BS EN 15074:2014

BSI Standards Publication

Chemicals used for treatment of swimming pool water — Ozone

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National foreword

This British Standard is the UK implementation of EN 15074:2014. It supersedes BS EN 15074:2006 which is withdrawn.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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Chemicals used for treatment of swimming pool water - Ozone

Produits chimiques utilisés pour le traitement de l'eau des piscines - Ozone

Produkte zur Aufbereitung von Schwimm- und Badebeckenwasser - Ozon

This European Standard was approved by CEN on 29 September 2014.

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Foreword

This document (EN 15074:2014) 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of an identical text or by endorsement, at the latest by May 2015, and conflicting national standards shall be withdrawn at the latest by May 2015.

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 15074:2006.

Significant technical difference between this edition and EN 15074:2006 is as follows:

- copy of Clause 3, Description, and Clause 5, Test methods, from EN 1278:2010 [1];
- updating of Subclause 6.2 in line with current legislation.

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 for swimming pools, caused by the product covered by this European Standard:

a) this European Standard provides no information as to whether the products 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 these products remain in force.

NOTE 1 Conformity with the European Standard does not confer or imply acceptance or approval of the products in any of the Member States of the EU or EFTA. The use of the product covered by this European Standard is subject to regulation or control by National Authorities.

NOTE 2 Ozone is a biocide product according to the 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.

1 Scope

This European Standard is applicable to ozone used for treatment of water for swimming pools. It describes the composition of ozone. It gives information on its use in swimming pool water treatment. It also determines the rules relating to safe handling and use (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)*

3 Description

3.1 Identification

3.1.1 Chemical name

Ozone.

3.1.2 Synonym or common name

None (has sometimes been called improperly “allotropic oxygen”).

3.1.3 Relative molecular mass

48.

3.1.4 Empirical formula

O_3.

3.1.5 Chemical formula

O_3.

3.1.6 CAS Registry Number[1]

10028-15-6.

3.1.7 EINECS reference[2]

Not applicable.

3.2 Commercial form

Ozone is generated on or near the site of use.

3.3 Physical properties

3.3.1 Appearance

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[1] Chemical Abstracts Service Registry Number.

[2] European Inventory of Existing Commercial Chemical Substances.

Bluish gas; the liquid is dark blue.

NOTE A weak absorption in the visual range between 435 nm and 475 nm.

3.3.2 Density

- Gas: 2,144 kg/m^3 at NTP (Normal Temperature Pressure, 273 K and 101,3 kPa);
- liquid: 1,574 g/ml at − 183 °C;
- solid: 1,728 g/cm^3.

3.3.3 Solubility in water

In pure water, the solubility values (S) expressed in grams per cubic meter water per (grams per cubic meter) gas at 101,3 kPa are given in Table 1.

Table 1 — Solubility in water

Temperature of water °C	**Solubility** S, in: $\frac{g/m^3 H_2O}{g/m^3 gas}$
0	0,64
5	0,5
10	0,39
15	0,31
20	0,24
25	0,19
30	0,15
35	0,12

NOTE 1 Recent surveys of literature data are given in Bibliography. See [2], [3] and [4].

NOTE 2 S is a ratio, not an absolute concentration.

3.3.4 Vapour pressure

The vapour pressure of ozone depending on temperature is given in Table 2.

Table 2 — Vapour pressure

Temperature °C	Vapour pressure kPa
- 183	0,014 7
- 180	0,028
- 170	0,188
- 160	0,897
- 150	3,306
- 140	9,892
- 130	25,331
- 120	56,928
- 110	115,322
- 100	2 139,079

3.3.5 Boiling point at 100 kPa[3)]

− 112 °C.

NOTE Vaporization heat: 681 kJ/m^3 at NTP.

3.3.6 Melting point

− 196 °C.

3.3.7 Specific heat (liquid)

Not applicable.

3.3.8 Viscosity (dynamic)

0,004 2 Pa.s at − 195 °C;

0,001 55 Pa.s at − 183 °C.

3.3.9 Critical temperature

− 12,1 °C.

3.3.10 Critical pressure

5 460 kPa.

3.3.11 Physical hardness

Not applicable.

3.4 Chemical properties

Ozone is a powerful oxidant. The standard redox potentials (25 °C) are:

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3) 100 kPa = 1 bar.

