BS EN 12672:2016

BSI Standards Publication

Chemicals used for treatment of water intended for human consumption — Potassium permanganate

National foreword

This British Standard is the UK implementation of EN 12672:2016. It supersedes BS EN 12672:2008 which is withdrawn.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 water intended for human consumption - Potassium permanganate

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Permanganate de potassium

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Kaliumpermanganat

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Contents

Page

European foreword

This document (EN 12672:2016) 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of an identical text or by endorsement, at the latest by November 2016 and conflicting national standards shall be withdrawn at the latest by November 2016.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 12672:2008.

The significant technical changes between this edition and EN 12672:2008 are as follows:

— deletion of reference to Directive 67/548/EEC of 27th June 1967 in order to take into account the latest Regulation in force (see [2]);

— amendment of subclause 6.2 according to [2].

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Introduction

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

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

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

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

1 Scope

This European Standard is applicable to potassium permanganate used for treatment of water intended for human consumption. It describes the characteristics of potassium permanganate and specifies the requirements and the corresponding test methods for potassium permanganate. It gives information on its use in water treatment. It also provides general information on potassium permanganate (see Annex A) and determines the rules relating to its 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 1233, *Water quality - Determination of chromium - Atomic absorption spectrometric methods*

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

EN ISO 11885, *Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885)*

EN ISO 12846, *Water quality - Determination of mercury - Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846)*

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

ISO 3856-2, *Paints and varnishes - Determination of "soluble" metal content — Part 2: Determination of antimony content - Flame atomic absorption spectrometric method and Rhodamine B spectrophotometric method*

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

ISO 8213, *Chemical products for industrial use - Sampling techniques - Solid chemical products in the form of particles varying from powders to coarse lumps*

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

ISO 17378-2, *Water quality - Determination of arsenic and antimony - Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

ISO/TS 17379-2, *Water quality - Determination of selenium - Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

3 Description

3.1 Identification

3.1.1 Chemical name

Potassium permanganate.

3.1.2 Synonym or common name

Permanganate of potash.

3.1.3 Relative molecular mass

158,04.

3.1.4 Empirical formula

$KMnO_4$.

3.1.5 Chemical formula

$KMnO_4$.

3.1.6 CAS Registry Number [1)]

7722-64-7.

3.1.7 EINECS reference [2)]

231-760-3.

3.2 Commercial forms

Solid product, consisting of rhombic crystals. For water treatment the commercial forms normally used are:

— technical grade to be dosed in liquid form, dissolved in water;

— free-flowing grade to be dosed either in solid form or dissolved in water.

3.3 Physical properties

3.3.1 Appearance

Crystals of a dark purple or bronze-like colour; almost opaque by transmitted light and of a blue metallic lustre by reflected light.

The free-flowing grade can present a different colour, usually greyish.

3.3.2 Density

The density of the product is 2,70 g/cm^3 at 20 °C.

The bulk density is between 1,45 g/cm^3 and 1,60 g/cm^3.

3.3.3 Solubility (in water)

The product is soluble in water.

The solubility in water is given in Table 1.

Aqueous solubility:

$$KMnO_4 \text{ (g/l)} = 30.55 + 0.796 \times (T, °C) + 0.039\ 2 \times (T, °C)^2$$

where

T is the solution temperature (°C).

1) Chemicals Abstracts Service Registry Number.

2) European Inventory of Existing Commercial Chemical Substances.

Table 1 — Solubility in water

Temperature °C	**$KMnO_4$** g/l
5	35,51
10	42,43
15	51,31
20	62,15
25	74,95
30	89,71

3.3.4 Vapour pressure

Not applicable.

3.3.5 Boiling point at 100 kPa[3)]

Not applicable.

3.3.6 Melting point

Product decomposes at 240 °C with emission of oxygen.

3.3.7 Specific heat

744,2 kJ/kg.K at 20 °C.

