



SLOVENSKI STANDARD
oSIST prEN 18087:2024
01-september-2024

Naprave za proizvodnjo biocidov na kraju samem - Klorov dioksid, proizveden iz natrijevega klorida z acidifikacijo (nakisanjem) ali oksidacijo

Devices for in situ generation of biocides - Chlorine dioxide generated from sodium chlorite by acidification or oxidation

Anlagen zur In-Situ-Erzeugung von Bioziden - Chlordioxid, hergestellt aus Natriumchlorit durch Ansäuren oder Oxidation

Équipements pour la production in situ de biocides - Dioxyde de chlore produit par acidification ou oxydation de chlorite de sodium

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Chlordioxid, hergestellt aus Natriumchlorit durch
Säurezugabe oder Oxidation

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 164.

If this draft becomes a European Standard, 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.

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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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prEN 18087:2024 (E)

European foreword

This document (prEN 18087:2024) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

This document is currently submitted to the CEN Enquiry.

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Introduction

In respect of potential adverse effects on human and animal health and the environment, caused by the product covered by this document, it provides no information as to whether the product may be used without restriction in any of the Member States of the EU or EFTA.

NOTE while awaiting the adoption of verifiable European criteria, attention is also drawn to national regulations that can apply.

Systems according to this document may be used in different fields of application, e.g. drinking water, swimming pool water, wastewater, air treatment, surface disinfection, etc. Additional requirements to this document should be observed, where appropriate for the specific application.

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prEN 18087:2024 (E)**1 Scope**

This document contains requirements for dosing systems for chlorine dioxide generation according to the chlorite-chlorine gas process, the chlorite-acid process and the chlorite-sodium peroxodisulphate process, which are used for the disinfection and oxidation of substances in water.

The chlorine dioxide (ClO₂) solution is produced on site (*in situ*) by automated mixing of chemical precursors. This document applies to the treatment of water for human consumption, rinsing water for filters for swimming and bathing pools as well as for other uses (e.g. cooling water, process water, etc).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 901, *Chemicals used for treatment of water intended for human consumption — Sodium hypochlorite*

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

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

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

EN 1717, *Protection against pollution of potable water in water installations and general requirements of devices to prevent pollution by backflow*

EN 12671, *Chemicals used for treatment of water intended for human consumption — Chlorine dioxide generated in situ*

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

EN 15363, *Chemicals used for treatment of swimming pool water — Chlorine*

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

EN ISO 10304-4, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 4: Determination of chlorate, chloride and chlorite in water with low contamination (ISO 10304-4)*

EN ISO 12100, *Safety of machinery — General principles for design - Risk assessment and risk reduction (ISO 12100)*

EN IEC 60751, *Industrial platinum resistance thermometers and platinum temperature sensors (IEC 60751)*

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

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp/>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

chlorine dioxide system

ClO₂ system

treatment system in which various chemical precursors are introduced by means of dosing devices in fixed or controlled proportions into a mixing chamber contained in the system with the intention of producing chlorine dioxide in situ and making it available for short-term use

3.2

precursor

substance that is fed to the chlorine dioxide system for production of the biocidal active substance

3.3

mixing chamber

component of a chlorine dioxide system in which the precursors are mixed and converted to ClO₂

3.4

bypass

partial flow to dilute chlorine dioxide solutions to lower concentrations, which can also be achieved by dilution with feed water

3.5

outgassing

release of chlorine dioxide from its aqueous solution

3.6

purification process

process for purifying the freshly produced chlorine dioxide from impurities from precursors and synthesis, e.g. via a gas phase transfer

3.7

reaction time

retention time of the precursors after complete mixing in the mixing chamber under operating conditions to achieve the nominal capacity

3.8

nominal capacity

maximum chlorine dioxide output of a chlorine dioxide system determined under specified conditions and declared by the manufacturer

3.9

metering device

device or assembly for dosing precursors, including dosing pump or injector, dosing line, mixing device, injection point and fittings

prEN 18087:2024 (E)**3.10****expert**

person who, due to their technical scientific training, work experience and knowledge of applicable standards and regulations, is capable to assess a chlorine dioxide system with regard to functions and safety

Note 1 to entry: This person can be from the manufacturer or an independent third-party organization (such as a test institution) without limitations, an inspector according to EN ISO/IEC 17020, Type C [17], fulfills this criterion.

