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« *Drinking water treatment* »

**CEN/TC 164/WG 9 N 936**

le :2005-06-22

**Pr EN**  
**Chemicals used for the treatment of water intended for  
human consumption**  
**Sodium permanganate**

### **Subject**

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Pr EN ..... "Chemicals used for the treatment of water intended for human consumption – Sodium permanganate"

### **Follow up**

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Revised draft established after the 33<sup>th</sup> meeting of CEN/TC164/WG9 ready for launching CEN Enquiry.

**CEN/TC 164**

Date: 2005-06

CEN/TC 164

Secretariat: AFNOR

## **Chemicals used for treatment of water intended for human consumption- Sodium permanganate**

ICS:

Descriptors:

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## Foreword

This document TC 164 WI 00164... 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.

This document will be based largely on EN 12672:2000 Chemicals used for water treatment intended for human consumption – potassium permanganate.

## 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 :

- 1) 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 ;
- 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 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 sodium permanganate used for treatment of water intended for human consumption. It describes the characteristics of sodium permanganate and specifies the requirements and the corresponding test methods for sodium permanganate. It gives information on its use in water treatment.

## 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 1483, *Water quality - Determination of mercury.*

EN ISO 3696, *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 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 8288, *Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods.*

ISO 9174, *Water quality - Determination of total chromium - Atomic absorption spectrometric methods.*

ISO 9965, *Water quality - Determination of selenium - Atomic absorption spectrometric method (hydride technique).*

ISO 11969 : *Water quality - Determination of arsenic – Atomic absorption spectrometric method (hydride technique).*

### 3 Description

#### 3.1 Identification

##### 3.1.1 Chemical name.

Sodium permanganate.

##### 3.1.2 Synonym or common name.

Permanganate acid sodium salt .

##### 3.1.3 Relative molecular mass.

141,93

##### 3.1.4 Empirical formula.

$\text{NaMnO}_4$

##### 3.1.5 Chemical formula.

$\text{NaMnO}_4$

##### 3.1.6 CAS Registry Number <sup>1)</sup>.

10101-50-5

##### 3.1.7 EINECS reference <sup>2)</sup>.

233-251-1

#### 3.2 Commercial forms

Liquid sodium permanganate product at 40% concentration for the treatment of drinking water.

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<sup>1)</sup> Chemicals Abstracts Service Registry Number.

<sup>2)</sup> European Inventory of Existing Commercial Chemical Substances.

### **3.3 Physical properties**

#### **3.3.1 Appearance.**

Liquid sodium permanganate is a dark purple coloured solution.

#### **3.3.2 Density.**

The density of 40,00 % liquid sodium permanganate is 1,37 g/cm<sup>3</sup> at 20 °C.

#### **3.3.3 Solubility (in water).**

Liquid sodium permanganate is soluble up to 40% and miscible with water in all proportions.

#### **3.3.4 Vapour pressure.**

Not determined for liquid sodium permanganate, however, very similar to water.

#### **3.3.5 Boiling point at 100 kPa<sup>3)</sup>.**

Greater than 101° C.

#### **3.3.6 Melting point.**

Not applicable.

#### **3.3.7 Specific heat**

Not determined.

#### **3.3.8 Viscosity (dynamic).**

Less than 5 centipoises.

#### **3.3.9 Critical temperature.**

Not determined.

#### **3.3.10 Critical pressure.**

Not determined.

#### **3.3.11 Physical hardness.**

Not applicable.

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<sup>3)</sup> 100 kPa = 1 bar.



### 3.4 Chemical properties

Sodium permanganate is a very strong oxidizing agent.

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

Note: the reaction with organics may be violent and is not recommended.

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

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

## 4 Purity criteria

### 4.1 General

This European Standard specifies the minimum purity requirements for sodium 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.

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 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 liquid sodium permanganate solution shall contain a sodium permanganate ( $NaMnO_4$ ) concentration of not less than 39,5 % (*m/m*).