3.3.8 Viscosity (dynamic)

Not applicable.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3.4 Chemical properties

Potassium permanganate is a very strong oxidizing agent.

It is soluble in water and also dissolves in various organic solvents (e.g. methanol, ethanol).

It decomposes at high temperature and also in the presence of concentrated acids, hydrogen peroxide and organic compounds in general.

It hydrolyzes in contact with air, reducing to manganese dioxide (MnO_2), a solid, brown to black colour product.

3) 100 kPa = 1 bar.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for potassium permanganate 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 the product standard.

Limits have been given for impurities and chemicals 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 leads to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

4.2 Composition of commercial product

The potassium permanganate content shall not be less than a mass fraction of 98,5 % in the technical grade, and a mass fraction of 97,5 % in the free-flowing grade.

4.3 Impurities and main by-products

MnO_2 (water insolubles): less than a mass fraction of 1,00 %.

Moisture (H_2O): less than a mass fraction of 0,50 %.

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]).

The content of chemical parameters shall conform to the requirements specified in Table 2.

Table 2 — Chemical parameters

Parameter		Limit mg/kg of product
Arsenic (As)	max.	20
Cadmium (Cd)	max.	50
Chromium (Cr)	max.	50
Mercury (Hg)	max.	10
Nickel (Ni)	max.	50
Lead (Pb)	max.	50
Antimony (Sb)	max.	50
Selenium (Se)	max.	50
NOTE Cyanide, which does not exist in a strong oxidizing medium such as potassium permanganate, is not a relevant chemical parameter. Pesticides and polycyclic aromatic hydrocarbons are not by-products of the manufacturing process.		

4.5 Flowability of free–flowing grade

The free-flowing grade shall pass the flowability test.

5 Test methods

5.1 Sampling

Observe the general recommendations of ISO 3165 and take account of ISO 6206. Prepare the laboratory sample(s) required by the relevant procedure described in ISO 8213.

5.2 Analysis

5.2.1 Determination of potassium permanganate (main product)

5.2.1.1 Principle

Reduction of potassium permanganate Mn(VII) to Mn(II) with sodium oxalate under acidic conditions. The excess of sodium oxalate is titrated with a standard volumetric solution of potassium permanganate.

5.2.1.2 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.

5.2.1.2.1 Potassium permanganate.

5.2.1.2.2 Sodium oxalate.

5.2.1.2.3 Sulfuric acid solution, 20 % (*m/m*).

5.2.1.2.4 Potassium permanganate standard volumetric solution $c(KMnO_4)$ = 1,000 g/l.

— Weigh 1,000 g of the potassium permanganate (5.2.1.2.1), transfer to a 1 l volumetric flask and dilute to volume with water. Allow to stand with occasional mixing for 15 min.

Standardize the solution as follows:

— Weigh 2,120 g of the sodium oxalate (5.2.1.2.2) and transfer to a 1 l volumetric flask. Add 20 ml of 20 % (*m/m*) H_2SO_4 (5.2.1.2.3) to the 1 l volumetric flask containing the oxalate, dissolve and allow to stand for 5 min.

Transfer 40 ml of the sodium oxalate solution by pipette into a small conical flask, heat to 70 °C to 80 °C and titrate with the potassium permanganate standard volumetric solution to a faint pink end-point that persists for 20 s to 30 s.

The standardization factor (*F*) is calculated as follows:

$$F = \frac{40}{V} \quad (1)$$

where

V is the volume, in millilitres, of potassium permanganate standard volumetric solution used in titration.

5.2.1.3 Apparatus

5.2.1.3.1 Ordinary laboratory apparatus and glassware.

5.2.1.4 Procedure

Weigh 1,000 g of the sample and 2,120 g of sodium oxalate on a watch glass and transfer quantitatively to a 500 ml conical flask. Add 150 ml of water and 20 ml of 20 % (*m/m*) H_2SO_4 (5.2.1.2.3). Heat while stirring to 70 °C to 80 °C and then titrate with the potassium permanganate standard volumetric solution (5.2.1.2.4) to a faint pink end-point that persists for 20 s to 30 s.