(E_{O}^{H} -values in volts):

$$O_3 + 2H^+ + 2e^- \rightarrow \qquad O_2 + H_2O \qquad E_{\mathrm{O}}^{H} = 2{,}07\ \mathrm{V} \tag{1}$$

$$O_3 + H_2O + 2e^- \rightarrow \qquad O_2 + 2OH^- \qquad E_{\mathrm{O}}^{H} = 1{,}24\ \mathrm{V} \tag{2}$$

$$OH^\circ + H^+ + e^- \rightarrow \qquad H_2O \qquad E_{\mathrm{O}}^{H} = 2{,}42\ \mathrm{V}\ \text{(calculated value)} \tag{3}$$

If the pH increases by one unit, the E^H -values shall decrease by 30 mV per electron transferred. At 100 kPa and 25 °C and pH = 7 the E^H -values, versus the normal hydrogen electrode, become:

- O_3 (1) = 1,66 V;
- O_3 (2) = 0,82 V;
- OH° (3) = 2,21 V.

In water treatment most of the direct reactions of ozone are dipolar cyclo-additions and electrophilic substitution reactions. Moreover ozone, in water, can generate radicals such as OH°: ($O_3 + H_2O \rightarrow 2\ OH^\circ + O_2$). The OH° radical is a strong general oxidant.

4 Purity criteria

4.1 Composition of product

Typical concentrations obtainable in air are in the range of 15 g/m^3 to 45 g/m^3 at Normal Temperature and Pressure, 273 K and 101,3 kPa (NTP).

The ozone concentration obtained under specified operating conditions shall be equal to or greater than the value declared by the manufacturer of the ozone generator.

4.2 Impurities and main by-products

Traces of nitrogen oxides can be formed during ozone generation.

5 Test methods

5.1 Sampling

Ozone generation is usually based on a continuous process gas flow mode positive pressure. Sampling of a volume is to be controlled with a totalizing volumetric flow meter, the volumes being expressed at Normal Temperature and Pressure (NTP).

In continuous monitoring methods the gas exit shall be open to ambient air or the gas pressure shall be controlled and the results corrected for effects of pressure.

Sampling lines shall be in stainless steel or in polyfluorocarbone material resistant to ozone. The transfer of the gas from the sampling point to the analyser shall be kept shorter than 1 min.

Expression of concentrations: concentration of ozone in a gas in g/m^3 (NTP), or kg/m^3 (NTP), and for traces in cm^3/m^3 (equivalent to ppm as volume fraction).

NOTE 1 1 g/m^3 (NTP) equals 466,4 × 10^{-6} (volume fraction) and 0,069 9 % (mass fraction) in oxygen or 0,077 3 % (mass fraction) in air.

NOTE 2 At conventional concentrations of about 20 g/m^3 (NTP), the effect of difference in gas densities between ozone and oxygen-nitrogen is negligible. This is not the case when higher ozone concentrations are generated, i.e. in oxygen.

5.2 Analyses

5.2.1 General

The present method concerns the determination of ozone in air, oxygen or other process gases. The method is directly applicable for ozone concentrations in the range of 1 g/m^3 to 200 g/m^3 (NTP).

5.2.2 Principle

Direct iodometric titration.

5.2.3 Reagents

All reagents shall be of a recognized analytical grade and the water used shall conform to grade 2 in accordance with EN ISO 3696.

5.2.3.1 Potassium iodide (KI) buffered solution.

Potassium iodide (KI) solution at 20 g/l with sodium hydrogen phoshate ($Na_2HPO_4.2\ H_2O$) solution at 7,3 g/l and potassium dihydrogen phosphate (KH_2PO_4) solution at 3,5 g/l.

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

5.2.3.3 Sulfuric acid, solution at 9 mol/l.

5.2.3.4 Potassium iodate (KIO_3) powdered.

5.2.3.5 Potassium iodide (KI) crystalline.

5.2.3.6 Hydrochloric acid standard volumetric solution $c(HCl) = 0,1$ mol/l **or sulfuric acid** $c(H_2SO_4) = 0,05$ mol/l.

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 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.

5.2.3.8 Standardization of sodium thiosulfate:

5.2.3.8.1 Reactions

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

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

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

$$3\ I_2 + 6\ S_2\ O_3^{2-} \qquad 6\ I^- + 3\ S_4O_6^{2-} \qquad (7)$$

5.2.3.8.2 Determination

Add 0,05 g of potassium iodate (5.2.3.4), 0,5 g of potassium iodide (5.2.3.5) into 50 ml water and a further 50 ml water in a conical flask. After mixing, add 10 ml standard volumetric solution acid (5.2.3.6). Titrate the liberated iodine immediately with the sodium thiosulfate solution (5.2.3.2).