### 4.3 Impurities and main by-products

For liquid sodium permanganate,  $MnO_2$  (matter insoluble) : less than 0,055 % (*m/m*).

### 4.4 Chemical parameters

The product shall conform to the requirements specified. in Table 1.

**Table 1 — Chemical parameters**

Parameter		Limit mg/kg of liquid $NaMnO_4$
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 Cyanides does not exist in a strong oxidizing medium . Pesticides and polycyclic aromatic hydrocarbons are not by-products of the manufacturing process. For parametric values of sodium permanganate on trace metal content in drinking water, see [1].
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## 4.5 Flowability

Not applicable for liquid sodium permanganate.

## 5 Test methods

### 5.1 Sampling

#### 5.1.1 General

Observe the general recommendations of ISO 3165 and take account of ISO 6206.

#### 5.1.2 Sampling from drums and bottles

##### 5.1.2.1 General

**5.1.2.1.1** Mix the contents of each container to be sampled by shaking the container, by rolling it or by rocking it from side to side, taking care not to damage the container or spill any of the liquid.

**5.1.2.1.2** If the design of the container is such (for example, a narrow-necked bottle) that it is impracticable to use a sampling implement, take a sample by pouring after the contents have been thoroughly mixed. Otherwise, proceed as described in 5.1.2.1.3.

**5.1.2.1.3** Examine the surface of the liquid. If there are signs of surface contamination, take samples from the surface as described in 5.1.2.2. Otherwise, take samples as described in 5.1.2.3.

##### 5.1.2.2 Surface sampling

Take a sample using a suitable ladle. Lower the ladle into the liquid until the rim is just below the surface, so that the surface layer runs into it. Withdraw the ladle just before it fills completely and allow any liquid adhering to the ladle to drain off. If necessary, repeat this operation so that, when the other selected containers have been sampled in a similar manner, the total volume of sample required for subsequent analysis is obtained.

##### 5.1.2.3 Bottom sampling

Take a sample using an open sampling tube, or a bottom-valve sampling tube, suited to the size of container and the viscosity of the liquid.

When using an open sampling tube, close it at the top and then lower the bottom end to the bottom of the container. Open the tube and move it rapidly so that the bottom of the tube traverses the bottom of the container before the tube is filled. Close the tube, withdraw it from the container and allow any liquid adhering to the outside of the tube to drain off.

When using a bottom-valve sampling tube, close the valve before lowering the tube into the container and then proceed in a similar manner to that when using an open sampling tube.

#### 5.1.3 Sampling from tanks and tankers

From each access point, take samples as follows:

- a) from the surface of the liquid, using a ladle as described in 5.1.2.2;
- b) from the bottom of the tank or tanker, using a sampling tube as described in 5.1.2.3 or using a specially designed bottom-sampling apparatus;
- c) from one or more positions, depending on the overall depth, between the bottom and the surface using a weighted sampling can.

## 5.2 Analysis

### 5.2.1 Determination of liquid sodium permanganate

#### 5.2.1.1 Principle

Reduction of sodium 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 , mass fraction 20 %.

5.2.1.2.4 Potassium permanganate standard volumetric solution  $c(\text{KMnO}_4) = 1,000 \text{ g/l}$ .

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

Calibration :

— 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  $\text{H}_2\text{SO}_4$  (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 solution prepared to a faint pink end-point that persists for 20 s to 30 s.

The standardization factor ( $F$ ) is given by the following equation :

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

where

$V$  is the volume in millilitres, of solution of potassium permanganate  $\text{KMnO}_4$  used in titration.

#### 5.2.1.3 Apparatus

Ordinary laboratory apparatus and glassware.

#### 5.2.1.4 Procedure

##### 5.2.1.4.1 Liquid sodium permanganate determination

Tare a weighing bottle and cap. Carefully add sample to the weighing bottle with a disposable pipette to a mass between 1,0 and 1,5 g.

Cap the bottle and record the exact mass ( $m_1$ ).

Pour the contents of the bottle into a 500 ml conical flask that contains a stir bar, and reweigh the empty bottle ( $m_2$ ). Rinse down the sides of the flask with water.