5.2.1.5 Expression of results

The content (P_1) in percentage by mass (% (*m/m*)) of potassium permanganate in the sample is calculated as follows:

$$P_1 = 100{,}00 - (0{,}1\, F \times V_1) \qquad (2)$$

where

F is the standardization factor determined as described in 5.2.1.2.4;

V_1 is the volume, in millilitres, of the potassium permanganate standard volumetric solution used in the titration.

5.2.2 Impurities

5.2.2.1 Manganese dioxide (MnO_2) (water insolubles)

5.2.2.1.1 Principle

Determination of mass fraction in (%) of manganese dioxide (MnO_2) in a sample of potassium permanganate, by spectrometric analysis of Mn(II). MnO_2 is separated from an aqueous solution of KMnO4 by filtration and subsequently reduced to Mn(II). The resulting solution is analysed according to EN ISO 11885.

5.2.2.1.2 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.

5.2.2.1.2.1 Hydrochloric acid, HCl, concentrated.

5.2.2.1.2.2 Hydrogen peroxide solution, volume fraction 0,5 %.

5.2.2.1.3 Apparatus

5.2.2.1.3.1 Ordinary laboratory apparatus and glassware.

5.2.2.1.3.2 ICP emission spectrometer.

5.2.2.1.4 Procedure

5.2.2.1.4.1 Separation and dissolution of MnO_2.

Weigh (5,000 ± 0,001) g of the sample, place on a glass filter (porosity grade P10 (4 µm to 10 µm)) and dissolve it to completion by washing the test portion repeatedly with water until the filtrate water is

free from $KMnO_4$ (colourless). Dissolve the residue on the filter with 10 ml of HCl (5.2.2.1.2.1) followed by 10 ml of a solution of H_2O_2, volume fraction 0,5 % (5.2.2.1.2.2). After repeated washing of the filter, transfer to a volumetric flask and dilute to 50 ml.

5.2.2.1.4.2 Determination of MnO_2 content.

The MnO2 content shall be determined by measuring the emission of the dissolved Mn(II) by ICP spectrometry according to EN ISO 11885.

The method will give the interim result (y), expressed in milligrams per litre of MnO_2, which needs to be corrected to give the final concentration according to 5.2.2.1.5.

5.2.2.1.5 Expression of results

From the interim results (y) (see 5.2.2.1.4.2), the content of MnO_2 (w_1) in the sample, expressed as a percentage by mass (%(m/m)), is calculated using the following formula:

$$w_1 = y \times \frac{5}{m \times 1\ 000} \tag{3}$$

where

y is the interim result (5.2.2.1.4.2);

m is the mass, in grams, of the test portion.

5.2.2.2 Moisture (H_2O)

5.2.2.2.1 Principle

Determination of percentage of H_2O in a sample of potassium permanganate ($KMnO_4$) by mass loss after heat treatment.

5.2.2.2.2 Apparatus

Drying oven.

5.2.2.2.3 Procedure

Weigh (10,00 ± 0,01) g of the sample in a watch glass. Place the test portion in a drying oven heated at 110 °C for 2 h. Cool in a desiccator and weigh.

5.2.2.2.4 Expression of results

The moisture (P_2) in percent by mass (% (m/m)) is calculated as follows:

$$P2 = \frac{m_1 - m_2}{m_1} \times 100 \tag{4}$$

where

m_1 is the initial mass in grams of the test portion;

m_2 is the mass in grams of the dried test portion.

5.2.3 Chemical parameters

5.2.3.1 Reagents

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

5.2.3.1.1 Hydrochloric acid, concentrated, HCI.

5.2.3.1.2 Hydroxylamine hydrochloride, $NH_2OH.HCI$, 99 % (m/m).

5.2.3.2 Test solution

SAFETY PRECAUTIONS: Addition of HCI to $KMnO_4$ will evolve chlorine gas. Hydroxylamine and potassium permanganate can react violenty. Add carefully and use adequate personal protection/goggles.