5.2.3.8.3 Calculation

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

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

where

c_a is the concentration, in moles per litre, of the acid (5.2.3.6);

V is the volume, in millilitres, of the acid (5.2.3.6);

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

5.2.4 Apparatus

Ordinary laboratory apparatus.

5.2.5 Procedure

5.2.5.1 Add the solution of potassium iodide (200 ml) to a standard gas washing vessel to give a depth of liquid of 10 cm to 15 cm. The use of fritted gas bubblers is not recommended.

5.2.5.2 Connect a second identical flask in series as a guard to check the ozone transfer and reaction.

5.2.5.3 For ozone produced with air, bubble the process gas containing ozone at a flow rate of about 1 l/min until a total expected quantity of approximately 1 mmol ozone (0,048 g) has passed. For process gases containing higher ozone concentration (100 g/m^3 to 200 g/m^3 (NTP), set the gas flow at the level to pass about 1 mmol of ozone.

5.2.5.4 Titrate the iodine formed in the flasks with the standard volumetric sodium thiosulfate solution (5.2.3.2) immediately after acidification with not less than 5 ml of the acidifying solution (5.2.3.3). After titration to a pale yellow colour, add 0,5 ml of starch indicator (5.2.3.7) and complete the titration and record the result.

5.2.6 Expression of results

The concentration of ozone, C, expressed in grams per cubic metre (NTP) is given by the following formula:

$$C = \frac{V \times c_t \times 24}{v} \tag{9}$$

where

V is the volume, in litres, of the sodium thiosulfate solution used;

c_t is the concentration, in moles per litre, of the standard volumetric sodium thiosulfate solution;

v is the inlet volume of gas passed, in cubic metres (NTP).

5.2.7 Accuracy

The detection limit is 0,1 g/m^3 (NTP), the standard deviation is 0,03 g/m^3 (NTP), for ozone produced from air at a nominal concentration of 20 g/m^3 (NTP). For higher concentrated ozone gases (range of 100 g/m^3 to 200 g/m^3 (NTP)), the standard deviation is 1 % of the measured result. Errors in gas flow and pressure measurement need to be taken into account.

5.2.8 Precautions

5.2.8.1 All upstream transfer and pressure reducing equipment shall be in materials which do not react with ozone, e.g. glass, polytetrafluorethylen (PTFE).

5.2.8.2 The gas contacting and transfer systems shall have a free exit to ambient pressure.

5.2.8.3 All gas flows shall be expressed at NTP (this equals 273 K and 101,3 kPa).

5.2.8.4 Gas flows shall be measured with an accuracy of 1 % (volumetric gas meter or bubble trap is recommended).

6 Labelling - Transportation - Storage

6.1 Labelling

Not applicable, except for safety instructions inside users' premises.

6.2 Risk and safety labelling according to the EU Legislation[4)]

Ozone is generated *in situ* therefore, at the date of the publication of this standard, risk and safety labelling is not applicable, except safety instructions inside of users' premises.

The legislation [5], 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.

6.3 Transportation regulations and labelling

At the date of the publication of this standard, ozone is not transported.

6.4 Marking

Ozone is generated *in situ* and therefore does not require marking.

6.5 Material acceptable for contact with ozone

For local buffer storage of brief duration and also in case of recycling of the process gas, stainless steel is preferable. Magnesium containing alloys shall be avoided. Cast aluminium is satisfactory and polyvinylchloride (PVC) (hard, 1,6 MPa standard) can be convenient if the plasticizer content is low but some formulations can be subject to ageing when exposed to ozone at high concentrations. Rubber and plastics materials e.g. for joints shall be proven specifically for resistance to ozone.

6.6 Stability

6.6.1 Temperature can influence the decomposition rate (see EN 1278).

6.6.2 The auto-decomposition of ozone is kinetically of first order.

6.6.3 In a dry process gas at 100 kPa and 25 °C, the half-life time of ozone is greater than 2 h.

[4)] See [5].

6.6.4 When dissolved in water the half-life time of ozone is in the range of 20 min to 30 min depending on the mineral composition of the water. The presence of reactive organic substances can promote the decomposition of ozone by reaction. In such cases the reactions are generally of second order.

6.6.5 Decomposition is accelerated in alkaline solution. A typical value of the pseudo first order overall kinetic constant is $k_1 = 2 \times 10^{-2} s^{-1}$ (at pH = 10 and an alkalinity in the range of 5 mg/l $CaCO_3$ to 500 mg/l $CaCO_3$).