Calculate the actual sample mass by subtracting the masses ( $m_2 - m_1$ ) recorded in step 4 (5.2.1.4.2.4) from the weight recorded in step 3 (5.2.1.4.2.3). Record this weight ( $m_3$ ).

Weigh an amount of sodium oxalate (5.2.1.2.2) that is equal to or slightly less than the mass of sodium permanganate solution ( $m_3$ ) onto a tared weighing paper. The mass shall be to the nearest 0,001 g. Record this mass ( $m_4$ ).

Transfer the sodium oxalate to the conical flask containing the sample of sodium permanganate and add sufficient water to cover the stir bar.

Add 25 ml of  $H_2SO_4$  (5.2.1.2.3) to the conical flask and rinse the sides with water.

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. Record this volume  $V_1$ .

##### 5.2.1.5 Expression of results

The content ( $P_1$ ) in mass fraction in (%) of sodium permanganate in the sample is given by the following equation :

$$P_1 = \frac{(0,4718 \times m_4) - (F \times V_1) \times 89,8}{m_3} \quad (2)$$

where

$m_3$  is the mass, in milligrams, of sodium permanganate;

$m_4$  is the mass, in milligrams, of sodium oxalate;

$V_1$  is the volume, in millilitres, of the potassium permanganate standard volumetric solution used for the titration;

$F$  is the standardization factor obtained in 5.2.1.2.4;

#### 5.2.2 Impurities

##### 5.2.2.1 Manganese dioxide (matter insoluble).

###### 5.2.2.1.1 Principle

Determination of mass fraction in (%) of manganese dioxide ( $MnO_2$ ) in a sample of sodium permanganate, by spectrometric analysis of Mn(II).  $MnO_2$  is separated from an aqueous solution of  $NaMnO_4$  by filtration and subsequently reduced to Mn(II).

NOTE Alternatively ISO 6333:1996 could be used.

### 5.2.2.1.2 Reagents

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

5.2.2.1.2.1 Hydrochloric acid, concentrate, HCl.

5.2.2.1.2.2 Hydrogen peroxide solution ,mass fraction 30 % .

### 5.2.2.1.3 Apparatus

Ordinary laboratory apparatus and glassware,

5.2.2.1.3.1 ICP emission spectrometer.

### 5.2.2.1.4 Procedure

#### 5.2.2.1.4.1 Separation and dissolution of MnO<sub>2</sub>

Weigh (12,500 ± 0,001) g of the sodium permanganate sample (5,000 g as NaMnO<sub>4</sub>). Place on a glass filter (porosity P10 (4µm to 10 µm)) and dissolve it to completion by washing the sample repeatedly with water until the filtrate water is free from NaMnO<sub>4</sub> (colourless). Dissolve the residue on the filter with 10 ml of HCl (5.2.2.1.2.1) and of H<sub>2</sub>O<sub>2</sub> (5.2.2.1.2.2). After repeated washing of the filter, transfer to a 50 ml volumetric flask and make up to volume with water .

#### 5.2.2.1.4.2 Determination of MnO<sub>2</sub> content

The MnO<sub>2</sub> content is measured by emission of the dissolved Mn<sub>(II)</sub> at an optimized wavelength of 217,610 nm by ICP spectrometry using an adequate calibration graph.

The method will give the interim result (y) expressed in milligrams per litre of MnO<sub>2</sub> which needs to be converted to give the final concentration according to equation 5.2.2.1.5.

### 5.2.2.1.5 Expression of results

From the interim result (y) determined (see 5.2.2.1.4.2), the content of MnO<sub>2</sub> (C<sub>1</sub>) in the sample expressed as a mass fraction in (%) is given by the following equation :

$$C_1 = y \times \frac{5}{m \times 1000} \quad (3)$$

where

y is the interim result (5.2.2.1.4.2) ;

m is the mass, in grams, of the initial sample.