Weigh 2,5 g of the sample. Dissolve in 100 ml of water in a 150 ml acid-washed beaker. Under a hood, acidify the solution with concentrated HCl (5.2.3.1.1) to a pH of less than 2. Add hydroxylamine hydrochloride (5.2.3.1.2) until the solution turns clear. Heat the solution gently to reduce the volume below 100 ml, making sure that it does not boil. Quantitatively transfer to a 100 ml acid-washed volumetric flask and make up to the mark with water.

5.2.3.3 Blank test solution

Prepare a blank test solution as in 5.2.3.2 without the sample.

5.2.3.4 Determination

Determine the content of chemical parameters in the test solution (5.2.3.2) and in the blank test solution (5.2.3.3) in accordance with the following methods:

— Total arsenic, in accordance with ISO 17378-2;

— Nickel, cadmium and lead, in accordance with ISO 8288:1986, method A;

— Chromium, in accordance with EN 1233;

— Mercury, in accordance with EN ISO 12846;

— Selenium, in accordance with ISO/TS 17379-2;

— Antimony, in accordance with ISO 3856-2 (FAAS method).

The method will give an interim result (y) expressed in milligrams per litre which needs to be corrected to give the final concentration according to the equation in 5.2.3.5.

5.2.3.5 Expression of results

From the interim results (y) (see 5.2.3.4), the content, C_2, expressed in milligrams per kilogram of each chemical parameter in the laboratory sample, is calculated from the following formula:

$$C_2 = y \times \frac{V_1}{m_1} \tag{5}$$

where

y is the interim result (5.2.3.4);

V_1 is the volume, expressed in millilitres, of the sample solution (5.2.3.2) (= 100 ml);

m_1 is the mass, expressed in grams, of the test portion.

5.2.4 Flowability of free-flowing potassium permanganate

5.2.4.1 Apparatus

5.2.4.1.1 Ordinary laboratory apparatus and glassware.

5.2.4.1.2 Funnel:

— top, diameter: 75 mm;

— stem length: 300 mm;

— stem, inside diameter: (12 ± 1) mm.

5.2.4.2 Procedure

Weigh out (100 ± 1) g of the sample. Add the weighed material to a suitable container (about 500 ml capacity) that has a tight-fitting lid.

Using water and a burette or pipette calibrated in 0,1 ml divisions, add 0,7 ml to the preweighed sample in the container, distributed evenly over the surface of the sample. Cover and shake during 3 min, so that the water and the sample are mixed thoroughly. Remove lid and pour the potassium permanganate sample into a funnel mounted on a ring stand.

5.2.4.3 Assessment

If the potassium permanganate mixed with the water flows freely through the funnel, then the sample passes the flowability test.

If the potassium permanganate mixed with the water does not flow freely through the funnel, then the sample does not pass the test.

6 Labelling - Transportation - Storage

6.1 Means of delivery

The product shall be delivered in steel drums certified for goods RID/ADR class 5.1.

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

6.2 Labelling in accordance with EU Legisation [4)]

At the time of publication of this European Standard, the following labelling requirements shall apply to Potassium permanganate:

4) See [2].

Figure 1 — GHS03

Figure 2 — GHS07

Figure 3 — GHS09

— Signal Word:

Danger

— Hazard Statements:

H272 May intensify fire; oxidiser.

H302 Harmful if swallowed.

H410 Very toxic to aquatic life with long lasting effects.

The Regulation [2] 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

Potassium permanganate is listed as UN Number [5]: 1490.

RID [6]/ADR [7]: Class 5.1, Classification code O2, Packaging group II.

IMDG [8]: Class 5.1 (packaging group II).