3.11**chlorine dioxide dosing**

controlled process of adding chlorine dioxide solutions

3.12**dosing capacity**

flow rate per time or flow rate of the metering device

3.13**feed water**

water supplied to the system in accordance with the chemical requirements of the corresponding manufacturer's specifications which, in addition to diluting the product or the precursors, can also be supplied to the reaction or used as motive water

3.14**dilution water**

feed water supplied to the system, which serves to dilute the chlorine dioxide produced or the precursors

3.15**buffer tank**

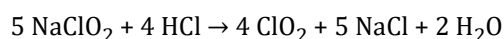
tank for temporary provision of the generated chlorine dioxide solution that is intended for the application

3.16**yield**

indication of how completely the reaction shown in the chemical reaction equation proceeds under practical conditions

Note 1 to entry: The difference between the actual yield and 100 % yield is due to unreacted precursors or side reaction products that were not represented in the chemical reaction equation

EXAMPLE If 9,5 g of chlorine dioxide are obtained in a reaction batch instead of according to the reaction equation

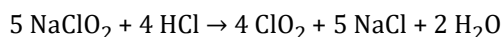


of the expected 10 g chlorine dioxide, the yield would be 95 %.

3.17**turnover rate**

indication of the percentage of molecules of chlorine dioxide that is formed from one molecule of the starting component according to the chemical reaction equation (i.e. the stoichiometric ratio)

EXAMPLE The chlorite-acid process is based on the following reaction equation:



From 5 molecules of the precursor sodium chlorite, 4 molecules of chlorine dioxide are formed, the turnover rate is therefore 80 %.

3.18

stability curve

representation of the concentration of chlorine dioxide and by-products at the specified temperature over time

Note 1 to entry: In systems with buffer tanks, this forms a basis in order to ensure that the active substance content and the amount of by-products such as chlorate in the generated chlorine dioxide solution in the buffer tank do not change unacceptably during the time between generation and metering the chlorine dioxide solution into the application

4 Processes for the preparation of chlorine dioxide solutions

4.1 General

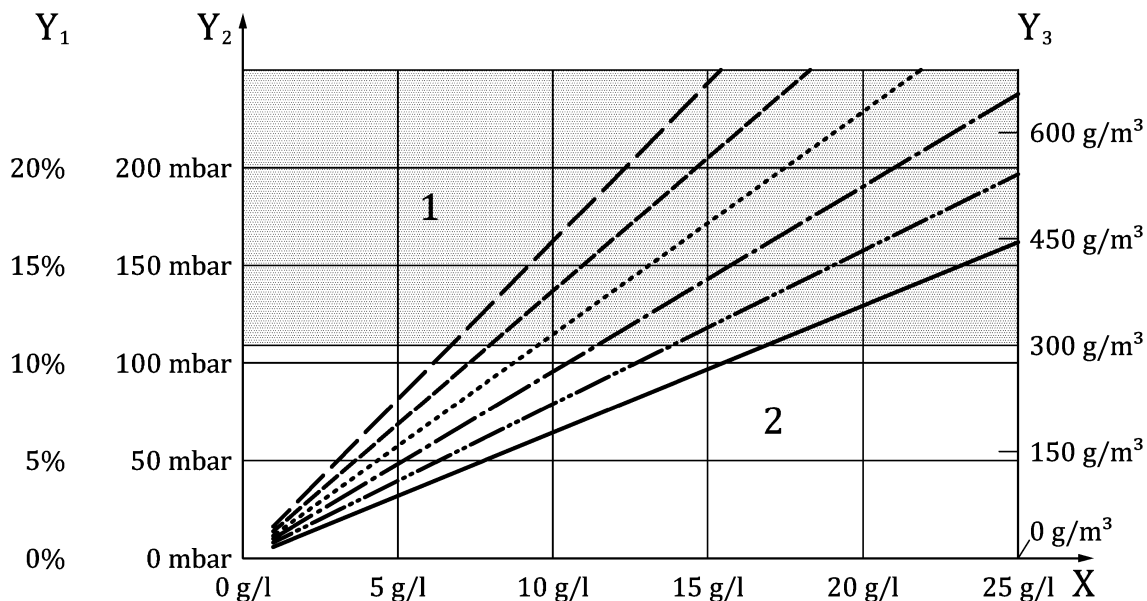
Chlorine dioxide is used in water treatment not only for disinfection but also for pre-oxidation, among other things, because its high normal potential oxidises phenols, other organic substances and complex-bound metals without forming chlorinated by-products. EN 12671 shall be applied to the treatment of water for human consumption.