## 5.2.3 Chemical parameters

### 5.2.3.1 Determination of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni) and selenium (Se)

#### 5.2.3.1.1 Principle

The elements arsenic, antimony, cadmium, chromium, lead, nickel and selenium are determined by atomic absorption spectrometry.

### 5.2.3.1.2 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.

**5.2.3.1.2.1 Hydrochloric acid**, concentrated, HCl.

**5.2.3.1.2.2 Hydroxylamine hydrochloride**,  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , mass fraction 99 % .

### 5.2.3.1.3 Test solution

**SAFETY PRECAUTIONS : Addition of HCl to  $\text{NaMnO}_4$  will evolve chlorine gas. Hydroxylamine and sodium permanganate can react violently. Add carefully and use adequate personal protection/goggles.**

Weigh (6,25) g of the liquid product (2,5 g as  $\text{NaMnO}_4$ ). Dissolve in 100 ml of water in a 150 ml acid-washed beaker. Under a hood, acidify the solution with concentrated HCl (5.2.3.1.2.1) to a pH value of less than 2. Add hydroxylamine hydrochloride (5.2.3.1.2.2) 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 volume with water.

### 5.2.3.1.4 Blank test solution

Prepare a blank test solution as in 5.2.3.1.3 without the sample.

### 5.2.3.1.5 Determination

Determine the content of elements in the test solution (5.2.3.1.3) and in the blank test solution (5.2.3.1.4) in accordance with the following methods :

- Arsenic, in accordance with ISO 11969 ;
- Nickel, cadmium and lead, in accordance with ISO 8288:1986, Method A ;
- Chromium, in accordance with ISO 9174 ;
- Mercury, in accordance with EN 1483 ;
- Selenium, in accordance with ISO 9965.
- 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 converted to give the final concentration according to equation in section 5.2.3.1.6.

### 5.2.3.1.6 Expression of results

From the interim result ( $y$ ) determined (see 5.2.3.1.5), the content,  $C_2$ , expressed in milligrams per kilogram of each element in the laboratory sample, is given by the following equation :

$$C_2 = y \times \frac{V_1}{m_1} \quad (4)$$

where

$y$  is the interim result (5.2.3.1.5) ;

$V_1$  is the volume, expressed in millilitres, of the sample solution (5.2.3.1.3) (= 100 ml) ;

$m_1$  is the mass, expressed in grams, of the initial sample.

## 6 Labelling - Transportation - Storage

### 6.1 Means of delivery

The product shall be delivered in steel drums or HDPE containers certified for goods

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 Risk and safety labelling according to the EU directives <sup>4)</sup>

The following labelling requirements shall apply to liquid sodium permanganate at the date of publication of this European Standard.

- Symbols and indications of danger :
  - X<sub>n</sub> : Harmful ;
  - O : Oxidizing.
- Nature of special risks attributed to dangerous substances :
  - R 8 : Contact with combustible material may cause fire;
  - R 22 : Harmful if swallowed.
- Safety advice concerning dangerous substances :
  - S 2 : Keep out of the reach of children.

NOTE Annex I of the Directive 67/548/EEC on Classification, packaging and labelling of dangerous substances and its amendments and adaptations in the European Union contains a list of substances classified by the EU. Substances not in this annex I should be classified on the basis of their intrinsic properties according to the criteria in the Directive by the person responsible for the marketing of the substance.

### 6.3 Transportation regulations and labelling

Sodium permanganate solution is listed as UN Number <sup>5)</sup> : 3214.

RID <sup>6)</sup>/ADR <sup>7)</sup> : Class 5.1, classification code O1; packing group II.

IMDG <sup>8)</sup> : Class 5.1, packing group II.

IATA <sup>9)</sup> : Class 5.1, packing group II.

### 6.4 Marking

The marking shall include the following information :

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<sup>4)</sup> See [2].

<sup>5)</sup> United Nations Number.

<sup>6)</sup> Regulations concerning International carriage of Dangerous goods by rail.

<sup>7)</sup> European Agreement concerning the international carriage of Dangerous goods by Road.

