solubility values

Temperature of water °C	**S value** : $\frac{g/m^3 H_2O}{g/m^3 gas}$
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.

---

2) European Inventory of Existing Commercial Chemical Substances.

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 Crystallisation 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

$HClO_2 + 3H^+ + 4e^-$	$\Rightarrow Cl^- + 2H_2O$	1,57
ClO_2 (dissolved gas) + $1e^-$	$\Rightarrow ClO_2^-$	1,15
$ClO_3^- + 1e^- + 2H^+$	$\Rightarrow ClO_2 + H_2O$	1,15
ClO_2 (dissolved liquid) + $1e^-$	$\Rightarrow ClO_2^-$	0,95
$ClO_2^- + 4e^- + 4 H^+$	$\Rightarrow Cl^- + 2H_2O$	0,78

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.

NOTE Users of this product should check the national regulations in order to clarify whether it is of appropriate purity for treatment of water intended for human consumption, taking into account raw water quality, required dosage, contents of other impurities and additives used in the product not stated in 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) may 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 [5]); for analysis see 5.2 and A.4.

4.4 Chemical parameters

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 into account ISO 6206;

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

— liquid samples for analytical control shall be introduced **directly** into the analytical reagent solutions; the sampling device and procedure shall take care 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 no -or only a little- a 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 best be carried out immediately after sampling plus 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

$$ClO_2 + I^- \Rightarrow ClO_2^- + 1/2\ I_2 \quad (1)$$