IATA [9]: Class 5.1 (packaging group II).

6.4 Marking

The marking shall include the following information:

— the name "potassium permanganate", the trade name and the grade;

— the net mass;

— the name and the address of supplier and/or manufacturer;

— the statement "This product conforms to EN 12672.".

6.5 Storage

6.5.1 Long term stability

The product is stable if stored in a cool dry area in closed containers.

6.5.2 Storage incompatibilities

Potassium permanganate produces spontaneous combustion in contact with products such as glycerin and ethylene glycol.

It also reacts violently with acetic acid, sulphuric acid, finely divided organic materials, charcoal, iron (II) salts, sulphites and peroxides. With hydrochloric acid, it releases chlorine.

5) United Nations Number.

6) Regulations concerning international carriage of dangerous goods by rail.

7) European Agreement concerning the international carriage of dangerous goods by road.

8) International Maritime Transport of Dangerous Goods.

9) International Air Transport Association.

Annex A
(informative)

General information on potassium permanganate

A.1 Origin

A.1.1 Raw materials

The raw materials for the production of potassium permanganate are:

— potassium hydroxide (KOH);

— pyrolusite (manganese ore, manganese dioxide (MnO_2)).

A.1.2 Manufacturing process

The principal manufacturing process of potassium permanganate is the oxidation of manganese dioxide in the presence of potassium hydroxide. The oxidation process consists of two stages: a chemical stage which yields potassium manganate (K_2MnO_4) and an electrochemical stage in which potassium manganate is oxidized to potassium permanganate.

A.2 Use

A.2.1 Function

The main applications of potassium permanganate include taste and odour control, elimination of algae and microorganisms, removal of iron (Fe) and manganese (Mn) by oxidation to insoluble oxides and regeneration of filtering material.

A.2.2 Form in which the product is used

The product is used as a solid or in aqueous solution.

A.2.3 Treatment dose

The treatment dose depends on the quality of the water to be treated. Effective oxidation of contaminants in water is achieved at dose rates under 10 mg of $KMnO_4$ per litre of water.

A.2.4 Means of application

When used as a solid, it should be applied using appropriate solid-feeding equipment.

When used in solution, it can be fed by gravity or by pumping.

A.2.5 Secondary effects

There are no secondary effects because, although the oxidation process yields a by-product, namely manganese dioxide, this by-product is insoluble in water at pH values between 2 and 11,5, biologically inert and removable by settling and filtration.

A.2.6 Removal of excess product

Excess product is removed by adding an aqueous solution of sodium thiosulphate or sodium bisulphite.

Annex B
(normative)

General rules relating to safety

B.1 Rules for safe handling and use

The supplier shall provide current safety instructions.

Personal protective equipment:

— eye protection : safety goggles / protective mask;

— hand protection : rubber gloves;

— respiratory protection: protective respirator;

— skin protection: rubber apron or safety overall.

B.2 Emergency procedures

B.2.1 First aid

In case of contact with skin, rinse immediately with plenty of water.

Contaminated clothing shall be removed and washed.

In the event of eye contact, rinse immediately with plenty of water for at least 15 min and seek medical advice.

If swallowed, drink plenty of water or if available drink sugared milk, orange juice or lemon juice. Seek medical advice.

B.2.2 Spillage

Spillage shall be swept up and removed immediately. Do not use sawdust or any other combustible material to collect the spill. Do not return the spilled product to the original drum.

To avoid the risk of combustion, the sweeping implement shall be washed immediately after use.

If possible, add sand to the spill before collection and disposal.

Disposal shall be carried out in accordance with local regulations.

B.2.3 Fire

The product is not flammable, but it favours combustion.

Cool fire-endangered containers with water.

Use water to extinguish fires.

Potassium permanganate decomposes spontaneously if exposed to high temperatures, releasing oxygen. In closed places, this decomposition can lead to explosion.

Bibliography

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

[2] 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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