<sup>8)</sup> International Maritime transport of Dangerous Goods.

<sup>9)</sup> International Air Transport Association.

- the name sodium permanganate solution", 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 .....".

## **6.5 Storage**

### **6.5.1 Long term stability**

The product is stable when stored ,in a cool and dry area, in closed containers.

### **6.5.2 Storage incompatibilities**

Sodium permanganate can produce spontaneous combustion in contact with products such as glycerine and ethylene glycol.

Also, sodium permanganate reacts violently with acetic acid, sulfuric acid, finely divided organic materials, charcoal, iron (II) salts, sulfites an peroxides. With hydrochloric acid it releases chlorine.



# **Annex A**

## **(informative)**

### **General information on sodium permanganate**

#### **A.1 Origin**

##### **A.1.1 Raw materials**

The raw materials for the production of sodium permanganate are :

- potassium hydroxide (KOH) ;
- pyrolusite (manganese ore, manganese dioxide (MnO<sub>2</sub>));
- sodium hexafluorosilicate (NaSiF<sub>6</sub>).

##### **A.1.2 Manufacturing process**

The principal manufacturing process of sodium permanganate is an oxidation of manganese dioxide in presence of potassium hydroxide. The oxidation process consists of two stages; one chemical which yields potassium manganate (K<sub>2</sub>MnO<sub>4</sub>) and another electrochemical which oxidises potassium manganate to potassium permanganate. The sodium permanganate is obtained by the conversion of potassium permanganate through an ion exchange of potassium with sodium using sodium hexafluorosilicate.

#### **A.2 Use**

##### **A.2.1 Function**

The main applications of sodium permanganate include taste and odour control, elimination of algae and micro-organisms, 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**

Sodium permanganate is used as the commercial product (aqueous solution with contents of mass fraction of 40 %)

##### **A.2.3 Treatment dose**

The treatment dose depends on the water quality to be treated. Effective oxidation of contaminants in water is achieved at dose rates under 10 mg of NaMnO<sub>4</sub> per litre of water.

##### **A.2.4 Means of application**

It is applied using a metering-pump, an injection feeder or a constant head gravity feeder.

##### **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**

The excess product is removed with a water solution of sodium thiosulfate or sodium bisulfite.

## **Annex B** (normative)

### **General rules relating to safety**

#### **B.1 Rules for safe handling and use**

The supplier shall provide current safety instructions.

#### **B.2 Emergency procedures**

##### **B.2.1 First aid**

In case of contact with skin, rinse immediately with plenty of water and remove and wash the contaminated clothing

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

In the case of ingestion , drink sugared milk, orange or lemon juice; if not possible, drink plenty of water. Seek medical advice.

##### **B.2.2 Spillage**

Contain the liquid by diking or collecting in a pit or holding area. Dilute the solution to make sure the concentration is approximately 6% ( $\text{MnO}_4^-$ ). Neutralize the permanganate using a solution of sodium thiosulfate, bisulfite, or ferrous salt.

To clean contaminated floors, flush with large quantities of water and discharge in accordance with the requirements/approval of the relevant authority.

Note : These products may ignite wood, cloth, and paper. If clothing becomes contaminated, wash off immediately. Can cause a fire if left on dirty rags or paper towels that have been thrown into the garbage. Be sure to dilute and neutralize any of these materials prior to disposal.

##### **B.2.3 Fire**

These products are not flammable, but they favour combustion.

Cool fire-endangered containers with water.

Use water to extinguish fires.

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

## Bibliography

- [1] 80/778 EEC : *Council Directive of 15th July 1980 relating to the Quality of Water intended for Human Consumption.*
- [2] 67/548/EEC : *Council Directive of 27th June 1967 on the approximation of the laws, regulations and administrative provisions relating to the classification, packing and labelling of dangerous substances.*
- [3] ISO 6333:1986, *Water quality - Determination of manganese - Formaldoxime spectrometric method.*
- [4] EN 12672, *Chemicals used for treatment of water intended for human consumption –Potassium permanganate.*