4.2 Properties

Chlorine dioxide is a yellow-orange substance with a boiling point of 11 °C and a melting point of -59 °C at atmospheric pressure. Unlike chlorine, for example, it dissolves in water as a gas without dissociation (see Henry's law) and therefore tends to outgas strongly. At 25 °C and under atmospheric pressure, the chlorine dioxide concentration in the aqueous phase is approx. 25 times higher than in the supernatant gas phase (see Don Gates et al. [3]).

Chlorine dioxide is not stable. When heated, under pressure or under the influence of light, it may explosively decompose into chlorine and oxygen. Gaseous chlorine dioxide is explosive above a concentration of 300 g/m³. The concentration of chlorine dioxide solutions with excess gas space shall therefore be kept below the explosion limit (see Figure 1).

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**Key**

X chlorine dioxide in water

Y1 chlorine dioxide in air (Vol% at 1 013 mbar)

Y2 chlorine dioxide in air (partial pressure)

Y3 chlorine dioxide in air (concentration at 1 013 mbar and 293 K)

A range of unsafe handling

B range of safe handling

— 5 °C

- · - · 10 °C

- - - 15 °C

· · · · · 20 °C

- - - - - 25 °C

- - - - - 30 °C

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<https://standards.itih.ai> **Figure 1 — Solubility of chlorine dioxide in water (see Gates et al. [3] and Ishi [12])** prEN-18087-2024

In a solution containing 8 g/l chlorine dioxide, there is a risk of the formation of an explosive atmosphere in the supernatant gas space at a temperature of more than 20 °C.

Depending on the pressure and temperature, liquid chlorine dioxide can precipitate in aqueous solutions. Pure chlorine dioxide in liquid status explodes above -40 °C with an explosive force equivalent to about 1/3 that of TNT (2,4,6-trinitrotoluene) (see Sattelberger et al. [9]).

In aqueous solutions, chlorine dioxide decomposes to chlorate (ClO_3^-), (chlorite ClO_2^-) and chloride (Cl^-) depending on temperature, light irradiation, pH-value and impurities. The rate of decay is essentially determined by the initial concentration of chlorine dioxide. While the chlorine dioxide concentration in solutions of 20 g/l at room temperature, for example, produced by the hydrochloric acid process, decreases by half within hours, diluted solutions can remain stable over longer periods of time (see also Annex A). Concentrated solutions are therefore either diluted to a concentration < 3 g/l immediately after preparation or dosed immediately into the water to be treated without intermediate storage. Further information on the decomposition reactions can be found in Annex A.

NOTE Solutions with a chlorine dioxide concentration < 3 g/l according to the CLP Regulation (Regulation (EC) 1272/2008 amended by Regulation (EU) 2018/1480 of 04. 10. 2018) do not require labelling.

Chlorine dioxide gas is very toxic and causes extremely life-threatening lung damage when inhaled. Therefore, when handling chlorine dioxide solutions, care shall be taken to ensure gas tightness. The occupational exposure limit of chlorine dioxide is 0,28 mg/m³ (0,1 ppm) and is below the odour perception limit.

Information on the determination of chlorine dioxide in the respective application concentration is given in Annex B and Annex C.

4.3 Requirements for the generation of chlorine dioxide

When designing chlorine dioxide systems, it shall be ensured that the precursors are completely mixed quickly and that the reaction time required for a high yield is maintained. Particularly in systems with alternating output, the residence time of highly concentrated chlorine dioxide solution in the mixing chamber shall be restricted in order to prevent the decomposition of the chlorine dioxide.

The quality of the water and the precursors for the production of the chlorine dioxide solutions shall not have any adverse effects on the production of chlorine dioxide. To this end, the purity criteria of the following document shall be met: among others, chlorine according to EN 937, sodium chlorite according to EN 938, sodium hypochlorite according to EN 901, hydrochloric acid according to EN 939 and sodium peroxodisulphate according to EN 12926.

When water is added together with precursors inside the mixing chamber by a metering device in order to achieve safe chlorine dioxide concentration, it shall be ensured that a sufficient dosage of water is added to prevent a potentially explosive chlorine dioxide liquid phase. Hence a proved safety system to monitor the water dosage shall be ensured, and if a risk assessment is performed according to EN ISO 12100, the severity and extend of the harm shall be estimated to the highest foreseeable severity, e.g. "death of several persons" (see chapter 5.5.2.2. in EN ISO 12100:2010).