6.6.6 Decomposition of ozone also occurs through synergetic processes (the so-called Advanced Oxidation Processes, “AOPs”), involving ozone together with hydrogen peroxide, UV-radiation or catalysts.

Annex A
(informative)

General information on ozone

A.1 Origin

A.1.1 Raw materials

Ozone for treatment of swimming pool water is obtained by processes involving the dissociation of molecular oxygen contained in air into oxygen radicals which can react with molecular oxygen to form ozone.

The concentration of hydrocarbons in the process gas should be minimized. At 1 % volume fraction of hydrocarbons in air, practically no ozone is generated; the drop in yield is linear with respect to the hydrocarbon content of the process gas. An optional analytical method for “methane index” is given in EN 1278.

A.1.2 Manufacturing process

The most common method is the silent electrical discharge, also called corona discharge, in which electrons are used as source of energy for the dissociation of oxygen in dry air (dew point below − 50 °C).

A.2 Use

A.2.1 Function

Ozone is applicable in swimming pool water treatment for disinfection, oxidation of organic contaminants and as a reagent promoting coagulation (“microflocculation”).

A.2.2 Form in which the product is used

Ozone is generated at or near the site of use and applied as a mixture in air.

A.2.3 Treatment dose

The required ozone dose depends on the swimming pool water quality and the objective of the treatment. General guidelines are at least 3 min contact time with a dissolved ozone concentration depending on the temperature as follows:

Water temperature	Ozone concentration
≥ 28 °C	≥ 0,8 mg/l
> 28 °C ≤ 32 °C	≥ 1 mg/l
> 32 °C ≤ 35 °C	≥ 1,2 mg/l
> 35 °C	≥ 1,5 mg/l

A.2.4 Means of application

Ozone is applied as a gas mixture injected into water. All technologies for mass transfer of gas to liquid are potentially applicable to ozonation. The most common technique used for the treatment of swimming pool water is a booster pump that forces pool water through an injector. The injector draws the air-ozone mixture from the generator into a mixer where intimate mixing of the gas bubbles with water occurs. Ozone transfer efficiency should be approximately 90 %.

A.2.5 Secondary effects

Ozone can form oxidation by-products. In certain conditions, limited formation of brominated trihalomethanes and of bromate can occur on ozonation of bromide containing waters.

A.2.6 Removal of excess product

Residual ozone shall be removed before the treated water is returned and should not be detected in the pool water. Normally this is effected by filtration through granular activated carbon or pyrolyzed coal material. Following the removal of ozone, chlorine or another disinfectant is added as a persistent disinfectant to avoid growth of opportunistic pathogens and to guard against cross-infection within the pool.

Excess ozone in the off-gas should be kept under appropriate control. Thermal or catalytic decomposition and adsorption with or without reduction can be effective.

Annex B
(normative)

General rules relating to safety

B.1 Rules for safe handling and use

Ozone is toxic on inhalation. The threshold limit value is defined as the maximum acceptable time-weighted average concentration in working rooms for 8 h per day exposure. The commonly adopted limit is a volume fraction of 0,1 ml/m^3. The ozone concentration in the ambient air shall be monitored. Premises potentially exposed to ozone leakage shall be naturally vented and forced venting equipment shall be installed in case of leakages of the hardware.

The risks of fire for ozone generating systems are the same as those for leakage in oxygen systems.

For electrical risks local standards and codes of practice shall be applied.

B.2 Emergency procedures

B.2.1 First aid

The first symptoms of intoxication are headache followed by irritation of respiratory passages, substernal pressure and feeling of suffocation. Aid measures are to vent the premises and to avoid any unnecessary physical efforts. In case of severe of exposure, practise artificial respiration, and call for medical assistance.

B.2.2 Spillage

In case of leakages, stop the generators and vent the premises. Destruction of residual ozone in the off-gas is required during operation.

B.2.3 Fire

No specific fire hazard is related to ozone at the concentrations that are generated. For electrical risks, standards and codes of practice shall be applied.

Bibliography

[1] EN 1278, *Chemicals used for treatment of water intended for human consumption - Ozone*

[2] Standard Method Nr 01/96 and Nr 002/87 of the International Ozone Association, Secrétariat; 83, avenue Foch, F 75116 Paris

[3] Ozone et Ozonation des Eaux. (1991) — Ed. Lavoisier-Technique et Documentation; 11, rue Lavoisier, F 75384 PARIS CEDEX 08

[4] Ozone in Water Treatment, ed. (1991) - AWWARF-CGE, published by Lewis Publishers Inc.; 121 South Main Street, Chelsea-Michigan (48118 USA)

[5] 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)

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