Chlorine dioxide is not a stable substance, but decomposes depending on temperature, pH value and the concentration of the chlorine dioxide solution to form chlorite (ClO₂⁻) and chlorate (ClO₃⁻):



Higher pH values, exposure to light, heat and even traces of impurities reduce the stability of the chlorine dioxide solution produced. Further information on the decomposition of chlorine dioxide to chlorate is given in Annex A. When selecting the production process and the conditions for dosing the chlorine dioxide or making it available for dosing, the shelf life shall be taken into account, including the application-specific requirements. To achieve the highest possible yield with minimum by-product formation at the same time, the following conditions shall be fulfilled:

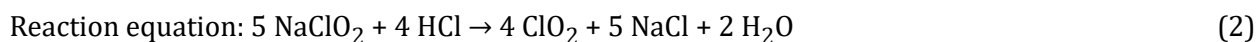
- optimized reaction time (depending on temperature, reaction process, precursors used);
- the highest possible reaction concentration (depending on the production process);
- rapid and complete mixing of the precursors;
- immediate consumption in the case of direct dosing or immediate rapid dilution of the highly concentrated mixing chamber effluent for more stable provision in the buffer tank.

The following processes are used for the *in situ* production of chlorine dioxide:

- 1) chlorite-acid process (chlorine dioxide generated from sodium chlorite by acidification);
- 2) chlorite chlorine gas process and chlorite sodium peroxodisulphate process (chlorine dioxide generated from sodium chlorite by oxidation).

prEN 18087:2024 (E)**4.4 Chlorite-Acid-Process (Chlorine dioxide generated from sodium chlorite by acidification)****4.4.1 Reaction conditions for the generation of chlorine dioxide**

The chlorite acid process is based on the reaction of sodium chlorite solutions according to EN 938 with hydrochloric acid according to EN 939 in excess.



Above a concentration of e.g. $c \geq 8 \text{ g/l}$ at $20 \text{ }^\circ\text{C}$, an explosive atmosphere of more than 300 g/Nm^3 chlorine dioxide develops in the gas space above the solution. No gas cushion may form in the mixing chamber. Immediately after preparation, the solution is usually diluted to a safe concentration of max. 3 g/l or added directly to the water to be treated without intermediate storage.

NOTE 1 In practice, a threefold molar amount of hydrochloric acid (related to the chlorite in reaction Formula 1a) has proven to be effective, e.g. by using commercial 9 % hydrochloric acid and 7,5 % sodium chlorite solution in a mixing ratio of 1 : 1.

NOTE 2 Other strong mineral acids such as sulphuric acid can also be used. However, a lower yield and increased chlorate formation is expected with these acids.

A common chlorine dioxide concentration in the mixing chamber is 20 g/l . Higher concentrations are possible, provided that a suitable combination of pressure and temperature ensures that no pure liquid, highly explosive chlorine dioxide can separate in the aqueous solution (see also 4.2). In particular, when using concentrated precursors such as e.g. 25 % to 36 % hydrochloric acid and 25 % to 31 % sodium chlorite, safe conditions for the chlorine dioxide concentration in the mixing chamber shall be ensured. A functional safety required for this shall be achieved e.g. by an intrinsically safe pre-dilution of concentrated precursors.

The temperature for preparing a solution of, for example, 20 g/l is at least $10 \text{ }^\circ\text{C}$ and should not exceed $35 \text{ }^\circ\text{C}$. The reaction time is strongly temperature-dependent and decreases with increasing temperature. An increase in temperature leads to increased formation of reaction by-products, therefore low temperatures are preferable. The reaction time should be at least at the following temperatures in the mixing chamber:

- $10 \text{ }^\circ\text{C}$ to $15 \text{ }^\circ\text{C}$: 15 minutes to 10 minutes;
- $15 \text{ }^\circ\text{C}$ to $25 \text{ }^\circ\text{C}$: 10 minutes to 7 minutes;
- $25 \text{ }^\circ\text{C}$ to $35 \text{ }^\circ\text{C}$: 7 minutes to 3 minutes.

NOTE 3 Systems working with other concentrations might have different reaction times at different temperature ranges and different maximum temperature limits.

4.4.2 Selection of the system**4.4.2.1 General**

A distinction is made between systems:

- a) with diluted or concentrated precursors;
- b) with continuous or discontinuous operation;
- c) with direct dosing of the prepared solution and systems with a buffer tank.